# Article

# **Open Access**

AN EXPERIMENTAL INVESTIGATION INTO ENHANCED OIL RECOVERY (EOR) BY POLYMER FLOODING IN SANDSTONE RESERVOIRS UNDER HIGH TEMPERATURE AND HIGH SALINITY CON-DITIONS USING A COMBINATION OF TWO SYNTHETIC POLYMERS

Ali Mohsenatabar<sup>1</sup>, Abbas Khaksar Manshad<sup>1</sup>\*, Ghasem Zargar<sup>1</sup>, Amir H Mohammadi<sup>2</sup>\*

<sup>1</sup> Department of Petroleum Engineering, Abadan Faculty of Petroleum Engineering, Petroleum University of Technology (PUT), Abadan, Iran

<sup>2</sup> Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

Received September 14, 2018; Accepted December 19, 2018

#### Abstract

Polymer flooding at high temperature and high salinity is a new challenge in the petroleum industry. Commonly used polymers are not effective at high temperatures and high salinity, and under harsh conditions, they are degraded and reduced viscosity. In this study, a combination of two synthetic polymers namely SAV37 and AN125VHM was used for polymer flooding tests. Initially, the stability of polymer solution in different weight percentages of the two polymers was investigated against increasing temperature and salinity. Then, 50% of each polymer was added to the flood in the 2000 ppm polymer concentration under the reservoir temperature of 85°C and the salinity of 150,000 ppm in the presence of divalent ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>). The results show that the combination of 50% of the two polymers increases the time of arrival of the injected flood to production, so the recovery factor has increased compared to water flooding. Also, the relative permeability curve was obtained after a history matching using one of the commercial numerical simulators, which indicates the control of the injected fluid mobility at high temperature and high salinity conditions.

Keywords: Polymer flooding; High Temperature; High Salinity; Synthetic Polymer; Enhanced Oil Recovery (EOR).

# 1. Introduction

Polymer flooding is a chemical enhanced oil recovery (EOR) method. In this method, by adding water-soluble polymers, the viscosity of the injected fluid is increased and prevents the fingering phenomenon <sup>[1]</sup>. This property brings the sweeping fluid into a porous medium piston-like in the direction of the production well, and the remaining oil content in the porous medium is minimized <sup>[2]</sup>. The polymers used in this method are divided into two general synthetic and natural polymer groups <sup>[3]</sup>. The base of the synthetic polymer is acrylamide group, the most famous of which is the hydrolyzed polyacrylamide polymers <sup>[4]</sup>. Xanthan is one of the most famous polymers in the category of natural polymers <sup>[5]</sup>. Most of the world's reservoirs are in deep areas with high temperatures and high salinity. Commonly used polymers, such as those mentioned earlier, cannot be used in such environments <sup>[6]</sup>. In fact, in a harsh environment with high temperatures and high salinity, these polymers are degraded, and the viscosity of the injected fluid is reduced <sup>[7]</sup>. Acrylamide-based polymers are hydrolyzed in the high-temperature environment and have a negative charge <sup>[8]</sup>. Due to the presence of single and divalent ions in the porous medium, molecules with a negative charge due to hydrolysis at high temperatures are trapped by dual-value ions <sup>[9]</sup>. This process causes both the viscosity of the polymer solution to be reduced, and the polymer injection cannot be carried out in real, and by polymer adsorption on the surface of the rock, the permeability of the reservoir is

reduced and causes problems when injected. Figure 1 shows the trapping of acrylamide molecules by divalent ions <sup>[10]</sup>.



Figure 1. Trapping the acrylamide molecule by divalent ion [11]

Natural polymers are also degraded under high temperatures and high salinity. In general, Xanthan gums are more stable than acrylamide at high salinity but are not stable at high temperatures <sup>[3]</sup>. As shown in Figure 2, these properties cause polymer molecules to be separated from the water phase and reduce the viscosity of the polymer solution, and in addition, by adsorption of polymer molecules on the surface of the rock, the permeability of the porous space decrease severely <sup>[12]</sup>.



Figure 2. The absorption of polymer molecules on the surface of the porous medium

Therefore, the use of new polymers in environments with high temperatures and high salinity is a new challenge in the polymer industry. Various polymers have been introduced for such environments. In the group of synthetic polymers, sulfate polymers and Co-polymer and Ter-polymers were designed for use at high temperature and high salinity conditions. Sulfate polymers are relatively expensive <sup>[13]</sup>. Some studies have been conducted on the development of acrylamide polymers. Hourdet et al. synthesized a high temperature resistant polymer that has poly (N-isopropyl acrylamide) (PNIPAM) and polyethylene (PEO) structures so that polymer is a series of blocks at low temperature in water that can be solubilized, but with increasing temperature the solubility of these blocks decrease, and polymer make the adhesion, and the viscosity decrease does not occur <sup>[14]</sup>. The main problem with this polymer is low molecular weight, and a high viscosity solution requires a high concentration of polymer, which has two major problems; one is the high cost of supplying polymer and other problems during the injection and low injection capacity <sup>[13]</sup>. In addition, the sulfating of polyacrylamide can make the polymer resistant to high temperatures. Therefore, polymers called AMPS were introduced. Although these polymers can withstand temperatures up to 120°C, they are very expensive, and the use of these polymers alone is not economical <sup>[15]</sup>. Also, new studies have shown that the use of nano silicates with polyacrylamide can create conditions that are stable at high temperatures and high levels of salinity <sup>[16]</sup>. In the group of the natural polymer, some studies have also been conducted that can be used at high temperature and high salinity conditions. The most recent of these polymers is the polymer of Schizophyllan. This polymer is obtained from the fungus of the body of dead trees <sup>[17]</sup>. This polymer is stable at high salinity (200,000 ppm) and high temperature (120°C) <sup>[18]</sup>. But economically it is not profitable and has a high cost than oil prices. In general, the use of synthetic polymers is better than natural polymer, since they are easy to produce and low cost, they are not subjected to bacterial degradation in the reservoir, and fewer problems with injection. Therefore, the production of acrylamide-based

synthetic polymers that can withstand high temperatures and salinity can have economic benefit. SNF has produced acrylamide-based polymers that can be used under high temperature and high salinity. As Figure 3 shows, polymer family of SAV is in the Super-pusher group, which can be used at high temperatures and high salinity.



Figure 3. Different group of polymers with temperature and salinity tolerance <sup>[19]</sup>

In this study, two samples of the company's polymers (SNF) were selected. By studying the rheological properties under the influence of temperature and salinity, a solution was used for flooding at high temperature and high salinity condition. To prepare a 6000 ppm polymer solution, two polymer samples, SAV37, and AN125VHM were combined in various weight percentages, each in brine and formation water with a salinity of 10,000 ppm and 150,000 ppm at 25 to 85°C. After studying the rheological properties of the solutions, the best weight percent composition of the polymer was chosen for injection. After determining the best polymer solution, its stability was studied over time. Then, by considering the oil viscosity, the 2000 ppm concentration of polymer was used for polymer flooding. The polymer flooding was applied on the sandstone core sample under constant pressure at 85°C, the salinity of the formation water of 150000 ppm and confining pressure of 2000 psi around the core.

# 2. Experimental

# 2.1. Materials

# 2.1.1. Core sample

Two sandstone samples were selected from Aghajari formation in one of the Iranian oil fields. After coring and cores preparation, their petrophysical properties including porosity and permeability were measured in different ways. Table 1 shows the characteristics of each sample.

Table 1.	Information of core samples.
----------	------------------------------

Core ID	S-1	S-2
Length (cm)	7.602	7.602
Diameter (cm)	3.686	3.687
Pore Volume (cm <sup>3</sup> ) @14.7psi	15.833	11.221
Porosity-Gas (%)	19.040	13.685
Porosity-Water (%)	19.519	12.145
Permeability (brine water-mD)	17.956	17.450

# 2.1.2. Crude oil

The sample of crude oil used in this study was selected from the Gachsaran oil field of Iran. This oil sample is light crude oil. The characteristics of the oil sample at two different temperatures are summarized in Table 2.

Table 2. Crude oil properties at two different temperatures

Temperature, °C/°F	Density, g/cm <sup>3</sup>	Viscosity, cP
25/77	0.8421	34.847
85/185	0.8515	5.0247

# 2.1.3. Electrolyte

Two samples of brine were used for injection, and one was considered as synthetic formation water. The brine used for water flooding and the polymer solution was concentrated in 10000 ppm of NaCl in deionized water. Brine was prepared by adding specific electrolytes with different percentages with a total concentration of 150000 ppm. The used electrolytes and the values of used weights are summarized in Table 3.

Table 3. Electrolytic Information for synthetic formation water

Electrolyte	Weight, g	Molecular weight, g/mol
NaCl	110	58.44
KCI	2	75.56
CaCl <sub>2</sub>	5	110.98
MgCl <sub>2</sub>	33	95.22

#### 2.1.4. Polymer

The SAV37, AN125VHM polymers from SNF Company were used to make polymer solutions. The AN125VHM polymer is a copolymer, 25% of which is made up of AMPS polymer. The SAV family of polymers is a polymer that has the N-vinyl-pyrollidone group in its structure. These specimens are known as high temperature and salinity resistant polymers worldwide. The characteristics of these two polymers are summarized in Table 4.

Table 4. Properties of polymers\*

Polymer	Company	Form	Molecular weight
SAV37	SNF SAS	White powder	2-5 MMD
AN125VHM	SNF SAS		6-8 MMD

\* More information is available upon request to the authors

As shown in Table 5, 5 polymer solutions at a salinity of 10000 ppm and 6000 ppm polymer concentration were studied from 25 to 85°C. Then the salts in the water were added to the solutions to achieve a salinity of 150000 ppm. The viscosity of the solutions was then measured at 25°C and 85°C. Then, a percentage of a mixture of two polymers was considered for flooding. A magnetic and thermal stirrer was used to make a polymer solution. Brookfield rheometer was also used to measure the viscosity of solutions.

Table 5. The combined percentages of the two used polymers

Solution	SAV37	AN125VHM
1	2 gr (100%)	0
2	1.4 gr (70%)	0.6 gr (30%)
3	1 gr (50%)	1 gr (50%)
4	0.6 gr (30%)	1.4 gr (70%)
5	0	2 gr (100%)

Total polymer concentration 6000 ppm

# 2.1.5. Core flooding

At first, the samples were saturated with water, then a sample of oil was injected into the core sample with varying oil rate to allow samples to reach the connate water saturation. Then, at different pressures, the oil rate was measured to determine the relative permeability of the oil in the connate water saturation. Then one of the samples was considered for water flooding. The 10000 ppm brine flooding was done under the constant pressure of 10 psi between two ends of the cores. When the flood was reached to residual oil saturation, the relative permeability of the water was measured. Regarding tests on different weight percentages of polymers, a polymer with 50% by weight of each of the polymers was considered. Therefore, another core sample was flooded with the polymer. Since the viscosity of oil at 85 °C was 5.247 cp, 2000 ppm concentration of polymer was considered for polymer flooding. Polymer flooding was performed under constant pressure of 14 psi at two ends of cores. When the injection reached to residual oil saturation, the relative permeability of the polymer solution was measured. Figure 4 shows the schematic of the flooding device.



Figure 4. A schematic of the flooding device

# 3. Results and discussion

# 3.1. Rheological properties of the polymer

In this study, the combination of two SAV37 and AN125VHM polymers with different weight percentages in the 6000 ppm of polymer concentration were studied. First, the stability of polymer solutions in salinity of 10000 ppm of salt was studied with increasing temperature so that the viscosity of the solutions decreases with increasing temperature according to Figure 5. Of course, with increasing concentration of polymer AN125VHM, the viscosity of the polymer solution increases and at high temperatures, the solution with a concentration of 100 % of the AN125VHM polymer has the highest viscosity.

The stability of polymer solution viscosity was investigated by increasing salt in solution in the presence of divalent ions  $(Ca^{2+}, Mg^{2+})$  and rising temperature from 25 to 85°C. As the following figures show, the viscosity of solutions decreases with increasing the salinity of the polymer solution from 10000 ppm to 150000 ppm (presence of divalent ions). According to the graphs shown in Figure 6, the variation in viscosity of the solution decreases when the percentage of concentration of AN125VHM is increased. Therefore, the graphs show that the concentration of this polymer is susceptible to divalent salts and reduces viscosity. But in lower percentages of this trend, viscosity reduction is less. Therefore, three different concentrations of the polymer were selected to increase the temperature.

As shown in Figure 7, the use of SAV37 in solution alone lowers viscosity in high salinity and temperatures. However, the viscosity of the solution increases with the addition of polymer AN125VHM. As the figure shows, the weight ratio of 50% per polymer shows a higher

viscosity in a saline solution of 150000 ppm with increasing temperature. Therefore, 50 weight percent of each polymer was selected for flooding.



Figure 5. Viscosity changes of polymer solution at 6,000 ppm concentration with increasing temperature in various weight percentages of two SAV37 and AN125VHM polymer.



Figure 6. Viscosity changes of polymer solutions at 25 °C with increasing salinity from 10000 ppm to 150000 ppm in the presence of dual value ions

In the reservoir under field conditions, due to the large dimensions of the reservoir, the viscosity of the polymer must be stable within the time course of polymer flooding. In this study, with regard to the fact that the injection of polymer in the concentration of polymer 2000 ppm was considered, the polymer viscosity was measured at 185°F for 30 days. According to the normalized viscosity curve (Figure 8), the solution was highly stable during this period.



Figure 7. Viscosity changes of polymer solutions in salinity of 150,000 ppm solution with increasing temperature in three different amounts of weight percentages of polymers



Figure 8. Under temperature viscosity stability for 30 days

# 3.2. Core flooding

Flooding results show that the combination of two polymers is 50% of each polymer which is effective under high temperature and high salinity, and the recovery of the oil is higher than the water flooding ratio. Also, the time of injected fluid arrival for production (break-through time) has increased, which in fact represents the control of the sweeping fluid mobility. Figure 9 shows the recovery of oil.

According to Figure 10, the amount of residual oil saturation in the polymer flooding is lower compared to water flooding, which in fact represents the mobility control in the porous medium due to the addition of the polymer.

As shown in Figure 11, water production was started during water flooding after 0.16 volume of pore volume injected, while in the polymer flooding the water was produced after injection of 0.28 volume of pore volume injected. Also, the amount of fluid injected has always been less than water flooding for polymer flooding.

Relative permeability curve for water and polymer flooding conditions were obtained using one of the commercial simulators after the history matching of production history using the

Corey relative permeability equation. As shown in Figure 12, the relative permeability diagram of the oil moves to the right, indicating that the oil is swept better during polymer flooding compared to water flood. Also, the relative permeability curve of the water shows a lower gradient and moves downwards indicating the mobility control by increasing the polymer and the efficiency of the polymer at high temperatures and high salinity.



Figure 9. Oil recovery curve in two modes of water and polymer flooding at high temperatures and salinity



Figure 11. Cumulative water production graph during water and polymer flooding



Figure 10. Curve of oil saturation during water and polymer flooding



Figure 12. The relative permeability curve of water and oil in the conditions of polymer and water flooding

# 4. Conclusion

By adding AN125VHM polymer, the viscosity of the water is higher in comparison with the condition when SAV37 polymer is added to the solution. But according to the obtained graphs, the AN125VHM polymer has a viscosity reduction at high temperatures and high salinity compared to SAV37. Among the combined percentages of these two polymers together, 50% for each, shows better stability and the high viscosity at high temperatures and high salinity. Therefore, in this combination, a percentage of each of the 2000 ppm polymer solution was selected for polymer flooding. As the results show, polymer flooding was effective at 85°C and salinity of 150000 ppm (in the presence of a large number of divalent ions), and a 23% increase in EOR was obtained in comparison with water flooding. Also, relative permeability diagrams indicate the mobility control of displacing fluid in polymer flooding compared to water flooding. Some experimental studies must be conducted in future on adsorption of polymer on the rock surface and its impact on residual oil saturation. Effect of ions (Na<sup>+</sup>, Ca<sup>2+,</sup> and Mg<sup>2+</sup>) on the rheology of the polymer solutions should be studied exclusively.

#### References

- [1] Shah DO. Improved oil recovery by surfactant and polymer flooding: Elsevier, 2012.
- [2] Taylor K, and Nasr-El-Din H. Water-soluble hydrophobically associating polymers for improved oil recovery: a literature review. in SPE International Symposium on Oilfield Chemistry, 1995.

- [3] Kamal MS, Sultan AS, Al-Mubaiyedh UA, Hussein IA. Review on Polymer Flooding: Rheology, Adsorption, Stability, and Field Applications of Various Polymer Systems. Journal Polymer Reviews, 2015; 55(3): 491-530.
- [4] Zhao X, Liu L, Wang Y, Dai H, Wang D, and Cai H. Influences of partially hydrolyzed polyacrylamide (HPAM) residue on the flocculation behavior of oily wastewater produced from polymer flooding. Separation and Purification Technology, 2008; 62: 199-204.
- [5] Ghoumrassi-Barr S, and Aliouche D. A Rheological Study of Xanthan Polymer for Enhanced Oil Recovery. Journal of Macromolecular Science, Part B, 2016; 55: 793-809.
- [6] Yanbiao ZFYGL, and Jiangbo L. Development of Chemical Oil Displacement Agent for High Temperature and High Salinity Reservoir. Advances in Fine Fetrochemicals, 2005; 5:
- [7] Wu Y, Mahmoudkhani A, Watson P, Fenderson TR, and Nair M. Development of new polymers with better performance under conditions of high temperature and high salinity. in SPE EOR Conference at Oil and Gas West Asia, 2012.
- [8] Rellegadla S, Prajapat G, and Agrawal A. Polymers for enhanced oil recovery: fundamentals and selection criteria, Applied Microbiology and Biotechnology, 2017; 101: 4387-4402.
- [9] Zhu D, Zhang J, Han Y, Wang H, and Feng Y. Laboratory study on the potential EOR use of HPAM/VES hybrid in high-temperature and high-salinity oil reservoirs. Journal of Chemistry, 2013; Article ID 927519.
- [10] Chen Q, Wang Y, Lu Z, and Feng Y. Thermoviscosifying polymer used for enhanced oil recovery: rheological behaviors and core flooding test. Polymer Bulletin, 2013; 70: 391-401.
- [11] Rashidi M. Physico-chemistry characterization of sulfonated polyacrylamide polymers for use in polymer flooding, 2010, PhD Thesis, The University of Bergen, Norway.
- [12] Kamal MS, Sultan AS, Al-Mubaiyedh UA, Hussein IA, and Feng Y. Rheological Properties of Thermoviscosifying Polymers in High-temperature and High-salinity Environments. The Canadian Journal of Chemical Engineering, vol. 93, pp. 1194-1200, 2015.
- [13] Wang Y, Lu ZY, Han YG, Feng YJ, and Tang CL. A novel thermoviscosifying water-soluble polymer for enhancing oil recovery from high-temperature and high-salinity oil reservoirs. in Advanced Materials Research, 2011, pp. 654-657.
- [14] Tamsilian Y, and Ramazani A. Smart polymer flooding process. ed: Google Patents, 2015.
- [15] Vermolen E, van Haasterecht MJ, Masalmeh SK, Faber MJ, Boersma DM, and Gruenenfelder MA.Pushing the envelope for polymer flooding towards high-temperature and high-salinity reservoirs with polyacrylamide based ter-polymers. in SPE Middle East Oil and Gas Show and Conference, 2011.
- [16] Zhu D, Wei L, Wang B, and Feng Y. Aqueous hybrids of silica nanoparticles and hydrophobically associating hydrolyzed polyacrylamide used for EOR in high-temperature and high-salinity reservoirs. Energies, 2014; 7: 3858-3871, 2014.
- [17] Wengel M, Kothe E, Schmidt CM, Heide K, and Gleixner G. Degradation of organic matter from black shales and charcoal by the wood-rotting fungus Schizophyllum commune and release of DOC and heavy metals in the aqueous phase. Science of the Total Environment, vol. 367, pp. 383-393, 2006.
- [18] Quadri SMR, Jiran L, Shoaib M, Hashmet MR, AlSumaiti AM, and Alhassan SM. Application of biopolymer to improve oil recovery in high temperature high salinity carbonate reservoirs. in Abu Dhabi International Petroleum Exhibition and Conference, 2015.
- [19] SNF. Available: http://www.snf-group.com/markets/oil-gas/

Dr. Abbas Khaksar Manshad, Department of Petroleum Engineering, Abadan Faculty of Petroleum Engineering, Petroleum University of Technology (PUT), Abadan, Iran

To whom correspondence should be addressed: Prof. Dr. Amir H Mohammadi, Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

# Article

ANALYSIS OF GEOLOGICAL AND TECHNICAL CONDITIONS FOR CREATION OF UNDERGROUND GAS STORAGE IN A DEPLETED GAS RESERVOIR OF YUZHNO-LUGOVSKOYE FIELD IN RUSSIA

Odunlami Kazeem Alani<sup>1</sup>, Chukwuemeka Augustine Okechukwu<sup>2</sup>

<sup>1</sup> Institute of Oil, Gas and Energy, Kuban State Technological University, Krasnodar, Russia <sup>2</sup> Akwa Ibom State University, Ikot Akpaden, Nigeria

Received September 24, 2018; Accepted December 21, 2018

#### Abstract

Around the world, gas produced in excess of demand during the warmer seasons is most often stored in depleted oil and gas reservoirs, water-bearing structures and in salt dome formations from which it is extracted in the cold season when industrial and household demand for natural gas is higher. This paper, in addition to presenting an overview of the geological and technical conditions for creating underground gas storage (UGS) in depleted reservoirs, carries out an analysis of Yuzhno-Lugovskoye field and calculates key parameters to determine the suitability of its depleted reservoirs for the purpose of underground gas storage.

The calculated parameters of the depleted reservoir in horizon III of the field are as follows: Total gas storage capacity,  $Q_{max} = 803.96 \times 10^{-6} \text{ m}^3$ , Maximum allowable pressure in the storage, (MPa) Pper = 9.5 MPa, and the vertical rock pressure, (MPa), Prock = 15.5 MPa. The pressure values satisfy the necessary condition,  $P_{per} \le (0.6 - 0.7) * P_{rock}$ , and therefore, guarantees that the integrity of the cap of the formation is not compromised and leakage of stored gas into the overlying strata or to the surface is prevented.

Based on the field's location and calculated reservoir properties the depleted reservoir of horizon III in Yuzhno-Lugovskoye field is an economically suitable site for underground gas storage.

Keywords: Underground storage; depleted field; natural gas; pressure; deliverability; maximum allowable pressure.

#### 1. Introduction

Home heating is one of the major uses of natural gas in some regions of the world. Varying temperatures and hence varying heating demands during the different seasons, lead to a fluctuation in gas demands. For instance, the demand for natural gas is more in winter than in mid summer. Therefore, storing the excess volume produced during the summer to compensate additional demands in the winter to ensure a regular and reliable supply of gas to the household and industrial facilities is a major task of the gas industry. To balance this fluctuation various forms of gas storage facilities including but not limited to underground gas storage (UGS) in depleted reservoirs are employed, which forms the subject of this paper.

Storage fields act as an underground warehouse that allow consumers to have a steady supply of natural gas year-round without interruption <sup>[1]</sup>. Underground storage of gas in depleted reservoirs entails injecting produced gas back into depleted reservoirs during low gas demand season, typically April to October and extracting the stored gas from these storages during high demand periods (November to March) to meet home and industrial needs. After solid removal, the produced gas is pumped to a gas metering station, after which it is compressed in a compressor shop, and then supplied to gas distribution stations. At this point, the general gas flow is divided in process lines which are connected to well loop. This permits the measurement of temperature and pressure of gas during an injection into each of the storage wells. The technological process of recovering stored gas from these underground storage

sites is principally the same as the process of extraction from gas fields, differing only in the necessity to extract the entire commercial volume of gas stored in an underground storage facility in the period of increased demand.

The first UGS became operational as early as 1915. Since then hundreds of facilities have been developed with some 150 in Europe and Central Asia, over 400 across the United States and 59 in Canada. Underground storage of natural gas has become a large and essential part of the natural gas delivery system and continues to grow as a result of continually increasing demand for natural gas. This calls for an enhancement of underground storage capacity and deliverability both by creating new facilities and by upgrading existing ones <sup>[2]</sup>.

UGS (underground gas storage) facilities largely contribute to the reliability of gas supplies to consumers. They level off daily gas consumption fluctuations and meet the peak demand in winter. UGS facilities are of particular importance in Russia with its cold climate and huge distances between resources and end users <sup>[3]</sup>, in addition to difference in climatic conditions between the southern and northern regions of the country.

This paper presents an overview of the various types of underground gas storage facilities, examines the factors that determine the suitability of a depleted reservoir for the construction of underground gas storage and carries out an analysis of Yuzhno-Lugovskoye field and calculates key parameters to determine the suitability of its reservoirs for underground gas storage.

# 2. Type of underground gas storage facilities

Most gas storage fields were, originally, gas fields, oil fields or aquifers that were converted to gas storage after depletion of native gas or oil reserves <sup>[4]</sup>. Depending on a number of factors, and to suit the different gas supply needs, various types of UGSs are distinguished as follows:

- Gas storage in depleted fields.
- Gas storages in a water-bearing structure.
- Gas storages in salt dome formations <sup>[5]</sup>.



Figure 1. Various types of underground gas storages [6].

Each storage type has its own physical characteristics (porosity, permeability, retention capability) and economics (site preparation and maintenance costs, deliverability rates, and cycling capability), which govern its suitability for particular applications <sup>[7]</sup>.

Several volumetric measures are used to quantify the fundamental characteristics of an underground storage facility and the gas contained within it. For some of these measures, it is important to distinguish between the characteristic of a facility, such as its capacity, and

the characteristic of the natural gas within the facility such as the actual *inventory level*. These measures are as follows:

Total natural gas storage capacity is the maximum volume of natural gas that can be stored in an underground storage facility in accordance with its design, which comprises the physical characteristics of the reservoir, installed equipment, and operating procedures particular to the site. Total gas in storage is the volume of natural gas in the underground facility at a particular time.

Base gas (or cushion gas) is the volume of natural gas intended as permanent inventory in a storage reservoir to maintain adequate pressure and deliverability rates throughout the withdrawal season.

Working gas capacity refers to the total gas storage capacity minus base gas. Working gas or active gas is the volume of gas in the reservoir above the level of base gas. Working gas is available to the marketplace.

Deliverability is most often expressed as a measure of the amount of gas that can be delivered (withdrawn) from a storage facility on a daily basis. Also referred to as the deliverability rate, withdrawal rate, or withdrawal capacity, deliverability is usually expressed in terms of million cubic feet per day (MMcf/d)

Injection capacity (or rate) is the complement of the deliverability or withdrawal rate – it is the amount of natural gas that can be injected into a storage facility on a daily basis. As with deliverability, injection capacity is usually expressed in MMcf/d<sup>[7]</sup>.

The measurements above are not fixed for a given storage facility. For example, deliverability depends on several factors, including the amount of gas in the reservoir and the pressure <sup>[8]</sup>.

Conversion of an oil or natural gas field from production to storage takes advantage of existing wells, gathering systems and pipeline connections. Depleted oil and natural gas reservoirs are the most commonly used underground storage sites because of their wide availability <sup>[6]</sup>.

# 3. Underground storage in depleted deposits

# 3.1. Factors that determine the suitability of gas reservoirs for construction of gas storage facility

Factors that affect whether or not gas reservoirs will make good storage reservoirs are both geographical and geological <sup>[9]</sup>.

Storage location is a very important consideration. For example, if the reservoir is not close to existing transmission lines or market areas, the developer may incur greater expenses to establish connection with pipelines <sup>[10]</sup>. Basic Storage Requirements: High porosity, high permeability, hold adequate volumes of gas, extract gas at high rates, contain and trap gas, and cushion gas <sup>[11]</sup>. The greater the porosity of the rock, the faster the rate of injection and withdrawal. The size of the reservoir, the thickness of the gas-bearing rock stratum and the extent to which the stratum covered by cap rock are also important <sup>[10]</sup>.

# 3.2. Construction of underground storage facilities in a depleted deposit

Depleted oil and natural gas reservoirs are considered to be the most economical, since:

- gas or oil reservoir is well studied: detailed information is available on the area, gas or oil content, capacity, reservoir parameters (geometric shapes and sizes, porosity, formation permeability), the degree of tightness of the cover, the volumes of gas and liquids recovered, the initial reservoir pressure and temperature, characteristics of wells and their operation mode;
- on the field, there is a certain number of drilled and equipped production wells, field equipment (compressor stations, separator, process pipelines), housing and cultural facilities that can be used for the underground storage of gases and liquids, and which generally reduce the capital investment on construction and operation costs;
- the time-frame for the creation of the storage and achievement of its design capacity are significantly reduced;

- when using oil deposits, it becomes possible to extract residual oil by increasing reservoir pressure.

The construction of underground storage facilities in a depleted deposit is usually performed in two stages. At the first stage, the inspection of landfilling facilities, repair and replacement of obsolete, worn out parts is carried out. The problems of automation, raising labor productivity, environmental protection and sources of drinking water are being addressed. At this stage, the industrial filling of the gas storage is also carried out. At the second stage, the testing and cyclic operation of the storage facility is carried out.

At the beginning of the extraction period, the gas is supplied by pressure in the gas storage facility, and then, when the pressure falls, the compressor switches on. Consequently, the compressor in underground gas storage facilities is used both for pumping gas into the formation and for feeding it to consumers during the selection process. Since gas returning from the reservoir is often moistened and contains mechanical impurities (mainly sand), facilities for purification and drying of gas are necessarily built at the underground storage facilities. A set of measures is also envisaged to prevent the formation of hydrate plugs in the wells and in the system of their connection.



Figure 2. Storage facilities in depleted gas reservoirs [12]

When designing the construction of an underground storage facility in a depleted gas field, the following parameters are determined:

- maximum allowable pressure;
- minimum required pressure at the end of the sampling period;
- volumes of active and cushion gas;
- number of injection wells;
- diameter and wall thickness of reservoir and connecting gas pipelines;
- type of compressor unit;
- total power of the compressor;
- type and size of the underground storage facility for gas purification from solid suspensions when injecting it into the formation and drying it during selection;
- the volume of additional capital investments, the cost of gas storage, the payback period of additional capital investments.

After that, technological condition of the wells, wellhead equipment, production gas pipelines, separators, compressors are inspected. The types of repairs, replacements, and the need to build new structures are also determined.

Particular attention is paid to determining the tightness of wells, the speed and intensity of the corrosion processes of metallic field equipment and the development of measures to combat it, the integrated automation of the operation of all elements of the underground storage facility, increment of labor productivity, environmental protection, and drinking water sources in the upper horizons.

#### 4. Geological and technical conditions for the construction of an underground storage facility

The prospects for the further development of underground storage of gases depend, first of all, on the geological, hydrogeological and mining technical conditions of occurrence of rocks. When assessing areas for the construction of underground gas storage facilities, it is necessary to take into account the features of the geological structure of the territory <sup>[13]</sup>. The rocks of the reservoir should have sufficient thickness, permeability, porosity and be characterized by relative lithological uniformity.

The creation of storage facilities in well-permeable and porous reservoirs with a small heterogeneity allows to apply increased depressions when filling gas storage facilities, to reduce the number of operational and observation wells, and to simplify control over the movement of reservoir waters during the extraction of gas from the storage.

The numerical values of the physical parameters of the reservoir bed intended for use as a storage facility can vary considerably. Tectonic disturbances always raise concerns about the tightness of the cap rock over the storage. The presence of faults, thrusts and other disturbances complicates the interpretation of geological and hydrodynamic data, makes difficult the choice of the gas injection scheme, complicates the technological calculations, etc.

The extent of formation water mobility and the magnitude of the reservoir bed elevation (the difference in the marks of the highest point of the reservoir bed and the deepest depth contours closed within the area under consideration) have some influences on the terms of creation of the storage and the mode of its operation.

When creating underground gas storage facilities, both in depleted fields and in watersaturated reservoirs, it is important to correctly establish the maximum permissible pressure in them.

Increasing the pressure in the storage to the maximum allowable contributes to reducing the time of construction of underground storage and positively affects the conditions of its operation as a whole. The greater the pressure in the storage, the greater the amount of gas stored and the less wells required to provide the required gas removal. Increasing the pressure in the storage during storage increases the compressor-free period of gas supply to the consumer from the storage process, reduces the capacity of the compressor station and improves the technical and economic performance of the gas supply system as a whole.

However, an excessive increase in pressure in the underground storage can lead to a breach of the tightness of the reservoir and gas losses, the breakthrough of gas on the daylight surface with the occurrence of explosions and fires, the formation of crystalline hydrates of hydrocarbon gases in the wells, and an increase in the cost of gas compression.

The maximum allowable pressure in the storage facility is due to many geological and technical factors and, first of all, depends on the depth of the formation; density, strength and ductility of the roof of the formation; the method of creating the storage and the rate of gas injection, the maximum compressor discharge pressure chosen for pumping gas into the storage and for taking gas out of it.

The maximum pressure is significantly affected by the structural and tectonic features of the formation, upper boundaries, bedrocks, and also the section of rocks above the reservoir.

When creating and operating underground storage facilities, one should also take into account the rate of increase in pressure during gas injection. The smaller the rate of increase in pressure, the greater the pressure in the storage can be increased.

Another important parameter for the operation of underground storage facilities is the minimum permissible depth of underground reservoirs, which is determined, first of all, by the vapor pressure of the stored product. This value is set taking into account that one atmosphere of the maximum working pressure of the product in the storage should be balanced by the pressure of the strata above the reservoir of at least six meters.

Approximate calculation of the storage depth of the storage (H) is carried out under the condition that the excess pressure in the storage ( $P_{ex,pre}$ ) is lower than the overburden rock pressure ( $P_{rock}$ ). It allows for the protection of the walls of the storage from destruction under the influence of internal pressure.

$$P_{ex.p} < P_{rock} = \rho_{rock} \cdot g \cdot H$$

(1)

where  $p_{\text{rock}}$  - average density of overlying rocks <sup>[13]</sup>.

When selecting a site and deciding on the suitability of the reservoir for the construction of a storage facility, the overall geological condition of the deposit is assessed in order to establish disturbed zones. The tightness of the storage can be disturbed by unfavorable tectonic conditions: faults, shifts, etc. Only a comprehensive analysis of the results of exploration makes it possible to conclude on the degree of tightness of underground storage, increasing its operational reliability <sup>[13]</sup>.

# 5. Geology and reservoir of the Yuzhno-Lugovskoye field

# 5.1. Characteristics of the Yuzhno-Lugovskoye field

The Yuzhno-Lugovskoye field is multi-layered and contains gas deposits in sediments of the lower Mazhuisk subhorizon at a depth of 700-1400 m. Type of collector - porous. The Yuzhno-Lugovskoye field is divided into three blocks: Zolataribni, Central and Northern. The northem block, starting from the ninth horizon up the section, is an arch of the South Lugovskaya structure, within which there are unlimited reservoirs of layers: III, IV, V, VI, VII, VIII. The gas storage operations are carried out on reservoir III. Gas water contact of III horizon of the Yuzhno-Lugovskoye field is determined in accordance with the interpretation of well log survey data at -669 m.

The main part of the studied rocks is characterized by low filtration properties (permeability from 1.68 to  $36.4 \times 10-3 \,\mu\text{m}2$ ).

# 5.2. Analysis of the parameters of the geological structure of the Yuzhno-Lugovskoye field from the point of view of the construction of an underground gas storage facility

During the selection of the reservoir for the creation of an underground storage, a number of the most appropriate horizons were studied. The choice of the facility was made in accordance with the conditions imposed by the UGS construction; on the interpretation of Geologic Information System GIS data, on structural constructions, on seismic studies, etc. In addition, the depth of the deposit is taken into account when choosing a horizon. This is due to the fact that a sufficiently high pressure must be created in the reservoir to ensure the storage of significant volumes of gas. The reservoir of horizon III was selected for underground gas storage. This reservoir being a depleted gas reservoir satisfies the conditions for the creation of an underground gas storage and saves the costs of additional research to verify reservoir integrity, an important factor that determines the ability of a reservoir to hold the stored gas.

# 6. Calculation of the main parameters of the underground gas storage

When calculating the parameters of the underground gas storage: the size and shape of the gas-saturated formation, the volume of the pore space of the deposit, the coefficients of porosity and permeability coefficients, the formation pressure and temperature, the composition of the gas, the placement of injection wells on the gas-bearing area, the coefficients of

the filter resistances, the change in the rate of gas pumped into the storage facility in time are known.

The purpose of this calculation is to determine:

- The maximum volume of gas pumped into the UGS (active),
- The total volume of gas in the storage,
- Cushion gas volume,
- Time of gas injection into the storage,
- The pressure at the bottom of the well at the end of the gas injection period,
- Pressure at the wellhead of the injection well at the end of the injection period,
- Vertical rock pressure,
- Bursting Pressure of the reservoir,
- Number of compressors.
- In the design and operation of underground gas storage facilities, active, cushion and total gas volumes are distinguished.
- Active volume is the volume of gas that is taken and pumped. This volume is determined by the formula below. For several years, its quantity in the storage can be considered permanent

$$Q_{act} = \Omega \frac{P_{max} - P_{min}}{z}$$

(2)

where  $\Omega$  is the volume of the pore space;  $P_{max}$  and  $P_{min}$  are the maximum and minimum pressure in the storage.

Cushion gas volume is the volume of gas that is not extracted from the underground gas storage, but necessary to maintain a certain minimum pressure for supplying gas to the surface, counteracting the introduction of formation water into the storage facility, etc.:

# $Q_{cushion=\frac{\Omega P_{min}}{7}}$

(3)

(4)

Cushion gas - the volume of gas that is constantly in the UGS during its operation. The volume of cushion gas in the underground storage depends on the depth of the trap, the physico-geological parameters of the reservoir, the thickness of the formation and the slope of the structure, and the mode of operation of the storage facility.

The costs of cushion gas and its injection into underground gas storage facilities are equivalent to capital investments in the construction of underground gas storage facilities. The volume of the cushion gas, the number of production wells and the power of the compressor are interrelated.

\*Total gas volume is the maximum amount of gas that can be placed in the storage:

# $Q_{total=\frac{\Omega P_{max}}{r}}$

When creating and operating underground gas storage facilities, the maximum permissible, maximum, minimum and average pressures are also distinguished.

Maximum permissible pressure is the greatest pressure in the storage, which can be assumed, based on the condition of reservoir (roof) preservation. The higher the pressure in the formation in which the storage is created, the more gas can be stored in it. However, if the pressure is increased excessively, the integrity of the roof of the formation may be compromised, and conditions for gas leakage into the overlying strata or to the surface are created.

To prevent this, the maximum permissible pressure in the formation is assumed to be somewhat less than the pressure of the overlying rocks (rock pressure):  $P_{per} \leq (0.6 - 0.7)P_{rock}$  (5)

The maximum is the pressure established on the basis of technical and economic calculations and corresponding to the active gas volume.

The minimum is the pressure established on the basis of technical and economic calculations and corresponding to the buffer volume of the stored gas.

# $\frac{Q_{cushion}}{P_{min}} = \frac{P_{min}}{P_{min}}$

 $Q_{act} = P_{max-P_{min}}$ 

The average pressure in the storage tank is determined from the expression below:

(6)

$P_{av} = \frac{1}{T} \int_0^T P(t) dt$	(7)
where T is the time equal to a year or a value that is a multiple of one y The injection time of the gas is determined from the ratio:	ear.
$t = \frac{Q_{act}}{N(t)}$	(8)
For an approximate determination of the pressures at the bottom of pumping gas at a constant rate, we use formula <sup>[14]</sup> .	injection wells when
$P_{bhp}^2 - P_k^2 = AQ + BQ^2$	(9)
$A = \frac{116\mu_0 z_0 T_0}{\pi k \ln T} \left( \ln \frac{R_k}{R} + \xi_1 + \xi_2 \right)$	
$mp_a r_c (m_c)$	(10)
$R = R_c + 1.5\sqrt{xt}$	(11)
$x = \frac{K P_k}{m \mu_0}$	(12)
$B = \frac{63.10^6 \rho_a T_0^2 [1 + \xi_1 + \xi_2]}{(k/m)^{3/2} 2\pi^2 h^2 T_c^2 R_c \rho_a .0.746.10^4}$	(13)
when R is reached, the $R_k$ value for uniform well placement on the gas a	area
$R_k = \sqrt{\frac{\Omega}{\pi hmn}}$	(14)
But in the case of battery placement of wells	
$R_k = L_k = \sqrt{\frac{\Omega}{\pi hmn}}$	(15)
The pressure at the mouth of the injection well is determined by the f	ormula GA Adamova:
$P_{whp} = \sqrt{P_{bhp}^2 e^{-2s} - \frac{1.377 \times 10^{-2} z^2 T^2 \lambda Q^2}{d^5}} \ (e^{-2s} - 1)$	(16)
$2s = 0.06833 \times \Delta L/zT$	
Bursting pressure	
$P_{bp} = P_{vp} - P_{res} + \sigma_p$	(17)
$P_{\nu p} = \frac{H \rho_r}{10}$	(18)
where $Pvp$ - vertical overburden pressure; $\sigma p$ is the rock stratification	n pressure (it can be

assumed that  $\sigma p = 1.5$  MPa)

The number of compressors necessary for pumping gas into the storage is found assuming that the compressor is located near the injection wells and the loss of gas pressure along the compressor path is small:

$$n_k = \frac{N(t)}{q_k} \tag{19}$$

where  $q_k$  is the flow rate of gas injected into the formation by a single compressor of a known type.

Table 1.	Basic data	of the	underground	gas	storage
----------	------------	--------	-------------	-----	---------

N⁰п	Initial data	Values
/п		
1.	Initial pressure in the storage, (MPa) Pinitial	7
2.	Volume of the deposit, (m3)	2,158,000
3.	Permeability, (µm2) k	0.5 × 10-3
4.	Porosity, m	0.3
5.	Viscosity, (MPa * s) µ	0.012
6.	Thickness of the formation, (m) h	12
7.	The radius of the well, (m) Rc	0.1
8.	Number of injection wells, n	5

№ п /п	Initial data	Values
9.	Constant flow of gas pumped into the storage facility by one well, $(m^3/day) N 1 (t)$	240000
10.	Maximum allowable pressure in the storage, (MPa) Pper	9.5
11.	Depth of borehole, (m) L	640
12.	Inside diameter of the production string, (m) d	0.132
13.	Coefficient of hydraulic resistance of pipes, $\lambda$	0.02
14.	The relative density of the injected gas through the air, $\Delta$	0.6
15.	Gas supercompressibility factor, z	0.85
16.	Coefficient of filtration resistance, B	0
17.	Stratification pressure of rocks, (MPa) $\sigma$	1.5
18.	Density of overlying rocks, pr	2.5
19.	The compressor capacity is 10 GHz/55-125, (m <sup>3</sup> /day).	842400

#### 7. Calculation, result and analysis

From equation (4), Total gas storage capacity  $Q_{max} = 803.96 \times 10^6 \text{ m}^3$ ; from (2), active gas volume  $Q_{act} = 211.56 \times 10^6 \text{ m}^3$ , from (3), cushion gas volume  $Q_{cushion} = 592.39 \times 10^6 \text{ m}^3$ ,  $Q_{act} + Q_{cushion} = Q_{max}$ 

Therefore, the sum of the active gas and the cushion gas gives the total gas storage capacity. From (8), time of gas injection into the storage, (d) T = $2.11,56 \times 10^6/1200000 =$  176.3 days.

From (19), number of compressors:

 $n_{K} = N(t)/q_{K} = 1200000/842400 = 1.424.$ 

Maximum allowable pressure in the storage, (MPa)  $P_{per} = 9.5$  MPa, which is less than than the vertical rock pressure, (MPa),  $P_{rock} = 15.5$  MPa.

This satisfied the condition in (5) that:  $P_{per} \leq (0.6 - 0.7)P_{rock}$ 

Therefore, the integrity of the roof of the formation will not be compromised, and conditions for gas leakage into the overlying strata or to the surface will also be prevented.

Table 2. Results of the calculation of the main parameters of the underground gas storage

№ п/п	The values obtained	Value	es
1.	The maximum volume of gas pumped into the UGS, $(m^3)$ Qact.	211568627.5	211,56×10 <sup>6</sup>
2.	Time of gas injection into the storage, (d.) T	176,3071895	
3.	Total gas storage capacity, (m <sup>3</sup> ) Qtot	803960784.3	803,96×10 <sup>6</sup>
4.	The pressure at the bottom of the well at the end of the gas injection period, (MPa) Pbh	10.12	
5.	Pressure at the wellhead of the injection well at the end of the injection period, (MPa) Pwhp	9.79	
6.	Storage radius, (m) Rk	356.7500283	
7.	Determine the number of compressors, n	1,424,501,425	thus 2 compressors
8.	Vertical rock pressure, (MPa) Prock	15.5	
9.	Bursting pressure, (MPa) Pb	10.5	
10.	Cushion gas, (m <sup>3</sup> ) Qcushion	592392156.9	$592.39 \times 10^{6}$
11.	Volume of pore space in the storage, $(m^3) \Omega$	71933333,333	$719 \times 10^{5}$
12.	The constant flow of gas pumped into the storage, (m <sup>3</sup> /day) N (t)	1200000	1.2× 10 <sup>6</sup>

# 8. Conclusions

- 1. Construction of underground storage facilities around the world has largely helped to contribute to the reliability of gas supplies to consumers.
- 2. The construction of underground gas storage comes with a lot of challenges. The prospects for the further development of storage of gases depend on geographical, geological and technical conditions of the reservoir.
- 3. At the end of this study, it has been shown that, for construction of underground storage in a depleted reservoir, some main parameters are considered and determined. These main parameters include: maximum allowable pressure; minimum required pressure at the end of the sampling period; volumes of active and cushion gases; diameter and wall thickness of reservoir and connecting gas pipelines; type of compressor unit; number of injection wells; type and size of the underground storage facility for gas purification from solid suspensions when injecting it into the formation and drying it during the selection.
- 4. As a result of the technological calculation, the investigated horizon can act as UGS, since the maximum and minimum pressures in the storage, the total volume of gas in the storage, the required number of new wells, and the compressor capacity have been determined.
- 5. From the analysis of geological and technological parameters, it is concluded that it is possible and also profitable to construct an underground storage on the chosen reservoir on the field.

# Acknowledgements

The authors wish to thank the Institute of Oil, Gas and Energy, Kuban State University of Technology for providing the materials for the research and giving us the opportunity to publish this paper. Also, special thanks to Ocheredko Tatyana Borisovna, Savenok Olga Vadimovna and Usov Sergey Vasilievich for their help and suggestions.

#### Nomenclature

В	Coefficient of filtration resistance	Prock	Overburden rock pressure, MPa
d	Inside diameter of the production string, m	Pvp	Vertical overburden pressure, MPa
g	Acceleration due to gravity, m <sup>2</sup> /s	Pwhp	Pressure at the wellhead, MPa
Н	Depth of the storage, m	Qact	Active volume, m <sup>3</sup>
h	Thickness of the formation, m	$\widetilde{Q}$ cushion	Cushion gas volume, m <sup>3</sup>
k	Permeability, µm2	Qtotal	Total gas volume, m <sup>3</sup>
L	Depth of borehole, m	qk	flow rate of gas injected, m <sup>3</sup> / day
т	Porosity	Rc	Radius of the well, m
MMcf/d	million cubic feet per day	Rκ	Storage radius, m
n	Number of injection wells	Т	Time of gas injection into the storage, d
Пĸ	Number of compressors	UGS	Underground Gas Storage
N (t)	Constant flow of gas pumped into the storage, m <sup>3</sup> /day	Ζ	Gas supercompressibility factor
Pav	Average pressure in the storage tank, MPa	λ	Coefficient of hydraulic resistance of pipes
Pbh	Pressure at the bottom of the well at the end of the gas injection period, MPa	μ	Viscosity, MPa * s
Pbp	Bursting Pressure, MPa	horock	Average density of overlying rocks, ka/m <sup>3</sup>
Pex.p	Excess pressure in the storage, MPa	$\sigma_{P}$	Rock stratification pressure, MPa
Pinitial	Initial pressure in the storage, MPa	Δ	Relative density of the injected gas through the air
Pmax	Maximum pressure in the storage, MPa	Ω	Volume of the pore space, $m^3$
Pmin Pres	minimum pressure in the storage, MPa Reservoir pressure, MPa	Pper	Maximum allowable pressure, MPa

#### References

- [1] Alleman N, Arthur JD, Tomastik T, and Andersen K. A Look at Underground Natural Gas Storage Operation and Regulation in the United States". Presented at the GWPC 2016 UIC Conference. Denver, CO. February 25, 2016.
- [2] <u>https://www.kappaeng.com/ugs/introduction</u>.
- [3] <u>http://www.gazprominfo.com/articles/gas-storage/</u>.
- [4] Muonnagor CM, Anyadiegwu CIC. Development and Conversion of Aquifer for Underground Natural Gas Storage in Nigeria; Pet Coal, 2014; 56(1) 1-12.
- [5] Aristova A, Gudmestad OT. Analysis of Russian UGS Capacity in Europe; International Journal of Energy Production and Management, 2016; 1(4) 313-321.
- [6] <u>http://www.energyinfrastructure.org/energy-101/natural-gas-storage</u>
- [7] Energy Information Administration., (2015): The Basics of Underground Natural Gas Storage; <u>https://www.eia.gov/naturalgas/storage/basics/.</u>
- [8] Sunday PHD, Singh VK. Geological Storage: Underground Gas Storage. 8<sup>th</sup> Biennial International Conference & Exposition on Petroleum Geophysics, HYDERABAD 2010.
  [8] https://www.lang.org/network.com/second/secon
- [9] <u>http://naturalgas.org/naturalgas/storage/</u>
- [10] Profile of underground natural gas storage facilities and market hubs: the INGAA Foundation, 1995.
- [11] Lord AS, Kobos PH, and Borns DJ. Geologic Storage of Hydrogen; Sandia National Laboratories 2009.
- [12] Falzolgher F. Underground storage of natural gas, Volume 1/Exploration, Production and Transport.
- [13] Narodny VP. Explosive work in the extraction of natural hydrocarbons, construction of main pipelines and underground storage facilities; edited by V.P. Narodny; NAS of Ukraine, Institute of Geophysics named after SI Subbotin. - Kiev, 2009. - Page 330, illustrations 127, tab. 72, bio.184.
- [14] Prytula N., et al (2017): Mathematical modelling of operating modes of underground gas storage facilities; Technology audit and production reserves No 4/1(36) 2017, ISSN 2226-3780.

To whom correspondence should be addressed: Odunlami Kazeem Alani, Institute of Oil, Gas and Energy, Kuban State Technological University, Krasnodar, Russia, email- kazeemodunlami@yahoo.com

# Article

# THE USE OF PROCESSED POLYETHYLENE PRODUCTS IN THE MANUFACTURE OF PLASTIC LUBRICANTS

Andrey Grigorov<sup>1</sup>, Oleg Zelenskii<sup>1,2</sup>

<sup>1</sup> National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine

<sup>2</sup> Ukrainian State Coal-Chemistry Institute, 61023, 7 Vesnina str., Kharkov, Ukraine

Received September 6, 2018; Accepted December 21, 2018

#### Abstract

It is proposed to expand the raw material base for the production of greases by using used motor oils and solid waste polyethylene products. The results of a laboratory study have been presented; they made it possible to establish that the optimal concentration of the thickener in oil fluctuates within a rather narrow range of 5.0-7.0 wt%. Thus, the obtained greases are identical in quality to the greases of the type Estan 2 (Exxon Co.) and AGIP Grease CC 2 but are much cheaper in production. The approach to attracting secondary energy resources to the technological process of greases production will meet the existing demand for lubricants and significantly reduce the environmental burden on the environment.

**Keywords**: secondary hydrocarbon raw materials; plastic grease; thickener; base oil; polyethylene products; quality indicators; adhesive ability.

# 1. Introduction

Over the past decade, there has been a rapid increase in the global fleet of construction and agricultural machinery, which in turn contributes to an increase in demand for lubricants, and it can be met in modern conditions only by expanding the resource base.

A promising direction in expanding the raw materials base for the production of lubricants, in particular, greases, may be the involvement in the process of various types of secondary hydrocarbon raw materials, the amount of which is capable of providing industrial production volumes and it will significantly reduce the cost of the final product, and also contribute to improving the environmental situation of the country.

# 2. The purpose and objectives of the research

The main components in the production of greases by classical technology are the base oil of a mineral or synthetic nature, a thickener (metallic soaps), fillers and additives <sup>[1]</sup>. Base oils other than the production of greases are widely used in the production of other lubricants so that they are always in great demand. Metal soaps, in turn, have a significant cost, and also for the creation of a spatial structure, they require deep purification of the base oil, which is added from tar-asphaltene substances <sup>[2]</sup>. Ultimately, this all significantly reduces the volume of industrial production of greases. It is possible to radically change this situation when secondary sources of hydrocarbon raw materials are involved in the grease production. In particular, the base oil can be replaced with various used oils, various functional purposes, wastes of selective cleaning of base oils, high boiling fractions of oil sludges, fuel oil, tar, and pre-prepared acid tar. But for this base (dispersion medium), classic thickeners – metal soaps are completely unsuitable and require their replacement by other substances that are not so demanding for the hydrocarbon composition of the dispersion medium. Such thickeners can be used plastic products, in particular, from polyethylene.

# 3. Results and discussion

There are a number of works in which it is proposed to use polyethylene as the main component of grease. For example, it was proposed in work <sup>[3]</sup> to use low molecular weight polyethylene, a waste product for the production of high-density polyethylene, as a dispersed phase in the production of greases.

It was proposed in work<sup>[4]</sup> to add various wastes and pure polymers (polyethylene, polypropylene and EVA copolymer) to lithium grease as modifiers of its viscosity. It has been established that the processed polymers significantly improve the rheological properties of the lubricant than the pure polymers. But in cases where the lubricant containing these polymers was subjected to significant mechanical stresses, its stability was deteriorated.

Also, the following studies have been carried out in the direction of the grease manufacture, by adding base oils of Group I and Group II (kinematic viscosity at  $40^{\circ}C = 160 \text{ mm}^2/\text{s}$ ) to the mixture. These oils are manufactured by Indian Oil Corporation Ltd. (Faridabad, India), a mixture of polypropylene and high-density polyethylene (PP+HDPE). The result of this work was the grease production with high rheological properties <sup>[51]</sup>.

Based on the mixing of two components, melted polypropylene or low density polyethylene in the base oil and the base oil that was thickened with sodium stearate, grease was obtained, which is 80-85 % more resistant to water than a conventional sodium lubric ant <sup>[6]</sup>.

Taking into account the positive properties of polyethylene as a thickener, we propose a plastic lubrication, which consists of SAE 10W-40 API SL engine oil, the amount of which and the negative impact on the environment predetermine the need for its utilization <sup>[7]</sup>, and crushed solid polyethylene products in the form of household packages and film. But to further study the properties and performance characteristics of such a lubricant, first of all, it is necessary to determine the necessary concentration of polyethylene – a thickener, which will meet the requirements of the regulatory documentation concerning the quality of greases.

In the laboratory, two plastic lubricants were obtained, one of which was thickened with crushed products from low-density polyethylene (LDPE), and the second one was obtained with crushed products from high pressure polyethylene (HDPE). The lubricants had a homogeneous, greasy brown-dark structure, and the concentration of the thickener in them varied within 1.0–10.0 wt%.

Further, it has been studied the change in the quality parameters of lubricants (penetration, colloidal stability, volatility, the temperature of sliding and dropping), characterizing their structure and properties <sup>[8]</sup>, from the change in their concentration of thickener (Fig. 1-5).





Fig. 1. Dependence of the colloidal stability of the lubricant on the concentration of the thickener: 1 – LDPE; 2 – HDPE

Fig. 2. Dependence of oil volatility on the thickener concentration: 1 – LDPE; 2 – HDPE

With an increase in the concentration of the thickener from 1 wt% to 10 wt%, the colloidal stability of the lubricants is improved (Fig. 1). Thus, for a lubricant that is thickened with LDPE, a decrease in the value is observed from 9.92 wt% to 1.65 wt%, and for greasing with HDPE: from 13.4 wt% to 5.87 wt%. Also, evaporation significantly decreases (Fig. 2): for

lubrication with LDPE – from 0.55 wt% to 0.29 wt%, for greasing with HDPE – from 0.99 wt% to 0.65 wt%. An important indicator, like lubricant penetration (Fig. 3), also decreases significantly, indicating a change in the consistency of the lubricant, that is, the compaction of its structure.



Fig. 3. Dependence of lubricant penetration on the thickener concentration: 1 – LDPE; 2 – HDPE



Fig. 5. Dependence of the dropping temperature of the lubricant on the thickener concentration: 1 – LDPE; 2 – HDPE



Fig. 4. Dependence of lubricant sliding temperature on the thickener concentration: 1 – LDPE; 2 – HDP

The temperature of sliding and dropping of grease (Fig. 4-5), at a concentration of the thickener at a level of 3 wt%, reach a certain level, which remains to 10 %, then their value slowly increases to 117°C and 119°C for greases with LDPE and 95°C and 110°C for HDPE lubrication respectively. It should also be noted that samples with LDPE at equal concentrations of thickener always have significantly better quality values than grease with HDPE. This is due to the difference in the melting point of these grades of polyethylene, which in some cases is about 40°C.

For the obtained lubricant samples, a very important indicator was also determined, and it characterized the possibility of using lubricant under certain conditions – the adhesive capacity <sup>[9]</sup>. Actually, according to this indicator, it was decided to determine the optimum concentration of thickener in the lubricant. It is proposed in work <sup>[10]</sup> to determine the adhesiveness of greases that contain various polymers and are used in sliding and rolling bearings using the method ASTM D 2979.

But we chose the method of determining the adhesive ability, which simulates the forces that affect the lubrication during the operation of the bearing. It consists in determining the rotational speed of the laboratory centrifuge, in which the layer of applied lubricant begins to drop from the surface of the metal plates fixed in it.

It was found that at 2000 rpm all the samples except those where 1 wt% of HDPE and LDPE were kept firmly on the plates. At 3500 rpm, only two samples are retained on the plates, with 5 wt% of LDPE and 7 wt% of HDPE. This indicates sufficiently high adhesion properties of these samples. At thickener concentrations of up to 3 wt%, the lubricant has a soft structure and centrifugal force discharges it from the plate. In the case of thickener concentrations of more than 10 wt%, a denser lubricant structure is formed, which also leads to deterioration of the adhesion properties, and as a result, dumping from the plate under the influence of centrifugal force.

# 4. Conclusion

Using solid household waste in the form of waste polyethylene products as thickener of the base oil, it is possible to obtain a rather wide range of plastic greases for various functional purposes. With this approach, there is no need to use distillate fractions as the base oil, and it is possible to use waste oil even without deep pre-treatment and various highly boiling fractions of oil residues.

It has been experimentally established that the optimal concentration of thickener fluctuates within a very narrow range of values, within the range of 5-7 wt%, depending on the method of polymer production. The greases obtained in this way are identical in quality to the greases of the type Estan 2 (Exxon Co.) and AGIP Grease CC 2, but are much cheaper in production.

Expanding the raw material base for the grease production by attracting secondary energy resources will help meet the existing demand for lubricants and significantly reduce the environmental burden on the environment.

#### References

- [1] Rizvi SQA. Lubricant Chemistry, Technology, Selection, and Design; ASTM International: West Conshohocken, PA, USA, 2009; p. 443.
- [2] Skobeltsin AS, Nemets VL. Study of the possibility of using used motor oils as a dispersion medium of soap greases. Oil refining and petrochemistry. 2005; 9: 32–37.
- [3] Diphare M, Pilusa J, Muzenda E, Mollagee M. A Review of Waste Lubricating Grease Management. 2nd International Conference on Environment, Agriculture and Food Sciences (ICEAFS'2013), Kuala Lumpur (Malaysia), 2013, p. 131–134.
- [4] Novichikhin DN, Voitik VS. Lubricant composition based on low-molecular-weight polyethylene. Chemistry and Technology of Fuels and Oils. 1998; 34(6): 352–355.
- [5] Martin-Alfonso JE, Valencia C, Sanchez MC, Franco JM, Gallegos C. Rheological modification of lubricating grease with recycled polymers from different plastic waste. Ind. Eng. Chem. Res. 2009; 48: 4136–4144.
- [6] Dixena R, Sayanna E, Badoni R. Recycled and Virgin HDPEs as Bleed Inhibitors and Their Rheological Influences on Lubricating Greases Thickened with PP and mPP. Lubricants. 2014; 2: 237–248.
- [7] Iheme C, Offurum J, Chukwuma F. Production and Blending of Sodium Based Water-Resistant Lubricating Greases from Petroleum and Petrochemical By–Products. American Journal of Computer Science and Engineering Survey. 2014; 2(1): 070–078.
- [8] Fuks IG, Shibryaev SB. Composition, properties, and production of greases, The State Oil and Gas Academy named after I.M. Gubkin: Moskow, 1992; p. 153.
- [9] Lugt P. M. Grease Lubrication in Rolling Bearings, John Wiley&Sons, Ltd: Chichester, 2013; p. 444.
- [10] Vargo D. The Adhesiveness of Grease. Functional Products Inc. Macedonia, Ohio, U.S.A. Presented at the NLGI 81st Annual Meeting Palm Beach Gardens, Florida, USA June 14-17, 2014: 1417-1426.

To whom correspondence should be addressed: Dr. Andrey Grigorov, National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine, <u>grigorovandrey@ukr.net</u>

# Article

**Open Access** 

# NATURE OF HIGHLY VISCOUS COMPONENT IN THE ALKYLBENZENE SULFONIC ACID TECHNOLOGY AND ITS INFLUENCE ON THE PROCESS EFFICIENCY

Irena O. Dolganova\*, Igor M. Dolganov, Ajur A. Bunaev, Maria A. Pasyukova

Institute of Natural Resources, Tomsk Polytechnic University, Russia

Received October 5, 2018; Accepted December 21, 2018

#### Abstract

The purpose of this article is to study the composition of feedstock and products of the process of production of linear alkylbenzene sulfonic acid as a main component of synthetic detergents. Light aromatic compounds, contained in sulfonation feedstock, form a highly viscous component as a result of dealkylation and polymerization reactions. This component is able to accumulate in the sulfonation reactor reducing efficiency and uniformity of the process and the duration of period between reactor washings.

Keywords: alkylbenzene sulfonic acid; sulfonation; highly viscous component; mathematical modeling.

# 1. Introduction

Akylbenzene sulfonic acid (ASA) is chemical with saturated hydrocarbon chain of 10-13 carbon atoms linked to one of sulfonic acid groups. These substances are common anions used in detergents production. ABSA is obtained by following steps <sup>[1-3]</sup>:

- 1) dehydrogenation of alkanes on Pt-catalyst with olefins obtaining;
- 2) hydrogenation of by-product (dienes);
- 3) alkylation of benzene with obtaining of linear alkylbenzenes (LAB) using HF as catalyst;
- 4) sulfonation of LAB with obtaining of ASA.

Given the impact of large number of different factors to work of coupled devices of technological scheme, study and optimization of these processes is of great complexity.

Aromatic compounds of unknown nature contained in feedstock make it difficult to simulate and optimize the sulfonation process. During sulfonation these compounds lead to the formation of highly viscous component, which is critical for the process in a thin film of organic phase. The uniformity of its distribution in the reactor is disturbed, the diffusion of SO<sub>3</sub> molecules in organic phase is hampered, the product color deteriorates, content of active component is reduced <sup>[4-5]</sup>.

The purpose of this work is to prove aromatics content in LAB and composition of active matter based on laboratory analyses of the selected samples, and analysis of trends of sulfonation parameters during the period between reactor washings using mathematical model.

# 2. Experimental

# **2.1.** Proving the aromatics content in LAB and composition of active matter based on laboratory analyses of the selected samples

The most probable composition of aromatics coming with strippant  $C_{11}H_{16}$ ,  $C_{12}H_{18}$ ,  $C_{13}H_{28}$ , isomers  $C_{11}H_{16}$ ,  $C_{12}H_{18}$ ,  $C_{13}H_{28}$ , probably 2-methylnaphthalene, 1- methylnaphthalene). Analysis of the content of organic compounds in feedstock of dehydrogenation reactor was carried out on the magnetic mass spectrometer Thermo Scientific<sup>TM</sup> DFS (Germany) (Tab. 1).

Compound	Content, % wt.						
Compouna	06.06.2014	18.11.2014	24.06.2015	11.06.2015			
Alkanes							
C <sub>10</sub> H <sub>22</sub>	13.131	15.885	11.583	10.647			
C <sub>11</sub> H <sub>24</sub>	22.083	23.768	27.370	25.051			
C <sub>12</sub> H <sub>26</sub>	30.135	27.951	25.791	33.179			
C <sub>13</sub> H <sub>28</sub>	29.105	24.116	31.265	29.120			
$C_{14}H_{30}$	0.644	0.635	0.637	0.456			
	n-alkylt	penzenes	-	-			
C <sub>11</sub> H <sub>16</sub>	0.039	0.077	-	-			
C <sub>12</sub> H <sub>18</sub>	0.019	0.170	-	-			
C <sub>13</sub> H <sub>28</sub>	0.044	0.189	-	-			
C <sub>16</sub> H <sub>26</sub>	0.009	0.035	-	-			
C <sub>17</sub> H <sub>28</sub>	0.031	0.036	-	-			
C <sub>18</sub> H <sub>30</sub>	0.020	0.015	-	-			
C <sub>19</sub> H <sub>32</sub>	0,012	0,009	-	-			
Metylalkylbenzenes (branched alkylbenzenes)							
Σ isomers C <sub>11</sub> H <sub>16</sub>	abs.	0.344	0.004	0.001			
Σ isomers C <sub>12</sub> H <sub>18</sub>	0.028	0.678	0.001	trace			
Σ isomers C <sub>13</sub> H <sub>20</sub>	0.014	0.857	0.001	trace			
$\Sigma$ isomers $C_{16}H_{26}$	0.032	0.087	-	-			
$\Sigma$ isomers $C_{17}H_{28}$	0.098	0.088	-	-			
$\Sigma$ isomers $C_{18}H_{30}$	0.090	0.104	-	-			
$\Sigma$ isomers C <sub>19</sub> H <sub>32</sub>	0.086	0.077	-	-			
$\Sigma$ isomers $C_{20}H_{34}$	0.047	0.038	-	-			
$\Sigma$ isomers $C_{21}H_{36}$	0.023	0.021	-	-			
Other hydrocarbons							
2-methylnaphthalene	0.036	0.189	-	-			
1- methylnaphthalene	0.027	0.071	-	_			
Σ isomers of dimethylnaph-	0 0 0	0 220	-	-			
thalene	0.009	0.229					
Unidentified compounds (prob-	4.238	4.331	3.348	1.546			

Table 1. Results of hydrocarbon group analysis of the feedstock for dehydrogenation process, wax fraction  $C_{10}-C_{13}$  (mixing unit)





n-alkylbenzenes, where R is the n-alkylbenzene radical ( $C_5$ - $C_{13}$ )

linear and branched radical, more detailed composition is impossible to determine due to the low content of compounds in the sample

The most probable composition of aromatics coming with strippant  $C_{11}H_{16}$ ,  $C_{12}H_{18}$ ,  $C_{13}H_{28}$ , isomers  $C_{11}H_{16}$ ,  $C_{12}H_{18}$ ,  $C_{13}H_{28}$ , probably 2-methylnaphthalene, 1- methylnaphthalene).

Unidentified compounds mostly consist of saturated hydrocarbons, individual composition is impossible to determine due to the low content of compounds in the sample (probably isoparaffines).

Obviously, feedstock of the dehydrogenation process includes wide variety of aromatic compounds that entered the inlet of the dehydrogenation reactor, both from the stage of adsorptive extraction of paraffins at Parex unit (with strippant:  $C_{11}H_{16}$ ,  $C_{12}H_{18}$ ,  $C_{13}H_{28}$ , isomers  $C_{11}H_{16}$ ,  $C_{12}H_{18}$ ,  $C_{13}H_{28}$ , probably 2-methylnaphthalene, 1-methylnaphthalene), and with recycle of unreacted paraffins after alkylation (LAB circulation).

In addition, a large number of different isomers prevail in the sample of feedstock for 18.11.2014 - 2,294% compared with the sample for 06.06.2014 (0,418%). It is also worth

emphasizing that both samples contain a significant number of unidentified compounds probably isoparaffines (4,238% – 06.06. and 4,331%–14.11), the sample of 2015 contain less of them. There are no isomers of  $C_{11}H_{16}$  in dehydrogenation feedstock for 06.06, while for 18.11. their concentrations is 0,344 %. In samples for 2015 traces of these isomers were found.

According to the experimental studies of samples of feedstock for 2015 using the method of chromatography-mass spectrometry traces of linear and branched alkylbenzenes were found in new samples, despite of the results for 06.06.2014 and 18.11.2014. Probably previous samples were contaminated. Or inefficient operation of Parex unit in 2014 led to difference in feedstock composition in 2014 and 2015.

Analysis of Parex strippant composition in June 2014. showed high aromatic content (average concentration in strippant is 1 % wt., average concentration in dehydrogenation feedstock in fraction  $C_{10}-C_{12}$ , is 0,67 % wt. and average concentration in fraction  $C_{13}$  is 0,72 % wt.). According to the results of IR spectroscopy there are 5,25% unidentified compounds contained in LAB, probably short chain aromatics.

LAB samples were analyzed using gas chromatography – mass spectrometry (GC-MS), Tab. 2.

	Content, % wt.				
Compound	06.06.2014	18.11.2014	LAB E-602 11.06.2015	FC-212 24.06.2015	
Methylalkylbenzenes (linear alkylbenzenes)					
C16H26	2.155	2.323	2.729	2.704	
C17H28	3.997	4.159	4.191	4.205	
C 18H30	3.959	4.165	4.326	4.429	
C 19H32	2.681	3.129	3.339	3.472	
Σ AB isomers C16	8.118	7.764	8.889	8.495	
Σ AB isomers C17	24.363	22.351	18.632	19.008	
Σ AB isomers C18	28.858	28.859	26.251	25.535	
Σ AB isomers C19	23.156	24.051	22.725	22.818	
Unidentified compounds (prob-					
ably tetraline and indane hom-	2.713	3.199	8.918	9.334	
ologues, polyalkylaromatics)					

Table 2. Results of hydrocarbon group analysis of LAB

Metylalkylbenzenes are compounds of this structure:





where R is the n-alkyl radical ( $C_9$ - $C_{12}$ ), or compounds of such type;

where R is the n-alkyl radical ( $C_8$ - $C_{11}$ )

R

where R is isomer of alkyl radicals  $(C_8-C_{11})$ , radical isomerism is impossible to establish without appropriate standards.

 $\Sigma$  isomers of alkylbensenes are mostly possible isomers of such structure

Accessory substances in LAB (tetraline and indane homologes, polyalkylaromatics), are most probable included in «Unidentified compounds» due to the complexity of their identification. Experimental studies of active matter of ASA were carried out using GC-MS, and showed its composition mostly contains unconverted alkylbenzenes  $C_{13}H_{27}$  and  $C_{12}H_{25}$ , their concentration is maximum.

The results of study were used in development of the unsteady mathematical model of sulfonation process which has prediction and optimization functions <sup>[6-11]</sup>.

# 3. Results and discussion

# 3.1. Analysis of LAB and active matter composition

Thus, despite the presence of aromatic hydrocarbons was detected in ASA samples (aromatic ring in target and by-product), the target product ( $(C_9-C_{14})-C_6H_4-SO_3H$ ), by-products: pyrosulfonic acid ( $(C_9-C_{14})-C_6H_4-SO_2-O-SO_3H$ ) and sulfones (( $(C_9-C_{14})-C_6H_4-SO_2-C_6H_4-(C_9-C_{14})$ ), active matter mostly consists of unreacted LAB (PhC<sub>12</sub>H<sub>25</sub> and PhC<sub>13</sub>H<sub>27</sub>). Presence of sulfo compound is not confirmed.

Previously completed researches showed that during operation of the sulfonation film reactor highly viscous component forms and accumulates. Highly viscous component contains of tetralins and sulfones. Tetralines are formed both at the stage of sulfonation as s result of interaction of LAB and ASA, and at the previous stages of dehydrogenezation and alkylation. This leads to a regular increase in the viscosity of the organic liquid film and as a result to the difficulties of diffusion SO<sub>3</sub> to the reagents and disturbing the uniformity of the sulfonation process. Therefore, the efficiency of the sulfonation process depends not only on ASA viscosity (the ammount of accumulated highly viscous conponent), but also on a current aromatic content in feedstock (LAB), and operational parameters at previous stages. Thus, the decrease in molar ratio at the dehydrogenezation stage leads to decrease in degree of dehydrogenezation of diolefin by-products, increasing the amount of aromatic structure in the sulfonation reactor feedstock.

Indirect parameter which shows the amount of accumulated highly viscous component is pressure of ASA recycle. By the end of the period between reactor washings it increases dramatically, this signals that concentration of viscous component reaches a critical value and indicates the necessity of reactor washings.

The mathematical model of the sulfonation process considers dynamics of highly viscous component accumulation and allows predicting changes of the main indicators of product guality during the period between reactor washings and also its duration. It also allows making recommendations on increasing in duration of the period between reactor washings while maintaining the required product quality as well as recommendations on optimal sulfur supply to the sulfonation reactor depending on the amount of the current concentration of highly viscous component. The more aromatics contains in the feedstock of the sulfonation reactor the more viscous component is formed, the contents of tetralines in LAB and the contents of tetralines and sulfones in ASA grows. When ASA is recycled viscous component is at the entrance of the switchgear, at the same time permeability of the flow is disturbed and the pressure increases. Trends of considered parameters correlate with each other. With maximum aromatic content in LAB – 8.35 % wt. there is maximum pressure of ASA recycle - 225 kPa (for 11.06.2016). This confirms a link between the pressure of ASA recycle as an indicator of necessity of the reactor washings with accumulation of highly viscous component formed from aromatics. The deposition of viscous component occurs not only on the film inside the reactor but also at the entrance to the reactor. This is confirmed by correlation between the pressure of ASA recycle and its color which is indirect parameter of viscosity.

As calculations showed at the dehydrogenation stage the aromatic dealkylation reaction is more likely to form paraffines. The aromatic dealkylation reaction to olefins is reversible. Dehydragenation of short-chain olefins to diolefins are less thermodynamically probable. Hydrogenation of light aromatics is less thermodynamically probable to dienes, probable to cycloalkanes, and also thermodynamically probable hydrogenation of naphthalene derivatives to bicyclic aromatic compounds (Tab. 2).

As a result of the reactions by-products (short-chain olefins) and aromatic compounds are formed, which:

1) At the alkylation stage form heavy alkylation products (tetraline and indane homologues, polyalkylaromatics, etc.);

2) At the sulfonation stage light aromatics less intensively enters the reactions of sulfonation, than LAB with the  $C_{10+}$  side chain, but more confirmed to dealkylation with the formation of short-chain olefins capable of further polymerization.

The results of calculation of the thermodynamic parameters of possible reactions at the stage of sulfonation show:

- 1) light aromatics reacting with SO<sub>3</sub> is less thermodynamically probable and close to equilibrium. Therefore a longer contact time is required for the sulfonation of light aromatics than of LAB with the  $C_{10+}$  side chain.
- 2) light aromatics dealkylation reactions are more thermodynamically probable, than LAB dealkylation reactions. The result of such reaction is formation of low molecular weight olefins with high reactivity in polymerization process with the formation of a polymeric compound film that deteriorates the quality of ASA.

# 3.2. Trends of sulfonation parameters during the period between reactor washings

Besides the main controlled parameters of the sulfonation process the mathematical model allows to calculate dynamics of accumulation of highly viscous component during the period between reactor washings (Fig. 1).



Figure 1. Dynamics of accumulation of highly viscous component during the period between reactor washings

The figure shows that during the period between reactor washings highly viscous component accumulates, which shows the deactivation of reaction medium. This additionally confirmed by trend of calculated sulfonation parameters during the period between reactor washings (Fig. 2).





The decrease in share of ASA and  $H_2SO_4$  associated with a decrease in reaction rate due to the deactivation of reaction medium with highly viscous component accumulation. Therefore, the reaction is not completed, and unreacted LAB transferred to the active matter. The conversion of SO<sub>3</sub> is reduced by reducing amount of SO<sub>3</sub> involved in target reaction.

The represented dependences fully correlate with experimental data. The effect of aromatic content on duration of period between reactor washings is represented in Tab. 3.

Date	Aromatic content in LAB,% wt.	Period between reac- tor washings, days	Real sulfur supply for combustion, kg/h	
05.01.2017	4.0	14		
	4.2	14		
	4.4	13		
	4.6	13		
	5.8	12		
	5.0	12	376.04	
	5.2	11		
	5.4	10		
	5.6	10		
	5.8	9		
	6.0	9		

Table 3. The effect of aromatic content on duration of period between reactor washings

Amount of days before washing depends on aromatic content in LAB. The more aromatics contained in LAB, the less period between reactor washings as viscous components are accumulated.

#### 4. Conclusions

It was shown that during operation of the sulfonation reactor highly viscous component accumulates, which contains of tetralins and sulfones. Tetralines are formed both at the stage of sulfonation as result of interaction of LAB and ASA, and at the previous stages of dehydrogenezation and alkylation. This leads to a regular increase in the viscosity of the organic liquid film and as a result to the difficulties of diffusion  $SO_3$  to the reagents and disturbing the uniformity of the sulfonation process. Therefore, the efficiency of the sulfonation process depends not only on ASA viscosity (the ammount of accumulated highly viscous conponent), but also on a current aromatic content in feedstock (LAB), and operational para-meters at previous stages. Thus, the decrease in molar ratio at the dehydrogenezation stage leads to decrease in degree of dehydrogenezation of diolefin by-products, increasing the amount of aromatic structure in the sulfonation reactor feedstock.

Indirect parameter which shows the amount of accumulated highly viscous component is pressure of ASA recycle. By the end of the period between reactor washings it increases dramatically, this signals that concentration of viscous component reaches a critical value and indicates the necessity of reactor washings.

The developed mathematical model of the sulfonation process which considers dynamics of highly viscous component accumulation is able to predict changes of the main indicators of product quality during the period between reactor washings and its duration. It also allows to make recommendations on increasing of the period between reactor washings duration while maintaining the required product quality as well as recommendations on optimal sulfur supply to the sulfonation reactor depending on the amount of the current concentration of highly viscous component.

# Acknowledgements

The work was financed by subsidy for state support to the leading universities of the Russian Federation in order to increase their competitiveness among the world's leading research and educational centers. The reported study was also funded by RFBR according to the research project № 18-38-00487.

#### References

- [1] Bannov PG. Processy pererabotki nefti. P.G. Bannov. M.: CNIITEHneftekhim. 2001. 625 p. [in Russian]
- [2] Eros LS, Kvitko IA. Himiya i tekhnologiya aromaticheskih soedinenij v zadachah i uprazhneniyah. - L.: Himiya. - 1971. — 496 p. [in Russian]
- [3] Roberts D. Optimisation of the Linear Alkyl Benzene Sulfonation Process for Surfactant Manufacture. Organic Process Research & Development, 2003; 7: 172–184.
- [4] Dolganova IO, Dolganov IM, Ivanchina ED, Ivashkina EN. Alkylaromatics in Detergents Manufacture: Modeling and Optimizing Linear Alkylbenzene Sulfonation. Journal of Surfactants and Detergents, 2018; 21(1): 175-184.
- [5] Dolganova IO, Ivashkina EN, Ivanchina ED, Dolganov IM. Influence of aromatics content in the feed stream on HF-catalyst regenerator and linear alkylbenzenes sulphonation reactor stability. Journal of Chemical Technology and Metallurgy, 2018;53(2): 390-394.
- [6] Zagoruiko AN, Belyi AS, Smolikov MD, Noskov AS. Unsteady-state kinetic simulation of naphtha reforming and coke combustion processes in the fixed and moving catalyst beds. Catal. Today, 2014; 220: 168-177.
- [7] Khlebnikova ES, Dolganova IO, Ivashkina EN., Koshkin SA. Modeling of Benzene with Ethylene Alkylation. MATEC Web Conf.,-2016; 49: 1-5.
- [8] Khlebnikova E, Ivashkina E, Dolganova I. Benzene alkylation with ethylene: The way to increase the process efficiency. Chem. Eng. Process. Process Intensification, 2017; 120: 234-240.
- [9] Belinskaya NS, Ivanchina ED, Ivashkina EN, Sejtenova G. Studying patterns of synthesis of low freezing distillates from atmospheric gasoil by means of mathematical modelling. Curr. Org. Synth., 2017; 14(3): 365-371.
- [10] Ivanchina ED, Ivashkina EN, Frantsina EV, Dolganova IO, Ivanov SY Increasing the selectivity of synthesis stages for linear alkyl benzenes. Curr. Org. Synth., 2017; 14(3): 342-352.
- [11] Belinskaya NS, Frantsina EV, Ivanchina ED, Popova NV, Belozertseva NE. Determination of optimal temperature of catalytic dewaxing process for diesel fuel production. Pet. Coal, 2016; 58(7): 695-699.

To whom correspondence should be addressed: Dr. Irena O. Dolganova, Chemical Engineering Department, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia<u>, e-mail</u>: <u>dolganovaio@tpu.ru</u>

# Article

EFFECT OF INITIAL GAS OIL RATIO, PRODUCED GAS RE-INJECTION AND FORMATION COM-PRESSIBILITY ON PREDICTED PRODUCTION PERFORMANCE OF A DEPLETION DRIVE RESERVOIR

Ikpeka Princewill Maduabuchi, Mbagwu Chinedu

Department of Petroleum Engineering, Federal University of Technology, Owerri, Nigeria

Received September 16, 2018; Accepted December 21, 2018

#### Abstract

Production from depletion drive reservoirs is mainly driven by the expansion of oil and gas originally dissolved in it. When the reservoir pressure drops below the bubble point, free gas evolves from solution and gradually begins to build up within the reservoir. When the critical gas saturation is reached, the free gas becomes mobile and starts flowing towards producing wells. The basic problem with such reservoirs is therefore low oil recoveries obtained since energy is lost as GOR rises. In this paper, a theoretical behaviour of depletion drive reservoirs was modelled with particular emphasis on early production performance, a stage at which reservoir pressure is above bubble point pressure and oil recovery is typically very low. This was achieved by examining the effects of initial gas oil ratio, formation compressibility and produced gas re-injection through the modification of the general material balance equation using PVT data obtained with correlations developed by Vasquez and Beggs and Petrosky and Farshad. The PVT data generation and material balance were carried out by a combination of PROSper software and Microsoft Excel. From the results obtained, this study proposed produced gas re-injection above the bubble point pressure at low initial gas oil ratio and high formation compressibility conditions as improved strategies that can be used to obtain higher oil recoveries from the early stages of production of depletion drive reservoirs.

**Keywords**: Depletion drive reservoirs; Solution gas oil ratio; formation compressibility; Production performance of depletion drive reservoirs; Material balance equation; Vasquez and Beggs; Petrosky and Farshad; Production modelling using PROSPER.

# 1. Introduction

A depletion drive reservoir is one in which the principal production mechanism is the expansion of oil and gas originally dissolved in it <sup>[1]</sup>. It is usually initially undersaturated (i.e. a situation in which the initial reservoir pressure is much higher than the bubble point pressure) and at such conditions, there is no free gas saturation in the reservoir. The pressure drop during this stage is always rapid because of the low compressibility of oil, rock and connate water.

When the reservoir pressure falls below the bubble point, dissolved gas begins to come out of solution, causing the oil to shrink slightly. The gas bubbles formed expand, oc cupying the volume of the produced oil thus ensuring less rapid pressure decline. The absence of water drive indicates little or no water production during the entire production life of such reservoirs unless the reservoir pressure drops to such an extent that there is sufficient expansion of the connate water to ensure mobility. But even at such conditions, water production is small <sup>[2]</sup>.

As the gas continues to accumulate in the reservoir, a point is reached when the critical gas saturation, is reached at which the gas becomes mobile. This trend often leads to an increase in the permeability of the formation to gas and a reduction in the permeability of the formation to oil leading to low oil recoveries and rapidly increasing gas to oil ratios (GOR). Oil production by depletion drive is usually the least efficient recovery method. This is a direct result of the formation of gas saturation throughout the reservoir. Ultimate oil recovery from depletion-drive reservoirs may vary from less than 5% to about 30%. The low recovery from

this type of reservoirs suggests that large quantities of oil remain in the reservoir and, therefore, depletion-drive reservoirs are considered the best candidates for secondary recovery applications. This makes secondary recovery schemes such as gas injection or water flooding an alternative field development solution for such reservoirs <sup>[3]</sup>

Secondary recovery is the result of human intervention in the reservoir to improve recovery when the natural drives have diminished to unreasonably low efficiencies <sup>[2]</sup>. However, before undertaking a secondary recovery project, it should be clearly proven that the natural recovery processes are insufficient; otherwise there is a risk that the substantial capital investment required for a secondary recovery project may be wasted (Ahmed 2006). In many cases, reservoir pressure is maintained by gas injection and oil is displaced by injected gas, thus making it an external gas drive mechanism <sup>[4]</sup>.

# 1.1. Statement of problem

Oil recovery for depletion drive reservoir is typically between 20% and 30% of original oil in place (i.e. low). Of this only 0% to 5% of oil is recovered above the bubble point <sup>[2]</sup>. There is usually no production of water during oil recovery unless the reservoir pressure drops sufficiently for the connate water to expand sufficiently to be mobile. Even in this scenario little water is produced <sup>[2]</sup>.

Early production of depletion drive reservoirs refers to the production stage above the bubble point, the stage at which oil recovery is primarily due to expansion of oil and rock. This is often a few percentages of oil initially in place, typically ranging from 0% to 5% <sup>[2]</sup>.

Ultimate recovery of depletion drive seldom exceeds 30%, this low oil recovery suggests that large quantities of oil remain in the reservoir and, therefore, solution gas drive reservoirs are usually considered the best candidates for secondary recovery such as gas injection to ensure continuous production of the reservoir and make maximum returns on investment.

# 1.2. Objective of the study

This study seeks to investigate the effects of Initial Gas Oil Ratio, Produced Gas Re-Injection and Formation Compressibility on Production Performance in a depletion drive reservoir.

# 1.3. Significance of the study

The economic limit of production for depletion reservoirs is typically reached at low ultimate oil recovery efficiencies which seldom exceed 30%. The rapid loss of gas (the expansion of which provides the main drive mechanism) from the reservoir is the reason for such poor recoveries. Improved depletion strategies are thus essential to make maximum returns on investment.

# 2. Literature review

Reservoirs can be classified on the basis of the boundary type, which determines the drive mechanisms <sup>[5]</sup>. To really understand reservoir behaviour and predict future performance, it is of a necessity to have knowledge of the drive mechanisms that control the behaviour of fluids within the reservoirs <sup>[3]</sup>. In performance prediction of a hydrocarbon reservoir under different drive mechanisms, different conditions arise during the exploitation of the reservoirs. With internal gas drive mechanism, volumetric undersaturated reservoirs are produced by liquid expansion and rock compressibility. As the reservoir pressure declines, oil phase contracts due to release of solution-gas and production is due to gas expansion. As gas saturation reaches the critical value, free gas begins to flow, resulting in high gas-oil ratios and low recoveries.

Bondino *et al.* <sup>[6]</sup> in their work on heavy oil systems identified three different regimes of bubble growth, depending upon capillary number and depletion rate. The three regimes are (a) the conventional capillary-controlled growth pattern at low capillary numbers, (b) viscous biased growth at intermediate capillary numbers, and (c) bubble mobilization and breakup leading to foamy behaviour at the highest capillary numbers and depletion rates. With external gas drive mechanism, saturated reservoirs are produced by depletion drive mechanism. In many cases, reservoir pressure is maintained by gas injection and oil is displaced by injected gas, thus making it an external gas drive mechanism. With the gravity segregation, high relief reservoirs with good along-dip permeability give favourable conditions for gravity segregation of injected gas or gas released from solution <sup>[4]</sup>.

# 2.1. Depletion drive mechanism

In depletion drive mechanism, the principal source of energy is a result of gas liberation from the crude oil and the subsequent expansion of the solution gas as the reservoir pressure is reduced <sup>[3]</sup>. It is also called solution gas or dissolved gas drive or internal gas drive. Depletion drive reservoirs may be initially undersaturated or saturated depending on the pressure <sup>[2]</sup>. If initially undersaturated, there will be no free gas present in the reservoir and production under such conditions is largely due to the expansion of oil, rock and connate water. The initial reservoir pressure in such conditions is above the bubble point pressure. Both black and volatile oils are amenable to solution gas drive <sup>[8]</sup>.

While focusing on heavy oil reservoirs, Alshmakhy and Maini <sup>[9]</sup> evaluated the contribution of gravitational forces under foamy flow conditions. Foamy Oil was observed to be the major reason for unusually high primary recovery factors (RFs) observed in numerous heavy-oil reservoirs. Foamy oils are non-Darcy flow involving formation and flow of gas-in-oil dispersion. It occurs when the wells are produced aggressively at high drawdown pressures that led to conditions in which the viscous forces become sufficiently strong to overcome the capillary forces in pushing dispersed bubbles through pore throats.



Depletion drive reservoirs usually undergo four stages of idealized production as illustrated in Fig. 1:

Stage 1- Production while initially undersaturated.

Stage 2- Production while saturated but the free gas in the reservoir is immobile.

Stage 3- Production while saturated and the free gas is mobile and the producing gas oil ratio is increasing.

Stage 4- Production while saturated and free gas is mobile and the producing gas oil ratio, (GOR) is decreasing <sup>[8]</sup>.

Fig 1 Depletion drive reservoir [11]

The solution gas drive process depends largely to an extent on fluid properties of the oil and gas <sup>[10]</sup>. However, the factor that exhibits the greatest influence on recovery is gas/oil relative permeability ratio as well as the critical gas saturation,  $S_g$  up to which the liberated gas is trapped within each pore in discrete bubbles. Ultimately, as the reservoir pressure declines to the abandonment pressure, the change in the gas formation volume factor offsets the increasing gas to oil mobility ratio and gas to oil ratio trend is reversed. The loss of gas from the reservoir increases the oil viscosity and decreases the oil formation volume factor <sup>[11]</sup>.

The economic limit of production for depletion reservoirs is reached at low ultimate oil recovery efficiencies. This typically ranges from 0 to 5% above the bubble point and 20 to

30% of the oil initially in place below the bubble point <sup>[2]</sup>. There is usually no water production during oil recovery unless the reservoir pressure drops sufficiently for the connate water saturation to expand sufficiently to be mobile. Even in such conditions, water production remains negligible. Other producing mechanisms may often augment the depletion drive mechanism. Its production performance is used as a benchmark to compare other producing mechanisms <sup>[8]</sup>.

Early production of depletion drive reservoirs refers to production above the bubble point, the stage at which oil recovery is primarily by the expansion of oil and rock. This is often a few percentage of the oil initially in place, typically ranging from 0 to 5% <sup>[2]</sup>. Improved depletion strategies are thus required in order to make maximum returns on investment on such reservoirs.

Almost all reservoirs experience an element of pore compressibility  $C_f$  as a result of pressure depletion. In most reservoirs, pore compressibility is small and remains almost constant during depletion. Typical values of ranges from  $3 \times 10^{-6}$  psi<sup>-1</sup> to  $6 \times 10^{-6}$  psi<sup>-1</sup>. Under these conditions, pore compressibility has only a marginal effect in enhancing oil recovery however; reduction in fluid pressure due to oil production causes a significant reduction in pore volume. This mechanism has been recognized as an important drive mechanism in Alberta and Vene-zuela heavy oils and oil sands <sup>[12]</sup>.

An increase of pore compressibility values on depletion drive had a great impact on the oil fractional recovery. This was further supported with reference to the Bachaquero field in Venezuela, and the Ekofisk field in the Norwegian sector of the North Sea. The Bachaquero field is one of the largest heavy oil fields in the Bolivar coast in Venezuela. The contributions of pore compressibility towards oil recovery were 45% and 48% respectively. This large reservoir dips between 1000–4000 ft. and has uniaxial compressibility in excess of  $100 \times 10^{-6}$  psi<sup>-1</sup>. The pore compressibility provided more than 50% of the total drive mechanism for the field. Since most of the production was done by primary recovery, there was considerable surface subsidence which indicated the significance of this compressibility [13].

The most significant effect of pore compressibility was in the Ekofisk field in the Norwegian sector of the North Sea. Ekofisk is one of the largest fields in the entire North Sea with a STOIIP of 6000 MMSTB<sup>[10]</sup>. The field had an abnormal degree of pore compressibility increasing from  $6 \times 10^{-6}$  psi<sup>-1</sup> to a maximum of  $100 \times 10^{-6}$  psi<sup>-1</sup>). The pore compressibility provided more than 30% of the total drive mechanism for the field. The undesirable effects of pore compressibility which caused subsidence of the sea bed cost the operator huge sum of money and created awareness for compaction studies for offshore fields produced primarily by pressure depletion <sup>[10]</sup>.

# 2.2. Fluid properties

Solution gas drive mechanisms depend to a large extent on PVT properties <sup>[10]</sup>. Onolemhemhen *et al.* <sup>[14]</sup> carried out a study to develop a correlation model that can estimate recovery factor under both primary and secondary recovery from oil reservoirs in the Niger Delta having water and depletion drive mechanisms. The results show that for both water and solution gas drive reservoirs; oil viscosity and residual oil saturation do have a strong correlation with recovery factor, while pressure, API gravity and gas oil ratio do have a strong correlation with recovery factor only in solution gas drive reservoirs.

These fluid properties are usually determined by laboratory experiments performed on samples of actual reservoir fluids. In the absence of experimentally measured properties, it is necessary for the petroleum engineer to determine the properties from empirically derived correlations <sup>[3]</sup>. Determination of PVT properties can also be achieved by Equation of state with appropriate calibrations and Artificial Neural Networks models <sup>[15]</sup>. The basic properties required to estimate a reservoir's performance includes solution gas oil ratio, oil formation volume factor and gas formation volume factor. Other properties such as density and compressibility are interrelated through the solution GOR <sup>[5]</sup>.

# 2.3. Fluid property correlations

The most accurate method for determining the behaviour of petroleum fluids is a laboratory PVT analysis. Several authors have done a lot of work on Pressure-Volume-Temperature (PVT) correlations. While some have fine-tuned older correlations others have propounded new ones altogether. PVT parameters are extremely critical input items into the material balance equation for performance prediction, as such the accuracy of such PVT parameters, or better still, the accuracy of the correlations by which they are predicted is very vital.

There have been a lot of correlations developed for crude oils from various geographic locations around the world. These include Standing, Vasquez and Begg's, Glaso, Petrosky and Farshad, Al-Marhoun etc. The accuracy of these correlations is often limited because reservoir fluids consist of varied and complex multicomponent systems with parameters such as gas gravity, oil gravity and GOR which depend entirely on the process by which the oil and gas are separated [16].

The development of neural networks for the modelling of PVT data indicates promising improvements over numerical modelling. Neural networks are mathematical models that acquires artificial intelligence; acquiring knowledge through a learning process <sup>[15]</sup>. They are information processing systems with similar performance characteristics with the biological networks <sup>[17]</sup>. They have the advantage of learning behaviour by self-tuning parameters, ability to discover patterns, fast response and confident prediction of PVT data [15].

# 2.3.1. Vasquez and Beggs Correlation – Worldwide Oil System

Vasquez and Beggs published correlations for gas oil ratio and oil formation volume factor in 1976. They were the first to categorize oil mixtures into two; above 30°API gravity and below 30°API gravity <sup>[18]</sup>. The correlation was developed with a wide variety of data points from over 600 laboratory measurements. An interesting feature of their study was the strong dependence on gas gravity. Realizing that the value of the specific gravity of the gas depends on the conditions under which it is separated from the oil, Vasquez and Beggs proposed that the value of the gas specific gravity as obtained from a separator pressure of 100 psig be used in the equation given below. This reference pressure was chosen because it represents the average field separator conditions <sup>[7]</sup>. The correlations are given as follows:

# i. Bubble point pressure Correlation

$$P_b = \left[\frac{R_{sb}}{C_1 \gamma_{gs} exp\left(\frac{C_3 \gamma_{API}}{T_R}\right)}\right]^{\frac{1}{C_2}}$$
(1)

# ii. Solution gas - oil ratio Correlation

The Vasquez and Begg's Correlations for solution gas oil ratio is given as follows  $R_{s} = C_{1}\gamma_{gs}P^{C_{2}}exp\left(\frac{C_{3}\gamma_{API}}{T_{R}}\right)$ (2) Where:  $T_{R}$  = Temperature, °R; P = Pressure, psia;  $\gamma_{API}$  =Stock tank gravity, °API;  $\gamma_{gs}$  =Gas gravity.

The values of the dimensionless constants are given in Table 1.

Table 1. Values of the dimensionless constants for solution gas oil ratio (Vasquez and Begg's Correlations)

Coefficient	γAPI ≤ 30	γAPI ≥ 30
C1	0.0362	0.0178
C2	1.0937	1.187
C3	25.724	23.931

# iii. Oil Formation Volume Factor Correlation for saturated oils

The correlation for saturated oils is given as follows  $B_o = 1 + C_1 R_s + (T_F - 60) \frac{\gamma_{API}}{\gamma_{as}} (C_2 + C_3 R_s)$ 

(3)
Where:  $B_o = FVF$  of oil conditions P, T rb/stb;  $R_s = Solution$  GOR at conditions P, T scf/stb;  $T_F =$ Temperature of the system, °F.

The values of the dimensionless constants are given in Table 2.

Table 2. Values of the dimensionless constants for Oil Formation Volume Factor Correlation for saturated oils (Vasquez and Begg's Correlations)

Coefficient	γAPI ≤ 30	γAPI ≥ 30
C1	4.677 × 10-4	4.670 × 10-4
C2	1.751 × 10-5	$1.100 \times 10-5$
C3	-1.811 × 10-8	1.337 × 10-9

Oil Formation Volume factor correlation for undersaturated oil ( $P > P_h$ )  $B_o = B_{ob} \exp[C_o(P_b - P)]$ (4)where  $B_{ab} = \text{oil formation volume factor at the bubble-point pressure, bbl/STB; } B_{ab} = \text{oil formation volume factor at the bubble-point pressure, bbl/STB; } B_{ab} = \text{oil formation volume factor at the bubble-point pressure}$  $P_b$  = bubble-point pressure, psia; $C_o$ =Isothermal compressibility.  $C_o = \frac{5R_{sb}+17.2T_F-1180\gamma_{gs}+12.61\gamma_{API}-1433}{2}$ mation volume factor at the pressure of interest, bbl/STB; P = pressure of interest, psia; (5) $P \times 10^5$ where:  $R_{sh}$  = Dissolved gas oil ratio at P<sub>b</sub>, scf/stb;  $T_F$  = Temperature, °F.

#### 2.3.2. Petrosky and Farshad's Correlation – Gulf Of Mexico Oil System

Petrosky and Farshad developed new correlations for Gulf of Mexico crudes in 1993 based on the modification of the Standing's correlations for bubble point pressure, solution gas oil ratio and oil formation volume factor <sup>[18]</sup>. They proposed a new expression for estimating  $B_{o}$ . The proposed relationship is similar to the equation developed by Standing; however, the equation introduces three additional fitting parameters in order to increase the accuracy of the correlation <sup>[7]</sup>. They also used Vasquez and Beggs oil compressibility correlation as a basis for developing the oil compressibility model. Their approach was to give the original correlation model a wide range of flexibility through nonlinear regression. This allowed each variable to have a multiplier and an exponent. Over 90 data sets from Gulf of Mexico was used to develop these correlations <sup>[18]</sup>.

The Petrosky and Farshad correlations are presented below

#### i. Bubble point pressure Correlation

$P_b = 112.727 \left[ \frac{R_s^{0.5774}}{\gamma_g^{0.8439} 10^X} - 12.340 \right]$	(6)
where $X = 7.916 \times 10^{-4} \gamma_{API}^{1.5410} - 4.561 \times 10^{-5} T_F^{1.3911}$	(7)

where  $X = 7.916 \times 10^{-4} \gamma_{API}^{1.5410} - 4.561 \times 10^{-5} T_F^{1.3911}$ 

## ii. Solution gas - oil ratio Correlation

$$R_{s} = \left[ \left( \frac{P_{b}}{112.727} + 12.340 \right) \left( \gamma_{g}^{0.8439} \right) 10^{X} \right]^{1.73184}$$
where:  $X = 7.916 \times 10^{-4} \gamma_{API}^{1.5410} - 4.561 \times 10^{-5} T_{F}^{1.3911}$ 
(8)

#### 2.3.2.3 Isothermal Oil Compressibility correlation

$$C_o = (1.705 \times 10^{-7}) \times R_s^{0.69357} \times \gamma_g^{0.1885} \times \gamma_{API}^{0.3272} \times T_F^{0.6729} \times P^{-0.5906}$$
(9)

## iii. Oil Formation Volume Factor Correlation

$$B_o = \left[a_1 + a_2 R_s^{a_3} \left(\frac{\gamma_g^{a_4}}{\gamma_o^{a_5}}\right) + a_6 T^{a_7}\right]^{a_8}$$
(10)

 $a_1 = 1.0113; a_2 = 7.2046e^{-5}; a_3 = 0.3738; a_4 = 0.2914; a_5 = 0.6265; a_6 = 0.24626; a_7 = 0.5371;$  $a_8$  = 3.0936;  $R_s$  = solution GOR, scf/stb;  $B_o$  = Oil formation volume factor, rb/stb;  $P_b$  = Bubble point pressure, psia; P = Pressure, psia;  $\gamma_a$  = Gas specific gravity;  $\gamma_o$  = Oil specific gravity;  $T_F$ = Temperature, °F.

## 2.4. Material balance calculations

The material balance equation (MBE) has long been recognized as one of the basic tools of reservoir engineers for interpreting and predicting reservoir performance <sup>[3]</sup>. The complete MBE is given by equation 11:

$$N_{p}[B_{o} + (R_{p} - R_{si})B_{g}] + W_{p}B_{w} = NB_{oi}\left[\frac{[(B_{o} - B_{oi}) + (R_{si} - R_{s})B_{g}]}{B_{oi}} + m\left(\frac{B_{g}}{B_{gi}} - 1\right) + (1 + m)\frac{(C_{w}S_{w} + C_{f})\Delta P}{1 - S_{wc}}\right] + W_{p}B_{w}$$
(11)

where:  $N_p$  = total Oil produced in STB;  $B_o$  = Oil Formation Volume Factor, RB/STB;  $R_p$  = Cumulative Produced Gas-Oil-Ratio (GOR), SCF/STB;  $B_a$  = Gas Formation Volume Factor, RB/SCF;  $W_p$  = Cumulative Water Produced STB; m = ratio of gas cap pore volume to oil leg pore volume;  $B_{oi}$  = Initial Oil Formation Volume Factor;  $R_s$  = Solution Gas-Oil ratio, SCF/STB; N = Initial oil-in-place, STB;  $S_{wc}$  = Initial Average Water Saturation;  $W_e$  = Cumulative Water Encroachment.

For a depletion drive or solution gas oil drive reservoir at initial pressure conditions, there is no initial gas cap, thus m = 0 and no water influx. Also, above the bubble point,  $R_p = R_{si} = R_s$ 

The general material balance equation now reduces to

$$\frac{N_p}{N} = \frac{\left[ (B_o - B_{oi}) + \frac{B_{oi}(C_W S_W + C_f)\Delta P}{1 - S_{WC}} \right]}{B_o}$$
(12)

AISO,

$$S_o = \frac{Oil \, volume}{pore \, volume} = \frac{(N - N_p)B_o}{\left(\frac{N B_{oi}}{1 - S_{wi}}\right)} = (1 - S_{wi})\left(1 - \frac{N_p}{N}\right)\frac{B_o}{B_{oi}}$$
(13)

As the solution gas evolves from the oil with declining reservoir pressure, the gas saturation (assuming constant water saturation,  $S_{wi}$ ) is simply given as

$$S_g = 1 - S_o - S_{wi} \tag{14}$$

Below the bubble point,  $R_p \neq R_{si} \neq R_s$ 

The general material balance equation now reduces to

$$\frac{N_p}{N} = \frac{\left[ (B_o - B_{oi}) + (R_{si} - R_s)B_g + \frac{B_{oi}(C_w S_w + C_f)\Delta P}{1 - S_{wc}} \right]}{B_o + (R_p - R_{si})B_g}$$
(15)

For the effect of gas injection in depletion drive reservoir, Above the bubble point, the equation becomes

$$N_{p}B_{o} = NB_{oi}C_{eff}\Delta P + G_{i}B_{gI}$$

$$C_{eff} = \left[\frac{C_{o}S_{o} + C_{w}S_{w} + C_{f}}{1 - S_{wc}}\right]$$
(16)
(17)
Since  $C_{o} = N_{e}P_{o}$  then the above equation now becomes

Since  $G_i = N_p R_{si}$  then the above equation now becomes  $N_p B_o = N B_{oi} C_{eff} \Delta P + F N_p R_{si} B_{gI}$ (18)

where F is the fraction of gas to be injected

Now re-arranging the above equation, we have that:

$$\frac{N_p}{N} = \frac{B_{ol}C_{eff}\Delta P}{B_o - FR_{sl}B_{gl}}$$
(19)

Below the bubble point pressure, the general material balance equation is modified as follows  $B_{-1}(C_{111}S_{111}+C_{-1})\Delta P$ 

$$\frac{N_p}{N} = \frac{(B_o - B_{oi}) + (R_{si} - R_s)B_g + \frac{-6i(-W - W - T_f)/2}{1 - S_{WC}}}{B_o + (R_p - R_{si})B_g - FR_{si}B_{gI}}$$
(20)  

$$R_p = \frac{\sum(\Delta N_p)R}{N_p} = \frac{\sum(\Delta N_p / N)R}{N_p / N} = \frac{N_{pb}R_{si} + (N_p - N_{pb})R_{avg}}{N_p}$$
(21)  
where  $R_{avg} = \frac{R_{si} + R_s}{2}$ (22)

 $G_i$  = Cumulative gas injected, scf;  $B_{ql}$  = injected gas formation volume factor, bbl/scf.

## 3. PVT Data

The solution gas oil ratio,  $R_s$  and oil formation volume factor,  $B_o$  used for this work were generated using two correlations already given in section 2 of this work: Vasquez & Beggs and Petrosky & Farshad. The use of these PVT correlations requires the following initial conditions specified as shown in Table 3.

Table 3. PVT properties used for the analysis

Properties	Values
Initially dissolved Solution gas oil ratio, Rsi	1200scf/stb to 300scf/stb
Specific gravity of Gas, $\gamma_9$	0.75
API gravity of Oil, γ <sub>API</sub>	40
Temperature of reservoir, T	660°R

Bubble Point pressures  $P_b$ , estimated using Vasquez & Beggs and Petrosky & Farshad correlation are presented in Table 4.

Table 4. Showing comparison of bubble point pressures predicted by the two correlations

Pa: (ccf/cth)	P♭ (psia) Vasquez	Pb (psia) Petrosky	
Ksi (SCI/SLD)	& Beggs	& Farshad	
1200	4393	4563	
1000	3767	3969	
700	2789	2971	
400	1741	1767	
300	1366	1283	

#### 4. Results

For an initially under-saturated reservoir,  $R_{\rm SI}$  values are expected to remain constant until the reservoir becomes saturated, at which stage a gradual decline in  $R_{\rm s}$  values should occur. The point at which this decline occurs is strongly dependent on the bubble point ( $P_{\rm b}$ ) of the reservoir as a result of solution gas released at this pressure. Fig. 2 shows the variation of solution gas oil ratio with pressure for a reservoir temperature of 200°F.





Fig. 3 Plot of *Bo* vs Pressure for *Rsi*=1200scf/stb

At an initial reservoir pressure of 5393psia, the Vasquez and Beggs correlation predicts 1200scf/stb of solution gas dissolved in the oil while the Petrosky and Farshad predicts 1200scf/stb of dissolved gas at 5563psia. The graphical plot shows that there is no evolution of solution gas at this point until the bubble point pressure is reached at 4393psia for the Vasquez and Beggs and 4563psia for the Petrosky and Farshad correlation. At these pressures, the first bubbles of free gas begin to appear. At 1593psia, the solution gas is 360.078scf/stb for the Vasquez and Beggs correlation and the average solubility is calculated as follows Average solubility =  $\frac{1200-360.078}{5393-1593}$  = 0.221scf/stb/psi

The prediction of gas solubility for the Petrosky and Farshad correlation for  $R_{si}$  = 1200scf/stb compare closely to that by Vasquez and Beggs as shown below

Average solubility  $=\frac{1200-35629}{5563-1563} = 0.211scf/stb/psi.$ 

On the other hand,  $B_0$  values are expected to increase slightly for an initially under-saturated reservoir, before a gradual decline below the bubble point pressure of the reservoir. The initial increase in  $B_0$  values are due to the slight compressibility of oil, which expands as reservoir pressure decline above the bubble point. Below the bubble point, oil expansion continues but is over-shadowed by a decrease in oil volume due to evolving dissolved gas coming out of solution as shown in Fig. 3.

## 4.1. Effect of Initial Gas Oil Ratio (*R*<sub>si</sub>) on Predicted Production Performance

From the results obtained from the material balance calculations using the Vasquez and Beggs and Petrosky and Farshad correlations, it is observed that  $R_{si}$  does not have significant effect on oil recovery above the bubble point. This is illustrated by the fact that recovery above the bubble point for  $C_f = 6 \times 10^{-6}$  psi<sup>-1</sup> was always low, varying between 1.89 to 2.43% for all values considered and always higher for  $C_f = 30 \times 10^{-6}$  psi<sup>-1</sup> varying between 5.86 to 5.38% as seen in Fig. 4 and Fig. 5. For gas re-injection, recovery above the bubble point was essentially the same for all  $R_{si}$  values considered, varying between 3.08 to 3.73% for all values considered with the two correlations.



Fig. 4. Plot of % Recovery vs Pressure for Rsi = 1200 scf/stb (Vasquez and Beggs)



Fig. 5. Plot of % Recovery vs Pressure for Rsi = 1200 scf/stb (Petrosky and Farshad)

However, below the bubble point, the effects of  $R_{si}$  becomes more significant with higher cumulative recoveries obtained at lower values for gas re-injection and  $C_f = 30 \times 10^{-6}$  psi<sup>-1</sup> by

the two correlations used. The oil cumulative recovery was observed to have increased with reducing  $R_{si}$  values and vice versa.  $R_{si}$  strongly influences the cumulative produced gas-oil ratio  $(R_p)$ , such that increases in  $R_{si}$  values correspond to an increase in  $R_p$ . Fractional recovery varies inversely with  $R_p$ , such that an increase in  $R_p$  corresponds to reduced fractional recovery.

## 4.2. Effect of Produced Gas Re-Injection on Predicted Production Performance

From the results presented in the earlier sections, it could be observed that re-injection of 70% produced gas provided an average recovery of 3.44% down to the bubble point pressure for all  $R_{si}$  values considered with both the Vasquez and Beggs and the Petrosky and Farshad correlations. This is a very small recovery fraction given that this is a percentage of the oil initially in place. At higher  $R_{si}$  values, cumulative recovery obtained is low whereas at very low  $R_{si}$  values i.e. 300 scf/stb, higher recoveries were obtained (See Fig A.1 and A.16). This behaviour is explained by the fact that at low  $R_{si}$  values, reservoir pressure is low and according to Boyles law, gas expands significantly, this is reflected by the increase in the gas formation volume factor,  $B_g$  values, gas volume is greatly reduced i.e. compression of gas occurs at high pressures.

It is the expansion of this gas that forms the secondary gas cap which provides energy or drive for increased oil recovery as observed in Fig. 6.



Figure 6. Showing recovery rates at bubble point as result of produced gas re-injection

# 4.3. Effects of formation compressibility on Predicted Production Performance

The effects of formation compressibility were investigated because at high values, it contributes to oil recovery by compaction drive mechanism. Values of  $C_f$  used in this study were  $6 \times 10^{-6}$  psi<sup>-1</sup>, typical in most reservoirs and  $30 \times 10^{-6}$  psi<sup>-1</sup>, which is high and can be obtained in chalky reservoirs with high porosities. With  $C_f = 6 \times 10^{-6}$  psi<sup>-1</sup>, it provided an average recovery of 2.22% above the bubble point for all  $R_{si}$  values considered with the two correlations but with  $30 \times 10^{-6}$  psi<sup>-1</sup>, recovery rates obtained above the bubble point doubled to an average of 5.18% for all values of  $R_{si}$  considered. However, in all cases, these recovery rates were lesser than those obtained with 70% gas re-injection considered. It is thus established that the higher the value of formation compressibility, the higher the oil recovery above the bubble point but the lower the cumulative recovery as compared to 70% gas re-injection considered. This is illustrated in Fig. 7 and Fig. 8. The increase in recovery obtained with high formation compressibility value of  $30 \times 10^{-6}$  psi<sup>-1</sup> above the bubble point is a result of increase in grain pressure as a result of withdrawal of fluids and subsequent production.



Figure 7. Showing recovery rates at the bubble point with  $C_f = 10^{-6} \text{ psi}^{-1} \text{ by the two correlations}$ 

Figure 8. Showing recovery rates at the bubble point with  $C_f = 30 \times 10^{-6} \text{ psi}^{-1}$  by the two correlations

## 4.4. Improved strategies for early production of depletion drive reservoirs

Early production of depletion drive reservoirs refers to the production stage above the bubble point. This is desirable for the following reasons

- 1. Maintaining production above the bubble point delays the evolution of free gas from the reservoir when gas treatment and or handling facilities are yet to be put in place. In view of the increasing ban on gas flaring, this is an alternative way of production without incurring prohibitive sanctions.
- To monitor reservoir performance (well flow rates, etc.) under depletion conditions before selecting an optimum secondary recovery strategy. This has the advantage of justifying the need to postpone artificial lift methods.

The investigation of the effects of formation compressibility and gas injection earlier discussed offer valuable insights to the development of improved strategies for increasing oil recovery at early stages of a depletion drive reservoir. The strategies are enumerated below.

## 4.4.1. Produced gas Re-Injection

Gas injection will give increased oil recovery above the bubble point for depletion drive reservoirs where initial solution gas oil ratio value is low and formation compressibility value is high. Where the  $R_{si}$  value is high, the effect of gas injection makes only small improvements on recovery.

High pressure associated with high  $R_{si}$  values will put a high economic premium on the gas compression facilities that is required for injection making it more unsuitable as an alternative secondary recovery method. There are a number of practical issues that may arise as a result of this strategy. In the first instance, high values of formation compressibility are closely associated with reservoir compaction. For this reason, geo mechanical analysis must be conducted as early as possible during field development of depletion drive reservoirs to screen, assess and engineer for compaction so as to utilize it a useful drive mechanism.

Another practical difficulty that may arise with this strategy is fingering. This occurs as a result of the downward displacement of oil due to the lower viscosity of gas. However, this effect can be minimized by keeping production rates as low as possible.

## 4.4.2. Water injection

At some point after gas injection is commenced at the upper section of the reservoir, water injection can also be used to increase oil recovery by helping the movement of fluids from upswept zones at the lower sections of the reservoir. The delay in starting water injection provides an opportunity to determine the dynamic characteristics of the aquifer. It is important

to note that with water injection, water cut will increase with time and as such, top side facilities must be designed or able to handle excess water production.

However, the combination of the two schemes could be carried out either as WAG (water alternating gas) or SWAG (simultaneous water and gas injection). In each case, there has to be provision of gas compression and injection facilities as well as water injection facilities. This has the capacity of substantially increasing the field economics.

## 4.4.3. Thermal recovery

At low  $R_{si}$  values there is a less amount of gas in solution, this however does not necessarily imply that the oil in the reservoir will have high viscosity. However, if the oil is highly viscous, then hot water flooding operations will provide a useful means of improving recovery by reduction of oil viscosity, enhancing interfacial tension and thus mobility.

Steam soaking or cyclic steam injection is another useful method of recovery for such viscous reservoirs. This method involves the injection of steam into the reservoir for several days before bringing the well on stream. However, the increase in carbon foot print associated with these operations alongside insulation and corrosion control requirements must be carefully considered before this strategy can be adopted.

## 5. Conclusion

Using the PVT data generated from the two empirical correlations, an increase in oil fractional recovery was observed with a decrease in dissolved solution gas-oil ratio ( $R_{SI}$ ). Reasons for this trend can be attributed to two major factors:

- i.  $R_{SI}$  strongly influences the cumulative produced gas-oil ratio ( $R_P$ ), such that increases in  $R_{SI}$  values correspond to an increase in  $R_P$ .
- ii. Fractional recovery varies inversely with  $R_{\text{P}}$ , such that an increase in  $R_{\text{P}}$  corresponds to reduced fractional recovery.

Cumulative oil recovery of Vasquez and Beggs was higher than that of Petrosky and Farshad for all case scenarios ( $C_f = 6 \times 10^{-6} \text{ psi}^{-1}$ ,  $C_f = 30 \times 10^{-6} \text{ psi}^{-1}$  and 70% gas re-injection). Also, cumulative oil recovery of  $C_f = 30 \times 10^{-6} \text{ psi}^{-1}$  was highest above bubble point and begins to drop below bubble point. For cumulative recovery of 70% gas re-injection, it is higher above bubble point but overtakes  $C_f = 30 \times 10^{-6}$  below bubble point and has the highest cumulative oil recovery for both correlations.

From the results of the material balance calculations carried out with the two correlation

- i. Formation compressibility is a significant factor that contributes to oil recovery at both undersaturated and saturated conditions in depletion drive reservoirs.
- ii. Initial gas oil ratio has no significant effect on the extent of oil recovery above the bubble point pressure for depletion drive reservoirs.
- iii. Produced gas re-injection is the most beneficial technique for improving oil recovery at low initial gas oil ratio conditions for depletion drive reservoirs.

#### 5.1. Further work

This study had a primary focus on the effects of the initial gas oil ratio in depletion drive reservoirs. There are a number of other factors that may affect oil recovery. As part of recommendations for further study, the effects of viscosity, reservoir porosity and permeability and critical gas saturation can be further investigated and results validated by computational simulation. An understanding of the interactions of these various parameters will determine the success of secondary recovery methods to be adopted.

Also, fractional oil recovery at values of  $R_{\rm SI}$  < 300 scf/stb should be investigated to further highlight the importance of this term to overall fractional recovery at pressure above and below bubble point.

## APPENDIX

*Ikpeka Princewill Maduabuchi, Mbagwu Chinedu:* Effect of Initial Gas Oil Ratio, Produced Gas Re-Injection and Formation Compressibility on Predicted Production Performance of a depletion drive reservoir, Pet Coal, 2019; 61(1): 31-49



Fig. A.1 Plot of Rs vs Pressure for Rsi = 1000 scf/stb



Fig. A.2 Plot of *Bo* vs Pressure for *Rsi* = 1000 scf/stb







Fig. A.4 Plot of % Recovery vs Pressure for *Rsi* = 1000 scf/stb (Petrosky)









Fig. A.6 Plot of *Bo* vs Pressure for *Rsi* = 700 scf/stb







Fig. A.8 Plot of % Recovery vs Pressure for Rsi = 700 scf/stb (Petrosky)





Fig. A.10 Plot of *Bo* vs Pressure for Rsi = 400 scf/stb





Fig. A.11 Plot of % Recovery vs Pressure for Rsi = 400 scf/stb (Vasquez)

Fig. A. 12. Plot of % Recovery Vs Pressure (Petrosky)





Fig. A.13 Plot of Rs vs Pressure for Rsi = 300 scf/stb





Fig. A.15 Plot of % Recovery vs Pressure for Rsi = 300 scf/stb (Vasquez)



Fig. A.16 Plot of % Recovery vs Pressure for Rsi = 300 scf/stb (Petrosky)

#### References

- [1] Dake LP. Fundamentals of Reservoir Engineering, Elsevier Publishing, New York, 1998.
- [2] Glover P. Reservoir Drives (Online). Available from: <u>http://www.gql.ulaval.ca/person-nel/paqlover/CD%20Contents/Formation%20Evaluation%20English/Chapter%203.PDF</u> (Accessed on 29th July, 2017).
- [3] Ahmed TK. Reservoir Engineering Handbook, Gulf Professional Publishing, New York, 2006.
- [4] Ambastha AK, Aziz K. Material Balance Calculations for solution Gas Drive Reservoirs with Gravity Segregation: The Society of Petroleum Engineers (SPE 16959). September 1987.
- [5] Williams CL, Guo B, Ghalambor A. Petroleum Production Engineering-A computer assisted approach. Elsevier Science and Technology books, New York, 2007.
- [6] Bondino I, McDougall SR, and Hamon G. Pore-Scale Modelling of the Effect of Viscous Pressure Gradients during Heavy Oil Depletion Experiments. Journal of Canadian Petroleum Technology 164: 45–55. SPE Paper 144467. February 2011.
- [7] Ahmed, T., Mckinney, P.D. Advanced Reservoir Engineering. Oxford, UK: Elsevier Incorporated. 2005
- [8] Lake, L.W. Reservoir Engineering Handbook, Society of Petroleum Engineers Publishing, Texas, United States of America. 2007
- [9] Alshmakhy A, and Maini BB. Effects of Gravity, Foaminess, and Pressure Drawdown on Primary-Depletion Recovery Factor in Heavy-Oil Systems. Journal of Canadian Petroleum Technology 164: 449–456. SPE 163067, November 2012.
- [10] Dake LP. The Practice of Reservoir Engineering, Gulf Professional Publishing, New York, 2001.
- [11] Schlumberger. Fundamentals of Formation Testing (Online). Available from: <u>https://www.slb.com/~/media/Files/evaluation/books/fundamentals formation test-</u> <u>ing\_overview.pdf</u>, 2006. (Accessed on 28th July, 2017).
- [12] Settari AT. Reservoir Compaction, Society of Petroleum Engineers, Journal of Petroleum Technology Volume 54, Issue 08, August 2002. SPE-76805-JPT.
- [13] Merle HA, Kentie CJP, van Opstal GHC, Schneider GMG. Bachaquero Composite Study of Analysis of the Behaviour of a Compaction Drive/Solution Gas Drive Reservoir, SPE 5529. In: Proceedings of the SPE 62nd Annual Technical Conference. Richardson TX: Society of Petroleum Engineers. 28 November – October 1st, 1975.
- [14] Onolemhemhen RU, Isehunwa SO, and Salufu SO. Development of Recovery Factor Model For Water Drive and Depletion Drive Reservoirs in The Niger Delta, paper SPE-184283-MS, presented at the SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, 2–4 August 2016.
- [15] Al-Marhoun MA. Reservoir Fluid Properties; State of the Art and Outlook for Future Development. SPE 101449 - DL. In: Proceedings of SPE distinguished lecturer program. Richardson TX. Society of Petroleum Engineers. 4 July, 2002.
- [16] Dindoruk B, Christman PG. PVT Properties and Viscosity Correlations for Gulf of Mexico Oils, SPE Reservoir Evaluation & Engineering Volume 7, Issue 06, December 2004. SPE-89030-PA.
- [17] Shahab MB. Virtual Intelligence in Petroleum Engineering Part 1 Artificial Neural Networks Society of Petroleum Engineers, Journal of Petroleum Technology,2000; 52(09): 64-73.
- [18] Al-Shammasi AA. Bubble Point Pressure and Oil Formation Volume Factor Correlations. SPE 53185. In: Proceedings of the SPE Middle East Oil show. Bahrain. Society of Petroleum Engineers. 20-23 February, 1999.

To whom correspondence should be addressed: Dr. Ikpeka Princewill Maduabuchi, Department of Petroleum Engineering,Federal University of Technology, Owerri, Nigeria

# Article

**Open Access** 

THE USING OF COAL BLENDS WITH AN INCREASED CONTENT OF COALS OF THE MIDDLE STAGE OF METAMORPHISM FOR THE PRODUCTION OF THE BLAST-FURNACE COKE. MESSAGE 2. ASSESSMENT OF COKE QUALITY

V. P. Lyalyuk, V. P. Sokolova, I. A. Lyakhova, D. A. Kassim, E. O. Shmeltser\*, D.V. Miroshnichenko

<sup>1</sup> Kryvyi Rig Metallurgical Institute, Ukraine National Metallurgical Academy, 50006, Kryvyi Rig, Ukraine <sup>2</sup> National Technical University "Kharkiv Polytechnic Institute",61002, Kharkiv, Ukraine

Received September 27, 2018; Accepted December 21, 2018

#### Abstract

Industrial tests show that the enrichment of coal blends containing more than 70% bituminous coals with high level of fluidity (HFC) must be increased in order to improve coke strength. However, it makes more sense to replace some of the HFC in the blend with an optimal quantity of low-metamorphic coal, and to reduce the degree of crushing, so as to ensure coke quality consistent with blast-furnace requirements (minimum strength  $M_{25} = 90\%$ ,  $M_{10} = 6\%$ ). **Keywords:** *oal batch; bituminous coal; crushing; clinkering properties; coke strength.* 

, , , , , ,

#### 1. Results and discussions

The table presents the characteristics of the coke, which was produced at the ArcelorMittal Kryvyi Rig.

				Chara	cteristi	cs, %			
Year	<b>W</b> <sup>r</sup> t	A <sup>d</sup>	S <sup>d</sup> t	M <sub>25</sub>	M <sub>10</sub>	>80 mm	<25 mm	CSR	CRI
2005	2.7	11.6	1.38	87.4	7.6	8.5	3.8	30.9	45.1
2006	2.9	12.3	1.08	88.4	7.5	9.1	3.1	42.0	37.1
2007	3.2	12.6	0.86	87.5	7.9	8.8	4.0	47.6	36.0
2008	3.5	13.1	0.80	85.0	9.3	12.4	5.8	41.2	40.4
2009	3.9	12.9	0.84	84.5	9.0	10.9	5.9	41.9	41.5
2010	4.4	12.9	0.88	83.4	8.6	7.3	6.8	41.2	41.5
2011	3.8	12.4	0.88	86.6	7.6	10.6	5.1	47.4	42.1

Table. Coke characteristics (2005–2011)

Analysis shows that the indices of resistance of coke abrasion ( $M_{10}$ ) and crushability ( $M_{25}$ ) deteriorated markedly from 2006 to 2010 and improved in 2011 insufficiently to meet blast-furnace requirements <sup>[1-5]</sup>.

Analysis of the decline in coke quality at ArcelorMittal Kryvyi Rig has identified factors such as the following <sup>[6-13]</sup>: the large number of coal suppliers; the instability of concentrate supplies (with 60–80 reconfigurations of the blend in some months); imprecise selection of the optimal degree of blend crushing (the content of the  $\leq$ 3 mm class), such that the blend density and content of the lean class (<0.5 mm) fluctuated impermissibly with the varying rank composition; poor blending of the blend after crushing (very poor blending in terms of some characteristics, such as the content of the <0.5 mm class); increased moisture and ash content of the coking blend; and extreme fluctuation in the coal and blend characteristics.

Insufficient attention has been paid to the selection of the optimal degree of blend crushing with a very high content of HFC. In the coking blend at ArcelorMittal Kryvyi Rig, the content of HFC fluctuated from 56 to 89% in 2011, according to petrographic data.

Semantic analysis (content analysis) of the information sources, which assesses the intensity of research in coke chemistry, clearly shows that very fine crushing of HFC is regar-ded as inexpedient in most publications (such as <sup>[14–22]</sup>). For example, with a considerable proportion of HFC in the blend, only the large concentrate need be crushed, with an overall level of crushing of 75–80% (that is, with 75–80% of the  $\leq$ 3 mm class), according to <sup>[14]</sup>. To obtain coke of optimal quality, 75% crushing of HFC, 80% crushing of low metamorphic coal, and 85% crushing of high metamorphic coal is recommended in <sup>[15]</sup>.

Industrial coking of blend with uncrushed concentrate consisting of blended HFC and lowmetamorphic coal shows the possibility of using larger blend, with reduction in the content of the  $\leq 3$  mm class from 78 to 74.5%. Such preparation of the batch does not reduce coke strength, and blast-furnace operation is satisfactory <sup>[16]</sup>.

At Kryvyi Rig coke plant, the crushing of low-metamorphic coal and a binary low-metamorphic + HFC blend corresponded to at least 80% of the  $\leq$ 3 mm class; for high-metamorphic coals, the corresponding figure was 90%; and HFC coal, which contained 76–77% of the  $\leq$ 3 mm class, were introduced in the blend without further crushing, according to <sup>[17]</sup>. Subsequently, at Kryvyi Rig coke plant, as a result of research with blend containing 65–95% of the  $\leq$ 3 mm class, the following levels were adopted: 75% for the blend as a whole; 75–76% for lowmetamorphic coal; 90–92% for lean coal; and 60–70% for HFC <sup>[18]</sup>.

At Zaporozhe coke plant, with a large proportion of low-metamorphic and HFC in the blend, the overall degree of crushing was reduced so as to improve coke quality by increasing the batch density: from 88.4 to 84.7% of the  $\leq$ 3 mm class. The content of the lean class ( $\leq$ 0.5 mm) was reduced from 46 to 38.1%, with gains in coke quality [<sup>19</sup>].

Excessive crushing of coal with good clinkering properties should be avoided according to <sup>[20]</sup>. Such crushing reduces the yield of liquid thermostable products, which bind the other components of the blend.

In studying the mutual penetration of the thermal-destruction products of different coals, it was established in <sup>[21]</sup> that, in all cases, decrease in grain size sharply reduces the motion of the destruction products of HFC, which is most fully converted to a liquid like plastic state. That explains why coke quality deteriorates as a result of fine crushing of HFC coal and the inclusion of a high content of such coal in the blend.

Large classes of HFC and high metamorphic coal obtained with cautious crushing are very similar in composition to grains of the same coal in the  $\leq$ 3 mm class and have better properties in coking, according to the experiments in <sup>[22]</sup>. Consequently, there is no need for fine crushing of such coal <sup>[22]</sup>.

Note that the foregoing applies to standard blend recommended for the production of blastfurnace coke of satisfactory quality. On average, standard blend consisting of coal from different basins contains no more than 30–55% HFC and 35–20% low-metamorphic coal (from the Donets and Karaganda basins, respectively)<sup>[23]</sup>.

The opposite opinion was advanced in <sup>[24]</sup>. According to that argument, since coking is based on the interaction of coal particles with different properties, the preparation of each component must take account of the properties of all the other components and their proportion in the blend. If the lean coal is very finely crushed, say, its clinkering properties may be further reduced on account of the higher content of the <0.5 mm class and, equally importantly, its specific surface may be increased so much that satisfactory coke cannot be obtained even from a blend of such coal with highly coking coal. Therefore, the optimal balanced degree of crushing must ensure the required contact between grains, without reducing the coking properties of the components (without increasing the content of the <0.5 mm class). On that basis, it was concluded in <sup>[24]</sup> that relatively fine crushing of HFC (in particular, of blend with moderate or poor coking properties) may improve the overall coking of the blend and increase the coke strength. In other words, additional crushing of HFC does not impair the coking properties and increases the contact area of the most valuable component in the blend with the other components, thereby resulting in greater coking. In a 2-kg furnace, coke of higher strength was obtained from blend containing 60% HFC with greater crushing in <sup>[24]</sup>.

We know that, with excessive HFC in the blend, the coke cracks, and small pieces predominate. The basic property of HFC is to hold together a considerable quantity of lean additives. Without sufficient additives, blend with a large content of HFC must be thoroughly crushed in order to prevent excessive coking properties.

As already demonstrated, the content of HFC in the coking blend at ArcelorMittal Kryvyi Rig may be as much as 89%. The blend is crushed in the coal preparation shop without any possibility of separate crushing of the HFC so as to reduce its coking properties. Since the degree of crushing in the coal preparation shop was increased from 76 to 89% in 2011, while the content of HFC rose from 56 to 89%, the influence of these two factors on the coke quality may be analyzed.

In Fig. 1, we show the coke strength  $M_{25}$  as a function of the content of HFC in the blend, in the range 56–89% (on the basis of petrographic analysis in 2011). We conclude that, with variation in the degree of blend crushing in the range 76–89%, increasing the content of HFC above 60–70% reduces  $M_{25}$ .



Fig. 1. Dependence of the coke strength  $M_{25}$  on the blend's content of HFC

At the same time, if we analyze the dependence of the coke strength  $M_{25}$  on the degree of blend crushing within the given range, when the blend contains 70–89% HFC (Fig. 2), we see that the strength increases with increase in the degree of crushing. This increase in coke strength is due to the blend's loss of coking properties.



Fig. 2. Dependence of the coke strength  $M_{25}$  on the degree of blend crushing with 70–89% HFC

In Fig. 3, we see the variation in content of the lean class (<0.5 mm) with increase in the degree of crushing of blend containing 70–89% HFC. It follows from Fig. 4 that, in production conditions, increase in content of the <0.5 mm class in blend with a high content of HFC boosts coke strength. Thus, increasing the content of the <0.5 mm class from 37 to 47% raises  $M_{25}$  from 85.6 to 87.3%, on average.



Fig. 3. Dependence of the content of the <0.5 mm class on the degree of batch crushing (the content of the  $\leq$ 3 mm class), with 70–89% HFC



Content of the  $\leq 0.5$  mm class in the blend, %

Fig. 4. Dependence of the coke strength M25 on the content of the <0.5 mm class, with 70–89% HFC

Note that, whereas reducing the coking properties of HFC (by increasing the content of the <0.5 mm class) is necessary in order to boost the quality of coke produced from blend with an excess of HFC, this is not recommended as a rational approach to the preparation of coking blend. If the coking properties of the blend are excessive, that may be addressed by introducing lean additives and petrographically no uniform coal. As we know, it is expedient to combine HFC with low metamorphic coal. In addition, given the current shortage of high metamorphic coal, it is expedient to increase the proportion of low metamorphic coal in the blend.

In coal blend, we must maintain an optimal HFC content of no more than 40-50% and also introduce up to 30% low metamorphic coal <sup>[25]</sup>.

As an example, we note the experience of Bagleisk coke plant, where the coking blend was of variable composition and contained up to 70% coal with limited coking properties. The quantity of low metamorphic coal was increased from 29.5 to 56%, with decrease in the content of HFC from 39 to 21% and in the content of coal with V<sup>daf</sup>~18–22% from 17 to 9%. The content of high-metamorphic coal varied in the range 13–18%. The degree of blend crushing was 78.2–80.0% in terms of the content of the  $\leq$ 3 mm class. With increase in the content of coal with limited coking properties, the coke quality deteriorated, but timely correction of the degree of blend crushing permitted the maintenance of relatively high coke quality. Thus, with

29.5% low-metamorphic coal in the blend,  $M_{25} = 88.7\%$  and  $M_{10} = 5.5\%$ . With 56% low-metamorphic coal, the coke quality deteriorated:  $M_{25} = 85.3\%$ ;  $M_{10} = 7.3\%$  <sup>[26]</sup>.

In 2011, according to petrographic analysis, the low metamorphic coal content in coking blend at ArcelorMittal Krivoi Rog fluctuated basically in the range 0-22%. As follows from Fig. 5, increase in the low-metamorphical coal content to 15% was accompanied by increase in  $M_{25}$ , with reduction in the HFC content of the blend.



Fig. 5. Dependence of the coke strength  $M_{25}$  on the blend's content of low metamorphic coal

## 2. Conclusions

In industrial conditions, if the content of HFC in the blend is too high (>70%), the coke strength may be increased by crushing the blend until it contains 88% of the  $\leq$ 3 mm class, on account of the increase in content of the lean (<0.5 mm) class.

However, this means of boosting coke strength is not recommended, because the properties of valuable HFC are wasted, along with the power required for crushing. A better approach is to introduce the optimal proportions of low metamorphic coal and HFC in the blend, with appropriate crushing, so as to ensure coke quality consistent with blast-furnace requirements (minimum strength  $M_{25} = 90\%$ ,  $M_{10} = 6\%$ ).

#### Symbols

 $W^{r}t$  – water content of coke, %;  $A^{d}$  – ash content of coke in the dry state, %;  $St^{d}$  – sulphur of coke in the dry state, %;  $M_{10}, M_{25}$  – indices of resistance of coke abrasion and crushability, respectively, %; >80, <25 – content of particles more and less 80 and 25 mm in coke accordingly, %. CRI, CSR – coke reactivity index and coke strength after reaction, %

#### References

- [1] Miroshnichenko DV, Ulanovskij ML. Reactivity of coke: Methods of measuring and influence factors. Koks Khim., 2009; 5: 21–31.
- [2] Ulanovskij ML, Miroshnichenko DV. Improvement in CSR of coke at Dofasco. Koks Khim., 2005; 12: 46–50.
- [3] Ulanovskij ML, Miroshnichenko DV. About method of 'NSC' company of determining the coke quality. Koks Khim., 2005; 6: 18–21.
- [4] Miroshnichenko DV. Influence of coal preparation and coking conditions on coke reactivity. Coke Chem., 2009; 52: 77–82.
- [5] Drozdnik ID, Kaftan YS, Miroshnichenko DV, Bidolenko NB. Assessing the technological value of coal in coking. Coke Chem., 2016; 59 (7): 249–253.
- [6] Sheremet VA, Lyalyuk VP, Kekukh AV, et al., Influence of the Decrease in Moisture Content of the Coal Batch on the Coke Quality. Metallurg. Gornorud. Prom., 2009; 5: 16–19.

- [7] Sheremet VA, Lyalyuk VP, Otorvin PI, et al., Boosting the Quality of Blast-Furnace Coke by Increasing the Density of the Coal Batch. Metallurg. Gornorud. Prom., 2010; 1: 27–31.
- [8] Sheremet VA, Lyalyuk VP, Kekukh AV, et al., Rational Crushing of Coal Batch to Boost Metallurgical-Coke Quality. Metallurg. Gornorud. Prom., 2010; 2: 48–52.
- [9] Lyalyuk VP, Sheremet VA, Kekukh AV. et al., Assessing the Uniformity of Coal Batch. Metallurg. Gornorud. Prom., 2010; 4: 18–21.
- [10] Lyalyuk VP, Sheremet VA, Kekukh AV. et al., Change in the Petrographic Composition of Coal Batch on Crushing. Metallurg. Gornorud. Prom., 2011; 2: 13–17.
- [11] Lyalyuk VP, Uchitel' AD, Lyakhova IA. et al., Quality of Batch Preparation for Coking. Coke Chem., 2011; 8: 2–19.
- [12] Lyalyuk VP, Sokolova VP, Lyakhova IA. et al., Stability of Coke Quality in Blast-Furnace Smelting. Coke Chem., 2012; 8: 19–24.
- [13] Lyalyuk VP, Uchitel' AD, Lyakhova IA. et al., Influence of the Moisture Content of the Coal Batch on Coke Quality. Coke Chem., 2012; 9: 2–8.
- [14] Glushchenko IM. Prognoz kachestva koksa (Predicting Coke Quality), Moscow: Metallurgiya, 1976.
- [15] Margolis AR, Kravchenko DN, Samoilov VI, and Smirnov YuA., Influence of Crushing on the Batch Density and Coke Quality, Metallurgiya i koksokhimika (Metallurgy and Coke Chemistry), Kiev: Tekhnika, 1977; 54: 50–53.
- [16] Gainicheva GR, Byzova VI, Nikitin LD. et al., Coking of Coal Batch with Uncrushed G and Zh Concentrate: Influence of Coke Quality on Blast-Furnace Performance. Coke Chem., 1990; 2: 12–13.
- [17] Ivanitskii VG, Shegolev SV, Solov'ev GD, et al., Optimizing the Granulometric Composition of Coal Batch to Increase Its Density. Coke Chem., 1976; 7: 4–6.
- [18] Fomin AP, Dovgaya AL, Shatokha IZ, and Mazurenko NA. Selecting the Degree of Crushing of Coal Batch on Economic Principles. Coke Chem., 1986; 2: 44–46.
- [19] Kuleshov PYa, Eidel'man AE, Golubchik AL, and Elenskii FZ. Enhancing Coke Quality at Zaporozhe Coke Plant. Stal', 1963; 1: 8–10.
- [20] Kharkhardin PP, Lyukanov AG, Berlin MYa. et al., Improving Coal and Batch Preparation for Coking by Rational Crushing. Coke Chem., 1982; 12: 21–24.
- [21] Aronov SG, and Svetlorusova LP. Influence of the Crushing of Coal and Batch on Coking. Coke Chem., 1958; 1: 5–11.
- [22] Kuznetsov MD, and Ayannaya ZG. Composition and Properties of Large Classes of Donets Coal. Coke Chem., 1960; 5: 10–13.
- [23] Glushchenko IM. Khimicheskaya tekhnologiya goryuchikh iskopaemykh (Chemical Technology of Fossil Fuels), Kiev: Vishcha Shkola, Golovnoe Izd., 1985.
- [24] Taits EM, Enik GI, and Rizaev VV. Crushing of Coal with Elevated Clinkering Properties and Coke Strength. Coke Chem., 1987; 11: 37–39.
- [25] Lyalyuk VP, Kassim DA, Lyakhova IA, and Sokolova VP. Influence of Coal-Batch Composition on Coke Quality. Coke Chem., 2012; 12: 13–19.
- [26] Gulyaev VM, Nagornyi YuS, and Glushchenko LI. Influence of Batch Composition and Preparation on Coke Quality. Coke Chem., 1992; 11: 11–13.

To whom correspondence should be addressed: Dr. E. O. Shmeltser, Kryvyi Rig Metallurgical Institute, Ukraine National Metallurgical Academy, 50006, Kryvyi Rig, Ukraine

# Article

**Open Access** 

INCREASE IN RESOURCE EFFICIENCY OF MOTOR GASOLINE PRODUCTION WITH THE HELP OF MATHEMATICAL MODELS

Vyacheslav A. Chuzlov<sup>1</sup>\*, Igor' M. Dolganov<sup>1</sup>, Irena O. Dolganova<sup>1</sup>, Gaini Zh. Seitenova<sup>2</sup>, Rizagul' M. Dusova<sup>1</sup>

<sup>1</sup> Tomsk Polytechnic University, Russia

<sup>2</sup> S. Toraighyrov Pavlodar State University, Pavlodar, Kazakhstan

Received September 18, 2018; Accepted December 21, 2018

#### Abstract

In this paper, the way of increasing resource efficiency of motor gasoline production by integration of heptane isomerization process was performed. The estimation of the efficiency of isomerization process integration to the oil refinery structure was carried out by using the performed models. These models are sensitive to changes in hydrocarbon composition and physical-chemical properties of the processed feedstock and operation conditions of industrial units. Integration to the finished motor gasoline process the technology of C7 isomerization allows to decrease in high cost flows (alkylate, toluene, MTBE) due to a significant increase in RON of low octane flows of the plant.

*Keywords*: mathematical modeling; isomerization; blending; resource efficiency.

#### 1. Introduction

One of the effective ways of production of high octane gasoline, which meets modern ecological restrictions, is the development of integrating complexes of high octane flows with low benzene and sulfur content. However, integration of these complexes in the structure of operative oil refinery leads to a number of complicated technological problems, for example providing desirable quality and quantity of the feedstock, supporting the optimal catalyst activity and supplying of the optimal operating conditions of every unit, taking into account the energy and resource efficiency of the production. The most effective solution of these similar complicated chemical-technological problems is to use forecasting mathematical models which are built on physical-chemical and macrokinetic regularities of industrial finished motor gasoline production processes.

#### 2. Object of research

In this paper, the object of research is process flow diagram of industrial finished motor gasoline production process, including stages of catalytic conversion of hydrocarbon feedstock and blending of high octane flows. (Fig. 1).

Currently, the process of catalytic isomerization of  $C_7$  fraction does not have any industrial application (dash line in the PFD). However, there are a number of researches that are directed on this process <sup>[1-4]</sup>. Authors have performed the kinetic model of this process in order to estimate the efficiency of the integration of this technology in the structure of the industrial plant.

#### 3. Method of research

The design of the physical-chemical reactor model, in general, includes the next stages: analysis of experimental data from the industrial unit, studying of the reaction mechanism on the catalyst surface, formation of the reaction list, which occurs due to the process, estimation of the thermodynamic probability of these chemical reactions, validation of the formalization level of the reaction scheme, composition of the system of differential equations of the kinetic model, estimation of kinetic parameters of the model using experimental data, calculation of the reactor and validation of the hydrodynamic model, verification of the model.



Figure 1. Block diagram of the finished motor gasoline production

Based on the experimental data from the laboratory isomerization unit the following reaction scheme was performed (Fig. 2).





According to the law of mass action, the elementary reaction rate due to constant temperature is proportional to the concentration of the substance in the power of the stoichiometric coefficient:

(1)

(2)

 $r = k.f(C)_i$ 

 $f(C) = C_1^{\nu 1} . C_2^{\nu 2} ... C_n^{\nu n}$ 

where r – reaction rate, k – rate constant,  $C_i$  – initial concentration,  $v_i$  – stoichiometric coefficient.

In this way the kinetic model of the isomerization reactor is performed by differential equations system of material balance for every component:

 $[nP_5] =$ - R[1] + R[2] - R[3] + R[4] + R[6] - R[31];  $[iP_5] =$ R[1] - R[2] - R[5] - R[35];R[3] R[4] + R[5] - R[6] + R[39] + R[41] + R[44]; $[N_5] =$  $[H_2] =$ R[3] - R[4] + R[5] - R[6] + R[9] - R[10] + 3\*R[11] - 3\*R[12] + R[13] -R[14] + R[17] - R[18] + 3\*R[19] - 3\*R[20] + R[21] - R[22] + R[25] - R[26] + 3\*R[27] - 3\*R[28] + R[29] - R[30] - R[31] - R[32] - R[33] - R[34] - R[35] -R[36] - R[37] - R[38] - R[39] - R[40] - R[41] - R[42] - R[43] - R[44]; - R[7] + R[8] - R[9] + R[10] - R[32]; $[nP_6] =$  $[iP_6] =$ R[7] - R[8] - R[13] + R[14] - R[36]; $[N_6] =$ R[9] - R[10] - R[11] + R[12] + R[13] - R[14] - R[39] + R[40] + R[43];  $[A_6] =$ R[11] - R[12];  $[nP_7] =$ R[15] + R[16] - R[17] + R[18] - R[33];[iP<sub>7</sub>] = R[15] - R[16] - R[21] + R[22] - R[37]; $[N_7] =$ R[17] - R[18] - R[19] + R[20] + R[21] - R[22] - R[40] - R[41] + R[42]; $[A_7] =$ R[19] - R[20];  $[nP_8] =$ - R[23] + R[24] - R[25] + R[26] - R[34];R[23] - R[24] - R[29] + R[30] - R[38];  $[iP_8] =$  $[N_8] =$ R[25] - R[26] - R[27] + R[28] + R[29] - R[30] - R[42] - R[43] - R[44]; $[A_8] =$ R[27] - R[28]; R[31] + R[32] + R[33] + R[34] + R[35] + R[36] + R[37] + R[38] + R[39] + $[C_1 - C_4]$ R[40] + R[41] + R[42] + R[43] + R[44];where R[1]-R[44] – chemical reaction rates from the formalized scheme.

Verification of the model was conducted by comparison of calculated and experimental isomerate compositions due to different temperatures (Table 1).

Table 1. Verification of the isomerization reactor model

	200	)°C	120	)°C
Component	Experiment,	Calculation,	Experiment,	Calculation,
	wt. %	wt. %	wt. %	wt. %
C1-C4	3.60	3.60	2.08	0.27
nC5	0.31	0.34	0.71	0.72
iC 5	0.82	0.84	0.38	0.41
N5	0.00	0.00	0.00	0.00
nC6	0.67	0.42	1.66	2.00
iC6	4.19	4.51	0.66	0.61
N6	2.65	2.54	3.40	3.48
<b>A</b> 6	0.00	0.01	0.00	0.01
nC7	15.99	16.04	26.05	26.13
iC7	48.76	49.01	32.09	33.05
N7	17.77	17.64	22.52	23.24
A7	0.00	0.00	0.00	0.01
nC8	1.14	1.18	1.14	0.86
iC8	2.99	2.73	7.19	7.13
N8	1.11	1.13	2.12	2.08
A8	0.00	0.01	0.00	0.00

Model verification shows low deviations of calculated end experimental values within 1-2 %, that allows to use it for real process description.

#### 4. Results and discussion

The composition of the isomerization feedstock can change in a wide range (for i-C<sub>5</sub>: 8.0-20.0, for n-C<sub>5</sub>: 17.0-32.0, for n-C<sub>6</sub>: 14.0-25.0 wt. %), which takes influence to the products quality and cases necessity to correct technological parameters of the industrial unit. The study of the influence of the feedstock composition on isomerate quality was carried out due to constant operation conditions (Table 2). The result of the research is performed in Fig. 3.

Table 2. Operation conditions of the isomerization process

Parameter	Value
Feedstock volume flow rate, h <sup>-1</sup>	90
Temperature of the reactor inlet, °C	200
Mole ratio H <sub>2</sub> /CH	3
Reactor pressure, MPa	2.5



Figure 3. The influence of the feedstock composition on isomerate (calculation)

It was established, that isomerate RON changes from 2 to 2.5 points in dependence on feedstock composition.

It was found, that for C<sub>7</sub> isomerization process the optimal temperature is 190-210°C. The contribution of the side reaction of gas formation becomes more significant at higher temperatures (Fig. 4).



Figure 4. The temperature influence on the C7 isomerization process: A – isomerate yield; B –isomerate RON

At low temperature, the isomerization rate is limited by a kinetic factor, which is conditioned by low values of reaction constants. At high temperature, the thermodynamic factor is manifested because isomerization is the exothermic process.

Thus there is an area of the optimal process temperature, which is determined by operation conditions, feedstock composition and equipment design of the process.

In this paper, the opportunity estimation of  $C_7$  isomerization process integration was performed. Results of research are shown in Fig. 5.



Figure 5. The estimation of the opportunity of C7 isomerization process integration: A – gasoline RON 92; B – gasoline RON 95

The estimation of heptane isomerization process integration to the oil refinery structure was conducted due to determined quality and quantity of blending components and present production level of finished motor gasoline. Low octane blending components was used as isomerization feedstock. According to results of research, isomerization process integration allows to decrease the percent of high coast blending flows such as alkylate, toluene, MTBE by significantly increasing of low octane flows RON.

#### 5. Conclusion

Kinetic model of  $C_7$  isomerization process can be used for forecasting in dependence on different feedstock composition and operation conditions of the reactor: – composition and yield of the product; – products RON.

Complex application of mathematical models of isomerization and blending processes allows conducting of the estimation of the feedstock composition and operation conditions influence on hydrocarbon composition and properties of blending components and finished motor gasoline recipes.

#### Acknowledgements

The work was financed by subsidy for state support to the leading universities of the Russian Federation in order to increase their competitiveness among the world's leading research and educational centers. The research was aslo supported by RSCF grant Nº 18-73-00086

#### References

- [1] Smolikov MD., Shkurenok VA, Yablokova SS, Kir'yanov DI, Paukshtis EA, Leont'eva NN, Belyi AS, Drozdov VA. Preparing and Studying Pt/WO<sub>3</sub>/ZrO<sub>2</sub> Catalysts for the Isomerization of n-Heptane. Catalysis in Industry,2017;9(1): 54–61.
- [2] Smolikov MD, Shkurenok VA, Yablokova SS, Kir'yanov DI, Doronin VP, Sorokina TP, Bikmetova LI, Gulyaeva TI, Paukshtis EA, Belyi AS. Effect of the Zeolite Modulus of Pt/MOR/Al<sub>2</sub>O<sub>3</sub> Catalysts on the n–Heptane Isomerization Reaction. Catalysis in Industry, 2016; 8(2): 121–127.
- [3] Smolikov MD, Shkurenok VA, Yablokova SS, Kir'yanov DI, Belopukhov EA, Zaikovskii VI, Belyi AS. Isomerization of n-Heptane on Pt/MOR/Al<sub>2</sub>O<sub>3</sub> Catalysts. Catalysis in Industry, 2014; 6(3): 223–230.
- [4] Shakun AN, Fedorova ML. Isomerization of light gasoline fractions: The efficiency of different catalysts and technologies. Catalysis in Industry, 2014; 6(4): 298–306.

To whom correspondence should be addressed: Dr. Vyacheslav A. Chuzlov, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, Russia

# Article

# **Open Access**

#### ASSISTED HISTORY MATCHING USING EVOLUTION STRATEGY ALGORITHM

Mohammed Abdelfetah Ghriga<sup>1\*</sup>, Mohamed Lamine Khelifi<sup>2</sup>, Ahmed Hadjadj<sup>1</sup>, Sofiane Belhocine<sup>3</sup>

<sup>1</sup> Laboratory of Hydrocarbons Physical Engineering, Faculty of Hydrocarbons and Chemistry, University M'Hamed Bougara of Boumerdes, Independence Avenue, 35000-Boumerdes, Algeria

<sup>2</sup> Petroceltic International PLC, 17 Khoudi Mohamed street, 16003 El Biar-Algiers, Algeria

<sup>3</sup> Software Integrated Solutions Segment-Schlumberger Algeria, Amara Activity Zone, 16002 Cheraga -Algiers, Algeria

Received September 12, 2018; Accepted December 21, 2018

#### Abstract

Predicting the behaviour of oil reservoirs depends crucially on the reliability of their numerical models. However, the latter have great uncertainties that push petroleum engineer to validate them periodically by the commonly known process of "History Matching (HM)". In practice, engineers perform this process manually, which is difficult and tedious. In this article, we aim to assist and accelerate this process using the Evolution Strategy algorithm implemented on Petrel RE software. We are evaluating for the first time the effectiveness of such an algorithm on a real numerical model. The latter is composed of nine production wells under a natural depletion regime with a historical production data of 6 years. For this, we have followed four steps, starting from the definition of an objective function, passing by sensitivity and uncertainty analysis on the model properties and finishing with the optimization process. As a result, the Algorithm was found to successfully match the historical production data of both the field and the wells and in a shorter time compared to the traditional method.

Keywords: Numerical Model; Manual History Matching; Assisted History Matching; Evolution Strategy; Optimization.

#### 1. Introduction

Optimizing the development of an oilfield (number of wells, well type, well location, and design operations, etc.) requires predicting its behavior under different scenarios, this is only possible using numerical models which represent the in-situ properties/conditions and can reproduce its historical production. Several disciplines (geology, geophysics, petrophysics, engineering, etc.) interact to build these numerical models by describing the best estimates of reservoir properties such as porosity, permeability, saturation, etc. Once a model is built, it can be used to predict the reservoir performance under different development strategies. However, a question is always raised: are these properties reliable? To answer this question, a simulation of the behavior of the model for a historical period of production is needed. The simulated results (flow rates, pressures, etc.) are in this case compared to the actual data (i.e., measured flow rates and pressures). However, and unless the engineer is very lucky, the initial model will never reproduce the behavior of the reservoir for the historical period. The estimated properties have always a great uncertainty especially in areas where the engineers have a lack of knowledge (i.e., deep in the reservoir). Therefore, it is necessary to adjust these uncertain properties, so the simulated results and production data are matched to a sufficient degree. This process is called: History Matching (HM).

The HM is an important step in the simulation studies. It allows validating and improving the numerical model and understanding the various phenomena of the reservoir. In practice, the engineer does it manually: he changes iteratively one uncertain parameter at a time and then simulates and evaluates the reduction in the mismatch. This makes the HM process very difficult and time consuming, first because of the multitude uncertainties in the properties of thousands of cells, or even millions of them. Secondly, because of the qualitative evaluations of the mismatch made by the engineer. To overcome these difficulties; the idea is to quantify the existing mismatch in an objective function, and then seeking the adequate values of the reservoir properties for which the objective function is minimal. This makes the history matching a nonlinear, multidimensional and a very complex optimization problem. To solve such a problem, a powerful optimization tool is thus necessary: this methodology is called Assisted History Matching (AHM). In our study, we will apply the Evolution Strategy algorithm in order to assist the process of HM.

The Evolution Strategy (ES) is a stochastic research optimization algorithm based on the population and which uses mathematical operators inspired by the Darwinian evolution theory such as mutation, recombination, and selection. It belongs to the family of metaheuristics Evolutionary Algorithms.

## 2. Overview of the History Matching

The HM process, as shown in Figure 1, was defined in the literature as "the process of changing the uncertain properties of the reservoir model until the simulated results for a historical period are "fit" with production data <sup>[1]</sup>".

In other words, it is the adjustment of the reservoir model using production history to reproduce the observed behavior <sup>[3]</sup>. The purpose is to determine the description of the reservoir (initial spatial distribution of properties) that minimizes the difference between the observed data and the results predicted by the simulator. Matheron was the first to make the initial approaches in the field of HM <sup>[4]</sup>. Later, Deutsch applied the HM in the oil reservoir models <sup>[5]</sup>. In recent years, the interest for matching the numerical models of oil reservoirs has increased, and this was expressed by the increase in the annual number of publications related to the HM, published in SPE (Society of Petroleum Engineers) and presented in Figure 2.



Fig.1. General History Matching process <sup>[2]</sup>



Fig.2. Annual number of publications related to the History Matching, published in the SPE papers and conferences <sup>[6]</sup>

#### 2.1. Manual history matching

The Manual History Matching (MHM) is a "trial and error" process: the engineer runs the simulation model for a historical period and compares the simulated results with measured data <sup>[7]</sup>. Once the results are compared, the engineer changes the reservoir properties iteratively and one by one trying to improve the calibration of the model

In general, MHM proceeds through three stages <sup>[8]</sup>:

- Pressure match phase.
- Saturation match phase.
- Productivity Index (PI) match phase.

Sadly, the MHM consumes up to 40 of the time during a numerical simulation study, which is even higher than the time needed to build the model as shown in Figure 3.



Fig.3 Time consumed by the MHM during a numerical simulation study



Fig. 4. 50 year of History Matching 1960-2010

## 2.2. Assisted history matching

The Assisted History Matching (AHM) consists in quantifying the offset (mismatch or misfit) between the observed data and simulated results in an Objective Function called the "error function". This function is then minimized by finding the optimal values of reservoir properties using coded optimization algorithms <sup>[7]</sup>. Therefore, this process converts the HM to an optimization problem.

Over than 40 successful AHM projects were conducted worldwide by the service company MEPO (Multipurpose Environment for Parallel Optimization) <sup>[11]</sup>. The time needed for numerical models with over than 600 properties and 1000 wells varied between 1 week to 9 months, according to the cluster's CPU time.

## 3. Evolution Strategy Algorithm (ES)

Throughout history, several optimization algorithms were used to reduce the time of the HM. Most of these algorithms are metaheuristics stochastic algorithms. Figure 4 shows the different algorithms used in the HM since the sixties until now <sup>[2]</sup>.

The ES was chosen in this case because of its flexibility (resolution of direct or inverse problems, minimizing or maximizing problems) and its ability to find the global optimum. It is a population-based research optimization algorithm that employs operators inspired from the Darwinian evolution theory such as selection, mutation, recombination and it belongs to the family of metaheuristics of Evolutionary Algorithms <sup>[9]</sup>. The algorithm was first proposed by Ingo Rechenberg in 1965 at Berlin Technical University, Germany. The method was then developed during the late sixties, mainly through the work of Rechenberg *et al.* on designing optimal aerodynamic profiles with the minimal friction with the air <sup>[10]</sup>. A general algorithm of the SE may be noted by  $(\mu/\rho, +\lambda)$ -ES, where :

 $\mu$ : the parents population.

- $\rho$ : Parents that will be combined to produce children.
- $\boldsymbol{\lambda}$  : the children population.
- , : « comma » selection.
- + : « *plus* » selection.

Figure 5 summarizes the steps of the ES Algorithm.

An application example of this algorithm is shown in Figure 6 <sup>[12]</sup> where the number of individuals of the parents and the children population is fixed at 8.





Fig. 5. Representative diagram of the principle of Fig. 6. Application example of the Evolution the Evolution Strategy Algorithm [11]

Strategy Algorithm [12]

To avoid the stagnation of the algorithm in local optimums, recombination and mutation operators allow better exploitation and exploration of the research space. The exploration, provided by the mutation, is to discover new areas in the research space. While exploitation ensured by recombination, is to benefit from the best individuals to achieve better individuals (Models). One should point out that a compromise between these two operators is needed to prevent the exploration-exploitation dilemma explained as follow: "Too exploitation results in convergence to a local optimum known as premature convergence, while too exploration leads to the non-convergence of the algorithm".

## 4. Case of application

## 4.1. Reservoir description



Fig. 7 General View of the reservoir

The Agaba reservoir is a sandstone reservoir which began production in January 2008 with 9 wells (A001, A002, P002A, P003A, P003C, P004A, P005A, and P005B). The reservoir (Figure 9) is a highly faulted oil reservoir with a gas cap. It has 4 main faults that divide the reservoir into 5 fault blocks. In some areas, the throw of the fault is so large that there is no sand-to-sand juxtaposition between the fault blocks. Geologists confirmed that fault 1 does not extend completely between fault block 3 and fault block 4. The geologist and geophysicists also agreed that there is very large aguifer

connected to the sides of the reservoir and that the uncertainty in the connection between the aquifer and the reservoir is directly related to the connection angle.

# 4.2. Problematic

The initial simulation of the numerical model (i.e., initial model) has shown (Figure 8) a huge mismatch between simulated and measured field and wells data over the 6 years for the water flow rate (WPR), the oil flow rate (PRO) and the gas flow rate (GPR).

# 4.3. Numerical model control mode

Each numerical model must have a control mode. This concept involves using the observed data of any parameter (oil flow rate, gas flow rate, water flow rate, reservoir pressure, reservoir volume) as initialization for calculating the results of the other parameters. For this, we have chosen the observed data of oil production as the control mode. The reasons for this choice were first the reliability of the observed oil production data compared to water or gas and secondly to reduce the number of parameters to match to only two parameters (water and gas). The simulator, in this mode, must reproduce the observed data of the oil and will calculate the flow of the other phases (gas and water) according to their mobility ratios. Consequently, as shown in Figure 9, the simulated results and observed for oil production were perfectly superposed. While the mismatch in the production of gas and water were persisted.





Fig. 8. Field cumulative observed production of water (a), oil (b) and gas (c) [11]



Fig. 9. Field cumulative production of water (a), oil (b), gas (c) in the oil control mode <sup>[11]</sup>

## 4.4. Assisted history matching

In order to implement an Assisted History Matching process in Petrel RE, we have followed four steps:

## 4.4.1. Definition of the objective function

The general objective function expresses the overall mismatch that should be minimized. It is defined by the following expression:

$$F = \sum_{Q} \sum_{I} w_{I} w_{Q} m(I,Q)$$

(1)

where: m(I, Q): the mismatch for the quantity Q in the well number I;  $w_I$ : weight on the well (higher values are assigned to wells with higher mismatch);  $w_Q$ : weight on the quantity (higher values are assigned to quantities with higher mismatch).

The general objective function given by equation (1) is the sum of the partial objective functions. The latter quantifies the mismatch for each quantity Q as shown in the following expression:  $F_0 = w_0 \sum_I w_I m(I,Q)$  (2)

In our case, we have two partial objective functions: one for water production rate and the other for gas production rate.

The observed results should be first inserted in the software, and four parameters should be defined:

- The measurement error "E": used to normalize the mismatch of each quantity, so the partial objective functions can be summed.
- The weight on the well " $w_I$ ": higher values are assigned to wells with a higher mismatch.
- The weight on the quantity " $w_Q$ " higher values are assigned to quantities with a higher mismatch.

The weight on time " $w_{\kappa}$ ": higher values are assigned to times with higher mismatch.

The chosen parameters for this case are resumed in Table.1.

Table 1. Objective function parameters

Quantity	Measurement error	Weight on the well	Weight on the quantity	Weight on the time
	"E″	wI	wQ	wK
Gas production rate (GPR)	10 MSCF/d	1	1	1
Water production rate (WPR)	5 STB/d	1	1	1

Errors on the gas and water flow rates are relatively high (10 MSCF/d and 5 STB/d) because of the technical and operational conditions such as the gauging conditions, three-phase flow metering, and the back allocation. In addition, these flow rates are not measured periodically as in the case of the oil. On the other hand, we have chosen to fix the weight of different parameters to 1, since the mismatch was observed for all quantities and for all the wells and we are looking to match them all.

After defining the objective function, an estimated value for the base case was obtained by running the first simulation. The results are summarized in Table.2. A value of "803.35" was obtained, and we will try to minimize it.

Table 2. Objective function of the base case

Base case	Objective1	Objective1_WPR	Objective1_GPR
HM	803.35	454.73	348.61
	100%	56.60%	43.40%

## 4.4.2. Sensitivity analysis

The purpose of a sensitivity analysis is the identification of the properties, which strongly influence the simulated results of the model. In this analysis, known also under the term "One Variable at One Time", one of the model properties is varied while keeping all the other variables constant. This process is then repeated for each uncertain property. The uncertain properties and their intervals are fixed by the engineer based on his analysis on the first simulation results. For this case, we have chosen the following properties:

Faults Transmissibility (Fault1, 2, 3, 4, 5): FTM1 [0; 1], FTM2 [0; 1], FTM3 [0; 1], FTM4 [0; 1], FTM5 [0; 1].

- Cells Transmissibility (X, Y, Z): MULTX [0.5; 2], MULTY [0.5; 2], MULTZ [0.5; 2].
- Aquifers contact angle (North/ South): AOF N[1: 360], AOF S[1: 360].
- Outer radii of (North/ South) aquifers: Ext Rad N [5000; 100000], Ext Rad S [5000; 1000001.
- Pore volume: PV [0.5; 1.5].



Fig.10. Tornado plot of the sensitivity study [11]

The results of the sensitivity analysis are visualized using a Tornado plot as shown in Figure 10, in this plot the effect of each property, on the objective function, is represented by a bar. As can be seen in this figure: Pore volume, South Aquifer contact angle, Cells Transmissibility in the X direction, Fault 5 Transmissibility, Fault 1 Transmissibility, Cells Transmissibility in the Y and Z directions, Fault 2 Transmissibility and Fault 3 Transmissibility, are the most influencing properties.

#### 4.4.3. Uncertainty analysis

This step involves samples from each sensitive property within the defined research space which are combined and simulated in a random way and then the objective function for the resulted models is evaluated. The samples are chosen using a numerical sampler to try to cover all the research space of each property.

A stochastic sampler "Monte Carlo" with the Latin-hypercube method was selected to choose a random 300 sample from each property. This will allow a better exploration of the research space and will provide us with a set of cases to initialize the optimization algorithm afterwards. The properties and their corresponding intervals that were selected for this analysis are:

- Faults Transmissibility (Fault1, 2, 3, 5): FTM1 [0; 1], FTM2 [0; 1], FTM3 [0; 1], FTM5 [0; 1].
- Cells Transmissibility (X, Y, Z): MULTX [0.5; 2], MULTY [0.5; 2], MULTZ [0.5; 2].
- (North/ South) Aquifer contact angle: AOF\_N[1; 360], AOF\_S[1; 360].
- Pore volume: PV [0.5; 1.5].

The properties "north aguifer outer radii, south aguifer outer radii, Fault 4 transmissibility" were not selected at this level, because of their neglected effect on the simulation results as shown by the tornado plot. However, the north aguifer contact angle was selected despite its minimal effect as we have estimated that it can still affect the simulation results. The simulation was then executed, where 300 numerical model were obtained. The results of the uncertainty analysis for four cases (randomly chosen among 300 cases) are presented in Table 3.

Case	HM_206	HM_344	HM_272	HM_224
\$PV	1.18	1.14	0.53	0.54
\$MULTZ	2.48	0.78	0.86	0.98
\$MULTY	1.77	0.57	1.76	1.68
\$MULTX	0.92	2.25	1.82	1.06
\$FTM5	0.87	0.49	0.34	0.25
\$FTM3	0.47	0.03	0.54	0.81
\$FTM2	0.49	0.54	0.97	0.28
\$FTM1	0.00	0.48	0.68	0.49
\$AoF_S	93.66	115.78	116.74	75.03
\$AoF_N	272.33	255.51	185.08	320.32
\$Objective1	416.80	530.82	2 624.78	3 247.80

Table 3. Uncertainty analysis results

From this table, one can see clearly that the Monte Carlo sampler has succeeded in exploring the research space by finding some interesting cases: the first two cases had an objective function value below the base case (803.35), and the other two unfavorable cases had an objective function value above the base case.

#### 4.4.4. Optimization

It is the heart of this study. the Evolution Strategy Algorithm is employed to generate numerical models with the lowest objective functions and which can match the observed data. First of all, we had to define the algorithm parameters (listed in table 4) in order to adapt the algorithm to our problem. This was done by running some trial tests. The chosen parameter values were summarized below (Table 4).

Parameter	Value	Parameter	Value
Maximum iterations	600	Required improvement	5%
Number of children	20	Improvement window	1 generation
Number of parents	10	Destabilization factor	2
Retain in population	yes	Random seed	1
Mutation standard deviation	0.1	Previous cases	Uncertainty cases
Parents par enfant	2		

Table 4. Evolution strategy algorithm parameters for the optimization process

The algorithm was then executed. The time needed to simulate all the 600 models was less than 12 hours thanks to the great capacity of the employed computer equipped with 5 CPUs. The results of the four best case obtained after the optimization was presented in Table 5.

Table 5. Best optimization results

Case	\$Obj1 WPR	\$Obj1 GPR	\$Obj1	% of reduction
HM938	102.392	220.425	322.817	60%
HM702	95.579	232.093	327.672	59%
HM751	92.994	236.824	329.818	59%
HM739	96.663	243.400	340.063	58%

According to Table 5, a total reduction of the objective function has reached up to 60% compared to the initial value (803.35) which is very remarkable for an HM process. Furthermore, three other cases reached up to 58% and 59% of reduction. Therefore, one can conclude that the optimization has provided several candidate models that can reflect the actual properties of the reservoir. Figure 11 and Figure 12 show the match obtained after the optimization at the field scale and for some wells (P003B, P004A and P005A) respectively. A perfect match was obtained for the water rate at both the field and well scale and for gas rate at the well scale. While the gas rate at the field scale had a less satisfactory match.



Fig. 11. Optimization results of the field [11].



Fig.12. Optimization results at the P3B (a), P4A (b), P5A (c) wells [11]

# 5. Conclusion

The History Matching (HM) had always required a lot of experience in reservoir engineering and the phenomena governing the reservoir and was always considered as an Art more than as a science; however, evolutionary algorithms can help in this task. In this study, a numerical model with 9 wells and two quantities (water and gas) with up to 13 uncertain properties needed for history matching. The task appeared impossible using the Manuel HM. Nevertheless, An Assisted HM using the Evolution Strategy Algorithm succeeded in matching it in less than 12 hours. At least four matched models were obtained with up to 60% reduction in the objective function. The success of the Evolution Strategy Algorithm in assisting the process of History Matching will certainly promote the use of such algorithms in other complex optimization problems in the oil industry.
#### References

- [1] Aziz K, and Settari A. Petroleum Reservoir Simulation, University of Calgary, Alberta, Canada, 1979.
- [2] Hajizadeh Y. Population-Based Algorithms for Improved History Matching and Uncertainty Quantification of Petroleum Reservoirs, Ph.D. Thesis, Heriot Watt University, Edinburgh, UK, March 2011.
- [3] Crichlow HB. Modern Reservoir Engineering A Simulation Approach, University of Oklahoma, 1977.
- [4] Matheron G. Principles of geostatistics. Economic geology, 1963.
- [5] Deutsch CV. Annealing techniques applied to reservoir modeling and the integration of geological and engineering (well test) data. Ph.D. thesis, Stanford University, 1992.
- [6] Corradi A. An example of particle iteration, 2010.
- [7] Ertekin T, Abou-Kassem JH, and King GR. Basic Applied Reservoir Simulation, Society of Petroleum Engineers SPE Textbook, Richardson, Texas, 2001.
- [8] Kossack CA. ECLIPSE Applied Reservoir Simulation Fundamentals, Schlumberger SIS, 2013.
- [9] Beyer HG, and Schwefel HP. Evolution Strategies: A comprehensive introduction, In Natural Computing, University of Dortmund, Germany, 2002.
- [10] Koumoutsakos P, Freund J, and Parekh D. Evolution Strategies for parameter optimization in jet flow control, University of California, Los Angeles, and Georgia Institute of Technology, 1998.
- [11] Khelifi ML, and Ghriga MA. Assistance de L'History Matching par l'algorithme de la Stratégie d'Évolution. Master Thesis. UMBB, 2015.
- [12] Larez CJ, Parades JE, and Pérez R. Evolution Strategy Algorithm through Assisted History Matching and Well Placement Optimization to Enhance Ultimate Recovery Factor for Naturally Fractured Reservoirs, SPE Paper 165943, 2013.

To whom correspondence should be addressed: Dr. Mohammed Abdelfetah Ghriga, Laboratory of Hydrocarbons Physical Engineering, Faculty of Hydrocarbons and Chemistry, University M'Hamed Bougara of Boumerdes, Independence Avenue, 35000-Boumerdes, Algeria, <u>ahrigafatah@yahoo.com</u>

# Article

**Open Access** 

THERMODYNAMIC ANALYSIS OF THE REACTIONS OF SULPHUR-CONTAINING COMPOUNDS IN THE PROCESS OF DIESEL FRACTIONS HYDRODESULPHURIZA-TION ON THE BASE OF QUANTUM-CHEMICAL CALCULATIONS

Evgeniya Frantsina\*, Nadezhda Krivtsova, Nataliya Belinskaya, Elena Kotkova

Department of Fuel Engineering and Chemical Cybernetics, National Research Tomsk Polytechnic University, Russia

Received August 31, 2018; Accepted December 21, 2018

#### Abstract

On the base of quantum-chemical calculations (DFT, B3LYP, 3-21G), thermodynamic parameters of the reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization were estimated. Based on the thermodynamic analysis, the probability of reactions occurrence was determined, the reaction scheme for hydrocarbon transformations was proposed, which can be used in mathematical modeling. It was shown that thermodynamic probability of the hydrogenolysis reactions increases in the series: dibenzothiophenes ( $\Delta Gr$ =-33.27 kJ/mol), benzothiophenes ( $\Delta Gr$ =-71.36 kJ/mol), thiophenes ( $\Delta Gr$ =-137.20 kJ/mol) and sulfides ( $\Delta Gr$ =-142.64 kJ/mol). It was found that hydrogenolysis of sulfides, thiophenes, and benzothiophenes proceeds irreversibly, and hydrogenolysis of dibenzothiophenes proceeds reversibly through the stage of aromatic hydrocarbons formation, followed by their hydrogenation to cycloparaffins. It was shown that in the series of thiophenes, benzothiophenes, and dibenzothiophenes, the thermodynamic probability of the hydrogenolysis reactions decreases with increasing molecular weight.

The values of the enthalpies of the sulfur-containing compounds reactions are calculated, and all reactions were shown to be exothermic. The greatest thermal effect is is observed for reactions of dibenzothiophenes hydrogenation to bicyclic paraffins ( $\Delta H_r$ =-514.89 kJ/mol), reactions of benzothiophenes to cycloparaffins ( $\Delta H_r$ =-398.71 kJ/mol), reactions of thiophenes to paraffins ( $\Delta H_r$ =-317.85 kJ/mol.

**Keywords**: thermodynamic analysis; hydrodesulphurization; diesel fractions; sulphur-containing compounds; quantum-chemical calculations.

#### 1. Introduction

Currently, the process of diesel fractions hydrodesulphurization is one of the basic processes in the oil refining industry and is widely used <sup>[1-2]</sup>. This is largely due to increased production of heavy oils with a high content of sulfur-containing compounds, as well as changing standards in the direction of strengthening environmental requirements <sup>[3-4]</sup>. In the process of diesel fractions desulphurization, reactions of removing heteroatomic compounds such as sulfur, nitrogen, oxygen, polycyclic aromatics and olefins occur <sup>[5]</sup>. However, the main purpose of the process is the removal of sulfur-containing compounds that cause corrosion of metal equipment and pollution of the environment due to the emission of sulfur-containing gases by diesel engines <sup>[6]</sup>. In addition, the process of diesel fractions hydrodesulphurization is an auxiliary process in catalytic technologies, which provides the removal of sulfur compounds that are catalytic poisons <sup>[7]</sup>. There are non-catalytic methods for removing sulfurcontaining compounds, for example, oxidative or adsorption methods <sup>[8-9]</sup>, however, catalytic hydrodesulphurization is currently the most efficient process. The direction of increasing the efficiency of the hydrodesulphurization process is important in order to increase the degree of removal of sulfur from complex hydrocarbons. To do this it is necessary to establish the thermodynamic probability of the hydrogenolysis reactions of various sulfur-containing compounds of the diesel fraction, mainly sulfides, thiophenes, benzothiophenes, and dibenzothiophenes. At the same time, it is relevant to estimate the probability of the hydrogenation reactions of sulfur-containing compounds in the same homologous series of different molecular weights in order to determine the most suitable methods of destruction of such compounds. The results of the thermodynamic analysis can be used to develop the scheme for the transformation of sulfur-containing compounds in the procedure of mathematical modeling of the process <sup>[10-11]</sup>.

Currently, molecular modeling methods, based on quantum-chemical calculations, are widely used to calculate various molecular properties, such as enthalpy, entropy, Gibbs energy, the total energy of a molecule and its most stable structure, and so on. They take into account the vibrational and rotational motions of atoms, the configuration of electronic orbitals, the effects of conjugation of double bonds, etc. <sup>[12-13]</sup>. These provide accurately calculate the energy parameters of molecular structures without binding to narrow classes of organic compounds.

The purpose of this work was to conduct thermodynamic analysis and determine the probability of the hydrogenolysis reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization based on quantum-chemical modeling.

### 2. Object of research

The process of diesel fractions desulphurization is the object of the current study. The main purpose of the process is the removal of sulfur-containing compounds such as sulfides, thiophenes, benzothiophenes, and dibenzothiophenes, proceeding on the nickel-molyb-denum catalyst at the temperature of 360°C and the pressure of 3.0 MPa. The feedstock was diesel fraction with the boiling range of 200-360°C, the total sulfur content of 1.40%wt., including 0.45%wt. of sulphides, 0.95%wt. of benzothiophene and dibenzothiophene.

#### 3. Method of research

The evaluation of the thermodynamic parameters ( $\Delta G_r$ ,  $\Delta H_r$ ) of hydrogenolysis reactions of various sulfur- containing compounds in the process of diesel fractions hydrodesulphurization was carried out using the software package Gaussian'09W, the Density Functional Theory (model of theoretical approximation B3LYP, basis 3-21G). The features of the method are, firstly, it accurately reproduces the structure and energy of hypervalent compounds and provides sufficient accuracy for the qualitative reproduction of many physical-chemical properties of the molecule. It is known that this method provides high accuracy for the calculation of hydrocarbon molecules containing heteroatoms and is used for thermodynamic analysis under conditions different from the standard ones <sup>[14-15]</sup>. The following average thermobaric conditions of the hydrodesulphurization process were used in calculations: the temperature of 360°C and the pressure of 3 MPa.

# 4. Results and discussion

With the use of the Gaussian'09W software package, the Density Functional Theory (model of theoretical approximation B3LYP, basis 3-21G), the main thermodynamic parameters of the reactions of sulfur-containing compounds that occur in the process of diesel fractions hydrodesulphurization were calculated at the average thermobaric process conditions (the temperature of 360°C and the pressure of 3 MPa).

To perform molecular modeling, a list of possible reactions with the most probable sulfurcontaining compounds presented in the diesel fraction was compiled. It is known that hydrogenation processes of sulfur-containing compounds, as well as the hydrogenation of monoand polyaromatic compounds, olefins, predominantly occur in the process of hydrodesulphurization. The list of reactions used for the study is presented in Table 1. Thermodynamic analysis showed (Table 2) that the thermodynamic probability of hydrogenolysis reactions decreases in the series: sulfides>thiophenes> benzothiophenes> dibenzothiophenes, which is associated with an increase in their stability and is confirmed by literature data <sup>[5]</sup>. In this case, the hydrogenolysis reactions of all sulfur-containing compounds are thermodynamically probable. The average Gibbs energy of hydrogenolysis reactions of sulfides, thiophenes, benzothiophenes and dibenzothiophenes to cycloparaffins is -142.64 kJ/mol; -137.20 kJ/mol; -71.36 kJ/mol and -33.27 kJ/mol, respectively.

Table 1. Hydrogenation reactions of various sulfur-containing compounds in the process of diesel fractions hydrodesulphurization

Reaction	Number of carbon atoms in the molecule
Thiophenes $\rightarrow$ Paraffins	4-9
$Benzothiophenes \rightarrow Cycloparaffins$	8-14
Benzothiophenes $\rightarrow$ Monoaromatic hydrocarbons	8-14
Monoaromatic hydrocarbons $\rightarrow$ Cycloparaffins	8-14
Dibenzothiophenes $\rightarrow$ Bicyclic paraffins	12-18
Dibenzothiophenes $\rightarrow$ Diaromatic hydrocarbons	12-18
Diaromatic hydrocarbons $\rightarrow$ Bicyclic paraffins	12-18
Sulphides $\rightarrow$ Paraffins	8-13
Olefins $\rightarrow$ Paraffins	6-11

Table 2. Thermodynamic parameters of sulfur-containing compounds reactions in the process of diesel fractions hydrodesulphurization (T=360°C, P=3 MPa

Reaction	⊿Gr, kJ/mol	∆Hr, kJ/mol
Thiophenes $\rightarrow$ Paraffins	-137.20	-317.85
Benzothiophenes $\rightarrow$ Cycloparaffins	-71.36	-398.71
Benzothiophenes  o Monoaromatic hydrocarbons	-30.71	-57.47
Monoaromatic hydrocarbons $\rightarrow$ Cycloparaffins	-39.72	-341.08
Dibenzothiophenes $\rightarrow$ Bicyclic paraffins	-33.27	-514.89
Dibenzothiophenes $\rightarrow$ Diaromatic hydrocarbons	-37.82	-70.87
Diaromatic hydrocarbons $\rightarrow$ Bicyclic paraffins	4.52	-444.04
Sulphides $\rightarrow$ Paraffins	-142.64	-115.24
Olefins $\rightarrow$ Paraffins	-52.83	-134.37

According to the thermodynamic analysis, the reaction of dibenzothiophenes hydrogenolysis are reversible. The average  $\Delta G_r$  is -33.27 kJ/mol, and these reactions pass through the aromatic hydrocarbon formation stage with subsequent hydrogenation to cycloparaffins. Reactions of sulfides, thiophenes, and benzothiophenes are irreversible. The average  $\Delta G_r$  is -146.64 kJ/mol, -137.20 kJ/mol and -71.36 kJ/mol, respectively. Herewith, benzothiophenes hydrogenolysis proceeds predominantly via the hydrogenation step, while the reaction of heteroatoms removing from dibenzothiophenes can pass both in the direction of hydrogenation and hydrogenolysis <sup>[5]</sup>. According to the value of the Gibbs energy of the reaction, the probability olefins hydrogenation is estimated, and it is shown that this reaction proceeds irreversibly ( $\Delta G_r$ =-52,83 kJ/mol).

Based on the calculated values of Gibbs energy of hydrogenolysis reactions of various sulfurcontaining compounds in one homological group, their thermodynamic probability is estimated depending on the molecular weight of the compounds (the number of carbon atoms in the molecule). It is shown that in the series of thiophenes, benzothiophenes, and dibenzothiophenes, the thermodynamic probability of hydrogenolysis reactions decreases with increasing molecular weight. The values of Gibbs energy increase with the number of atoms in the molecule from -153.3 kJ/mol to -134.5 kJ/mol (for thiophenes from  $C_4H_4S$  to  $C_9H_{14}S$ ), from -92.5 kJ/mol to 62.9 kJ/mol (for benzothiophenes from  $C_8H_6S$  to  $C_{14}H_{18}S$ ) and from -39.4 kJ/mol to -30.6 kJ/mol (for dibenzothiophenes from  $C_{12}H_8S$  to  $C_{18}H_{20}S$ ) (Figure 1).

Similar dependence is observed for hydrogenation reactions of benzothiophenes and dibenzothiophenes to mono- and diaromatic hydrocarbons (Figures 2, 3, respectively), followed by their saturation to cycloparaffins, which is due to the greater energy stability of heavy sulfurcontaining molecules. The values of Gibbs energy increase with the increase in the number of carbon atoms in the molecule from -39.1 kJ/mol to -25.3 kJ/mol (for hydrogenation reactions of benzothiophenes (from  $C_8H_6S$  to  $C_{14}H_{18}S$ ) to monoaromatic hydrocarbons), from -53.4 kJ/mol to -37.3 kJ/mol (for hydrogenation reactions of monoaromatic hydrocarbons (from  $C_8H_8$  to  $C_{13}H_{18}$ ) to cycloparaffins) (Figure 2).



Figure 1. The thermodynamic probability of hydrogenolysis reactions as a function of the number of carbon atoms in the molecule of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization (T=360°C, P=3 MPa)



Figure 2. Thermodynamic probability of consecutive stages of benzothiophene hydrogenation reactions as a function of the number of carbon atoms in the molecule in the process of diesel fractions hydrodesul-phurization (T=360°C, P=3 MPa)

Similarly, the following dependencies were observed for dibenzothiophenes: the Gibbs energy values increase with the increase in the number of carbon atoms in the molecule from - 41.7 kJ/mol to - 39.9 kJ/mol (for hydrogenation reactions of dibenzothiophenes (from C<sub>12</sub>H<sub>8</sub>S

to  $C_{18}H_{20}S$ ) to diaromatic hydrocarbons), from -20.2 kJ/mol to 9.3 kJ/mol for hydrogenation reactions of diaromatic hydrocarbons (from  $C_{12}H_{10}$  to  $C_{18}H_{22}$ ) to bicyclic compounds (Figure 3).



Figure 3. Thermodynamic probability of consecutive stages of dibenzothiophenes hydrogenolysis reactions as a function the number of carbon atoms in the molecule in the process of diesel fractions hydrodesulphurization (T=360°C, P=3 MPa)

The thermodynamic analysis of the thermal effects of hydrogenolysis reactions of various sulfur-containing compounds performed on the base of estimated reactions enthalpies at  $T=360^{\circ}$ C, P=3 MPa, showed (Table 2) that all reactions are exothermic. The highest thermal effect is observed for hydrogenation of dibenzothiophenes to bicyclic paraffins ( $\Delta H_r$ =-514.89 kJ/mol), benzothiophenes to cycloparaffins ( $\Delta H_r$ =-398.71 kJ/mol), thiophenes to paraffins ( $\Delta H_r$ =-317.85 kJ/mol). The thermal effect of hydrogenation reactions of sulphides and olefins to the corresponding paraffins is  $\Delta H_r$ =-115.24 kJ/mol and -134.37 kJ/mol, respectively.

Based on the results of the thermodynamic analysis of the reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization, the probability of various hydrocarbon conversions and their reversibility were evaluated. The proposed scheme of hydrocarbon reactions is shown in Figure 4. The combination of hydrocarbons in groups was made on the basis of the probability of the reactions proceeding with regard to their reversibility. The probability and reversibility of the reactions were determined from the values of Gibbs energy under the thermobaric conditions of hydrodesulphurization process (T=360 °C, P=3.0 MPa) according to the following criterion: the reaction is thermodynamically probable and reversible if -50 kJ/mol $<\Delta G_r < +50$  kJ/mol, the reaction is thermodynamically probable and irreversibly passes in the forward direction if  $\Delta G_r < -50$  kJ/mol, the reaction does not occur in the forward direction if  $\Delta G_r > +50$  kJ / mol [<sup>161</sup>].



Figure 4. The scheme of hydrocarbon reactions in the process of diesel fractions hydrodesulphurization

This reaction scheme can be used to create the model of diesel fractions hydrodesulphurzation process in order to simplify the mathematical description without loss of the model's sensitivity to the reactivity of sulfur-containing compounds of various homologous groups. The mathematical model of the process can be used to predict the residual sulfur content at the output from the installation, to study the influence of technological parameters and to solve various scientific and applied problems.

#### 5. Conclusions

Based on the results of the thermodynamic analysis performed using the quantum-chemical methods of calculation under the thermobaric conditions of diesel fractions hydrodesulphurization process (T=360°C and P=3 MPa), it was established that hydrogenolysis reactions of all sulfur-containing compounds are thermodynamically probable.

It is shown that the thermodynamic probability of hydrogenolysis reactions increases in the series: dibenzothiophenes ( $\Delta G_r$ =-33.27 kJ/mol), benzothiophenes ( $\Delta G_r$ =-71.36 kJ/mol), thiophenes ( $\Delta G_r$ =-137.20 kJ/mol) and sulphides ( $\Delta G_r$ =-142.64 kJ/mol). The probability of olefins hydrogenation reaction is estimated from the value of Gibbs energy and it was shown that this reaction proceeds irreversibly ( $\Delta G_r$ =-52.83 kJ/mol).

It was found that under the taken thermobaric conditions, hydrogenolysis of sulfides, thiophenes, and benzothiophenes proceeds irreversibly, as for dibenzothiophenes, hydrogenolysis proceeds reversibly through the stage of aromatic hydrocarbons formation, followed by their hydrogenation to cycloparaffins.

The thermodynamic probability of hydrogenolysis reactions of various sulfur-containing compounds in one homological group is estimated depending on the number of carbon atoms in the molecule. It was shown that in the series of thiophenes, benzothiophenes, and dibenzothiophenes, the thermodynamic probability of hydrogenolysis reactions decreases with increasing molecular weight. A similar dependence was observed for the hydrogenation of benzothiophenes and dibenzothiophenes to mono- and diaromatics, respectively, followed by their saturation to cycloparaffin hydrocarbons, which is due to the greater energy stability of heavy sulfur-containing molecules.

The enthalpy values of the reactions of sulfur-containing compounds were calculated, and all reactions were shown to be exothermic. The highest thermal effect is observed for hydrogenation of dibenzothiophenes to bicyclic paraffins ( $\Delta H_r$ =-514.89 kJ/mol), benzothiophenes to cycloparaffins ( $\Delta H_r$ =-398.71 kJ/mol), thiophenes to paraffins ( $\Delta H_r$ =-317.85 kJ/mol). The thermal effect of hydrogenation reactions of sulphides and olefins to the corresponding paraffins is  $\Delta H_r$ =-115.24 kJ/mol and -134.37 kJ/mol, respectively.

Based on the thermodynamic analysis of the reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization, the reaction scheme for the transformations of hydrocarbons is proposed, which can be used to create the mathematical model of the process for solving various scientific and applied problems.

#### Acknowledgements

Ministry of Education and Science of the Russian Federation (10.8306.2017/6.7) supported the research. The research is carried out at National Research Tomsk Polytechnic University and within the framework of National Research Tomsk Polytechnic University Competitiveness Enhancement Program grant.

#### References

- [1] Akhmetov SA, Physical-chemical technology of deep oil and gas processing; UGNTU: Ufa, Russia, 1997.
- [2] Solodova NL, Terentyeva NA. Hydrofining of fuels; Publishing house KSTU: Kazan, Russia, 2008.
- [3] Kondrasheva NK, Kondrashov DO. Technological calculations and theories of hydrotreating process; Monograph: Ufa, Russia, 2008.

- [4] Zabotin LI. Chemistry and technology of secondary processes of oil refining; Samara State Technical University: Samara, Russia, 2014.
- [5] Kim JH, Ma X. Energy&Fuels. 2005; 19: 353-364.
- [6] Taflan RA, Karamangil MI. Fuel. 2012; 102: 41-48.
- [7] Fahim MA, Sahhaf TA, Elkilani AS. Fundamentals of Petroleum Refining; Elsevier, 2010.
- [8] Xiong J, Li H, Yang L, Luo J, Chao Y, Pang J, Zhu W. AlChE Journal. 2017; 63(8): 3463-3469.
- [9] Al-Degs YS, El-Sheikh AH, Al Bakain RZ, Newman AP, Al-Ghouti MA. Energy Technology. 2016; 4: 679-699.
- [10] Belinskaya NS, Frantsina EV, Ivanchina ED. Chemical Engineering Journal. 2017; 329: 283-294.
- [11] Frantsina EV, Belinskaya NS, Ivanchina ED. Korean Journal of Chemical Engineering. 2018; 35(2): 337–347.
- [12] Baskin II, Polyulin VA, Zefirov NS. Bulletin of Moscow University. 2001; 42(6): 387-389.
- [13] Poleshchuk OH, Kizhner DM. Chemical studies by methods of calculating the electronic structure of molecules; TPU Publishing House: Tomsk, Russia, 2006.
- [14] Li H, Zhu W, Zhu S, Xia J, Chang Y, Jiang W. Zhang M, Zhou Y, Li H. AlChE Journal. 2016; 62(6):2087-2100.
- [15] Valencia D, Laura P, Garcia-Cruz I. International Journal of Quantum Chemistry. 2012; 112: 3599-3605.
- [16] Sykes P. A guidebook to mechanism in organic chemistry; Longman Group Ltd, 1986.

To whom correspondence should be addressed: Dr. Evgeniya Frantsina, Department of Fuel Engineering and Chemical Cybernetics, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia, e-mail: <u>evf@tpu.ru</u>

# Article

LONG-TERM MONITORING OF OIL CONTAMINATION OF PROFILE-DIFFEREN-TIATED SOILS ON THE SITE OF INFLUENCE OF OIL-AND-GAS WELLS IN THE CENTRAL PART OF THE BORYSLAV-POKUTTYA OIL-AND-GAS BEARING AREA

Vasyl Karabyn<sup>1</sup>, Vasyl Popovych<sup>1</sup>, Ihor Shainoha<sup>2</sup>, Yaroslav Lazaruk<sup>3</sup>

<sup>1</sup> Lviv State University of Life Safety, Lviv, Ukraine <sup>2</sup> Ivan Franko National University of Lviv, Ukraine <sup>3</sup> Institute of Geology and Geochemistry of Combustible Minerals, Lviv, Ukraine

Received September 12, 2018; Accepted December 21, 2018

#### Abstract

The dynamics of oil contamination of profile-differentiated soils of the Precarpathian region in the area of influence of deep wells of the Vilhivska oil exploration area of the Boryslav-Pokuttya oiland-gas bearing area is investigated. The research was conducted during 2007-2016. Soils were tested in the intervals of the distribution of humus-eluviated (H (e) gl), eluvial-humous (Eh (gl)), iluvial (Ih (gl)) horizons, iluviated parent rock (Pigl), and unchanged parent rock (Quaternary sediments) to the depth up to 2.0 m. The concentrations of oil products in pollution sources are analyzed. The zoning of the research territory according to the distribution of elementary geochemical landscapes is carried out. Within the various elementary geochemical landscapes, reqularities in the horizontal and radial distribution of oil products have been revealed. The highest pollutants concentration is established in the silts of elementary transsuperagual landscapes in the number up to 1750 mg/kg. In deeper horizons, the concentration of pollutants decreases nonlinearly, and the dynamics of this process is different in various elementary geochemical landscapes. The dynamics of the change in the oil concentration over time during the 9-year period of field observations were established. In particular, 1.5 years after the drilling operations cessation, the average concentration of oil products in the interval of the humus-eluviated horizon decreased 2.7 times and more than 4 times after 2.5 years. In the interval of the eluvial-humus horizon, the dynamics of the pollutant concentration change was less intensive, as the processes of desalination and decomposition of oil products were accompanied by the introduction of new pollutant amounts from the upper horizons.

Obtained results are unique considering the natural conditions and long duration of the study (9 years). It can be useful in predicting changes in the concentration of oil products in soils, in designing environmental protection measures and civil protection measures. Highlighted in the article, the results of research support and develop the theory of geochemistry of technogenesis, the theory of geochemical landscapes, creating a reliable experimental basis for improving the scientific methods of ecological and crisis monitoring.

**Keywords**: emergency situation; environmental safety; crisis monitoring; ecological monitoring; elementary geochemical landscape; geochemistry of technogenesis.

#### 1. Introduction

The development of the oil and gas industry is impossible without the discovery of new deposits. Economically attractive is the discovery of new deposits in oil-and-gas producing regions with developed infrastructure, a competition of highly professional personnel, well-established logistics of extraction, transportation, and processing of raw materials. Such long-standing and well- equipped oil-and-gas producing areas exist in a large number of countries in the world: the Los Angeles, Ventura, Uinta, Utah, North Albert, Williston Basin (USA), the Cas-

pian oil-and-gas province (Kazakhstan, Russia), the oil-and-gas provinces of the northem Sahara (Algeria), West Africa, Potwar (Pakistan), Absheron petroleum- bearing region (Azerbaijan), Oiloibiri oil field (Nigeria), Douala (Cameroon), the Rhine basin (Germany), the Westem Canadian basin (Canada), Pechelbronn field in Alsace (France)<sup>[1-5]</sup>. The territories with long oil production include the Carpathian oil-and-gas bearing province, where oil is extracted since the 16th century<sup>[5]</sup>.

The main oil area in the Carpathian oil-and-gas bearing province is the Boryslav-Pokuttya oil-and-gas bearing area, which has thousands of drilled oil wells. During the long-term oil production, the environment has undergone an intense man-made impact, which is manifested primarily in contaminated soil, surface, and groundwater. The contamination of the geological environment components with organic substances, primarily oil products, phenols, hydrocarbon gases <sup>[6-7]</sup> is one of the most dangerous. Such an intensive technogenic impact can lead to an emergency situation.

**The purpose of the given article** is to characterize the hazard factors for soils caused by oil wells drilling and, based on the results of the field and laboratory studies, to establish spatially and time patterns of oil products distribution in profile-differentiated soils using an example of the Vilhivska area in the central part of the Boryslav-Pokuttya oil-and-gas bearing area of the Carpathian province (Ukraine).

**The object of the research** is the processes of transformation of hydrocarbon contamination of soils of a podzolic type as a part of the geological environment at the site of deep wells influence in the central part of the Boryslav-Pokuttya oil-and-gas bearing area of the Carpathian province.

### 2. Experimental

Ecological and geochemical studies on assessing the effect of wells in the central part of the Boryslav-Pokuttya oil-and-gas bearing area of the geological environment were conducted at the site of the search well Vilhivska-34.

# 2.1. Field studies

Five main and three additional stages of field observations were conducted to trace the time of ecological-geochemical changes, intensity and level of soils and silts contamination within the research area. Fieldwork was carried out in May and October. The stages of observations were tied to the particular hydro-meteorological stages, which marked the end of the peak seasonal receipts to the surface of the meteorological waters. The main stages of field research were conducted during 2007-2009. Additional stages were carried out in May and October 2010-2011 and in May 2012, 2014, 2016.

The main stages of the field work at the site of the influence of the Vilhivska-34 oil exploration well were provided for testing the soils and rocks of the aeration zone with a uniform square grid of geochemical wells with a density of  $100 \times 100$  m, which, depending on the situation, branched out into the fan-shaped profiles from the oil-and-gas well construction sites down the terrain. Thus, the initial detail of the eco-geochemical survey was at least 1: 1000 (1 geochemical well per 1 ha of an area). To determine the thickness, lithological, and mechanical composition of soils in the rocks of the aeration zone, as well as the intensity of their contamination, geochemical wells with a depth of up to two meters, were drilled in the section of the mechanized-manual sections, with a soil sampling interval. Samples of soils were selected from intervals of 0.1-0.2 m, 0.3-0.5 m, 0.8-1.0 m, 1.3-1.5 m, and 1.8-2.0 m. In addition to the samples from geochemical wells, ravine and mountainous catching ditches silt were analyzed. Additional stages of fieldwork included testing of soils and silts at the selected representative points in the intervals of 0.1-0.2 m and 0.3-0.5 m. The test points were clamped on the ground with reference marks for ecological and geochemical monitoring. The binding was carried out using a compass and GPS. Soil and water samples were collected and preserved according to the requirements of the state standard of Ukraine DSTU 4287: 2004. The soil samples meant for adsorbed gases testing were sampled in the glass jars (0.5 I) and hermetically preserved. The period between sampling and determination of organic compounds did not exceed 7 days.

#### 2.2. Analytical studies

The concentration of oil products was mainly determined by infrared spectroscopy by measuring the absorption in the region of  $2700-3100 \text{ m}^{-1}$ . Preparation of the sample included the extraction of oil products with carbon tetrachloride and chromatographic purification from polar compounds in a column with active alumina. The calculation of oil products was carried out by IHS-29. The device was calibrated with a mixture of decane (56% vol.), iso-octane (19% vol.), and benzene (25% vol.). The lower limit of the determination was 0.1 mg/L or 0.1 mg/kg with relative error 15%.

### 2.2.1. An object of research

In the administrative aspect, the research area is located in the Ivano-Frankivsk region, in Ukraine.

From the point of view of orography, the area is characterized by low-mountain relief with the well-developed hydrographic network. The absolute elevation marks range from 450 m in valleys to 600-800 m on the watersheds. The climate of the region is moderately continental. The average annual rainfall is 700-800 mm.

According to the landscape-geochemical zoning, in the territory of Precarpathians from the scarp of the Outer Carpathians to the river Dniester, the landscapes of the acid-calcium class with forest-lush vegetation on the profile-differentiated gleyed soils developed on the deluvium of sandy-argillaceous formations are widespread. Directly the research site is covered with profile-differentiated gleying argillo-arenaceous soils on the old eluvial sediments. The territory is intensively dissected by ravines.

According to the classification of elementary geochemical landscapes <sup>[8]</sup>, within the research area, we have distinguished an elementary autonomous eluvial landscape, an elementary transeluvial landscape, and an elementary transsuperaqual landscape.

# 2.2.2. Geological structure and oil-and-gas content

Geologically, the research area is located in the central part of the Boryslav-Pokuttya zone of the Precarpathian mountain trench. This territory is located between one of the largest hydrocarbon deposits of the Carpathian region, namely Dolynskyi and Bytkiv-Babchynskyi ones. The geological structure of the region includes deposits of Upper Cretaceous, Paleocene, Eocene, Oligocene, Miocene, and Pliocene. The entire stratum is represented by a flechesite complex of rocks that differ in cement (limestone, siliceous), the granulometric composition of rocks, the distribution of micaceous minerals, and the thickness of measures. In addition, the menilitic suite of the Oligocene is characterized by high bitumen content. The rocks of the upper Eocene sediments and the Oligocene menilite suite of the Paleogene system are oiland-gas bearing ones.

Dozens of wells (1–, 2–, 3–, 5–, 7–, 8–,11–, 15–, 16–, 20–, 21–, 24 – (Vilhiv); 2–, 6– (Pidlisiv); 6–, 9–, 12–, 16–, 17–,18–, 19–, 21– (Strutyn) were drilled on the Vilhivska search area near Strutynske mine field. At least 5 new deep wells were planned to be drilled. Drilling of the wells in the research area was carried out using barns and burial of drilling waste on site, which created additional risks of contamination of the geological environment and an emergency.

# 2.2.3. Characteristics of soils

According to the soil-geographical zoning, the research area refers to the subboreal soilbioclimatic belt of the Western European subboreal forest region of the Carpathian mountainlarval province of the brownish-podzolic zone of gleyed soils of the Carpathian region <sup>[9]</sup>. According to the soil maps compiled according to the classification of soils of the UN Food and Agriculture Organization, profile-differentiated gleyed soils (Stagnic Cutanic Albeluvisols) dominate in the territory of the Carpathian Mountains. S.M. Polchyna <sup>[9]</sup> determines this soil type as brownish-podzolic gleyed soils. Distribution of profile-differentiated gleyed soils of Prykarpattya is controlled by the main tectonic elements of the Carpathian folded structure. These soils are also widely distributed in Western and Central Europe <sup>[10]</sup>.

The profile-differentiated gleyed soils in the research area are described according to the work of <sup>[9]</sup>. The following soil horizons are distinguished: 0-5 cm - sod (Ho), or arable layer; 5-17 cm - humus-eluviated horizon, clayly (H (e) gl) 17-31 cm - humus-eluvial, clayly (HEgl) 31-48 cm - eluvial-humus, clayly (Eh (gl)); 49-110 cm - illuvial (Ih (gl)); 110-155 cm - illuviated parental rock (Pigl).

The boundaries of soil horizons are established as a result of three soil sections documenting. The highest variability is found in the thickness of the illuvial horizon (Ih (gl)) with sole ranged between 98 and 118 cm, and the illuviated paternal rock (Pigl) with lower distribution boundary fixed at a depth of between 147 and 169 cm.

Thus, the soil sampling intervals correspond to the following soil horizons:  $0.1-0.2 \text{ m} - \text{humus-eluviated}(H(e) \text{ gl}); 0.3-0.5 \text{ m} - \text{eluvial-humous}(Eh(gl)); 0.8-1.0 \text{ m} - \text{illuvial}(Ih(gl)); 1.3-1.5 \text{ m} - \text{illuviated} \text{parental rock}(Pigl); 1.8-2.0 \text{ m} - \text{unchanged} \text{parental rock}(Quaternary sediments}).$ 

Among the features of profile-differentiated gleyed soils that can affect the migration of oil products, the fillowing should be noted: a relatively high content of physical clay; the increased compactness and hygroscopicity of the soil with depth, which cause favorable conditions for water stagnation in the upper soil; low content of organic carbon (up to 2-4% in the range of 5-10 cm, the amount of which does not exceed 1% already at a depth of 40 cm) <sup>[9]</sup>; wide development of gleying processes; the presence of neoplasms in the form of concretions, peas, ortsands <sup>[11]</sup>.

#### 3. Results and discussion

#### 3.1. Sources of oil products entering the soil

Pollution of the environment of oil-and-gas bearing areas is caused by natural and maninduced processes. Natural ones, for example, include the flow of hydrocarbon fluids to the surface out of oil-and-gas deposits, caused by their vertical unloading with tectonically-weakened channels out of the deep zones of excess pressure. However, the natural component of pollution is negligible, and man-induced pollution is predominant. The man-induced pollution of the environment is already observed at the early stages of exploration for oil and gas, in particular, at the stage of the drilling rig installation. This is due to the imperfection and violation of environmental protection requirements, as well as the chemical composition of drilling mud flush components and drilling waste enrichment by harmful compounds in the middle of the opening of the reservoir during the oil-and-gas wells constructing.

The rocks of the menilite suite, oil, and formation water are primary sources of natural oil pollution of the environment components of the Carpathian region in the process of deep wells constructing. The man-made sources include separate components of drilling mud, combustive-lubricating materials, and drilling waste.

The Boryslav-Pokuttya area of the Carpathian oil-and-gas province is characterized by difficult drilling conditions, namely: absorption of drilling mud in the deposits of the Yamnenska suite; the rocks shedding in the menilite deposits; frequent oil-gas and water showings in different intervals of drilling; desalination in the sediments of the Stebnytska and Vorotyshchenska suites. Difficult geological conditions require the use of highly inhibited (such as potassium) low-filtration drilling fluids, often on an oil basis, which harmfully affects the environment.

Within the Vilhivskyi polygon, two mud flush formulations were used in accordance with the project. In the interval 0 – 1120 m, potassium mineralized mud flush with a density of 1.24 g/cm<sup>3</sup> was used. The solution was treated with the carboxymethylcellulose (CMC), condensed sulfide alcohol spirits (CBSS), potassium chloride and oil with sulfonol. In the interval 1120 –

1860 m, a polymer-potassium mud flush with a density of  $1.12 \text{ g/cm}^3$  was used. The mud flush was treated with CMC, CCB, potassium chloride, oil, and sulfonol.

According to the results of our research, the mud flush and drilling wastewater are the dangerous sources of contaminants at the Vilhiv ecological and geochemical range. In particular, mud flush with mineralization of 7.4 g/dm<sup>3</sup> contained oil products (11.85 mg/dm<sup>3</sup>); the indicator of chemical oxygen consumption reached 66.85 mg  $O_2/dm^3$ . The drilling wastewater with mineralization of 0.56 g/dm<sup>3</sup> contained 106.5 mg/dm<sup>3</sup> of liquid hydrocarbons. At the site of the operating wells of the Strutynskyi deposit, liquid waste contains 41.8 g/dm<sup>3</sup> of oil products.

All these sources of pollutants create significant risks of environmental pollution outside drilling sites.

### 3.2. Distribution of oil products in soils

According to the results of the first stage of the monitoring observations (October 2007) in the interval of 0.1-0.2 m (humus-eluviated horizon), oil products were found in concentrations 0 730 mg/kg, in silts – up to 1750 mg/kg. The morphology of the anomalies reflects the features of the relief. In particular, the most contrasting anomalies are established in the ravines silts and in the parts of the lowered parts of the relief (Fig. 1).



Fig. 1. Schemes of oil products distribution in the humus-eluviated horizon of profile-differentiated soil in the area of influence of Vilhivska-34 down hole (as of October 2007, the beginning of drilling a well)

In May 2008, the drilling operations were at the final stage. The average concentrations of oil products increased in the humus-eluviated horizon and decreased in the eluvial-humous horizon and unchanged paternal rock. Subsequently, the concentration of OP along the soil profile was nonlinearly decreased in total. The most intensive decrease in the content of OP was recorded in the interval of 0.1-0.2 m from October 2007 till October 2009. At the same time, in the intervals of 1.3-1.5 and 1.8-2.0 m, the content of OP increased (Fig. 2).

During 2010-2016, with a variable dynamics, there was a further decrease in the intensity of soils and silts pollution with oil products. It is worth emphasizing that the increase of the concentration of oil products in the spring of 2013 and 2016 compared with the previous periods of research. Such geochemical field bifurcations are likely associated with the additional entering the hydrocarbon substances out of neighboring oil and gas exploration areas with meltwater (Fig. 3). The graph of the change in the concentration of OP in the interval 0.1-0.2 m is well approximated by the exponential and in the interval 0.3-0.5 m – by

the linear dependence. The reliability of the dependencies was confirmed by the determination coefficient within the confident interval.



Fig. 2. Dynamics of changes in the average concentration of oil products in soils with depth and time. Sampling intervals, m: 1 - 0.1 - 0.2, 2 - 0.3 - 0.5, 3 - 0.8 - 1.0, 4 - 1.3 - 1.5, 5 - 1.8 - 2.0.



Fig. 3. The dynamics of the change in the concentration of oil products in various parts of the research site in the interval of 0.1-0.2 m (a) and in the interval of 0.3-0.5 m (b): 1 – the silts of the elementary transsuperaqual landscape, 2 – the soils of the elementary downslope (transeluvial) landscape, 3 – the soils of elementary autonomous eluvial landscape, 4 – the soils and silts of the entire research area, 5 – trend line for the graph of the change in the average content of the OP

It should be noted that the decrease in the oil products content occurred most intensively in the May-October period, while in the spring, on the contrary, we recorded a decrease in the dynamics of self-cleaning of the soil or a slight increase in the concentration of the pollutant. After the well drilling was stopped during 2008-2012 in the interval of 0.1-0.2 m, the average number of oil products in the spring period was 87% compared to the previous autumn period. At the same time, in autumn, the oil products content averaged 52% compared with the oil products content in the previous spring period. In the interval of 0.3-0.5 m, in spring, the oil products content averaged 103% compared to the concentration in the same horizon in the previous autumn period. At the same time, in autumn, the number of oil products was only 64% compared to the previous spring period. The increase in the intensity of degradation of oil products in soils in summer can be explained by the influence of temperature and better access to oxygen in comparison with the winter period. In spring, during the melting of snows, the average concentration of contaminants in the soil may increase due to their leaching and subsequent migration from localized sources within the drilling site.

Based on these results, in the case of limited funding or other obstacles to the implementation of monitoring studies twice a year, it is essential to conduct monitoring studies within the technogenic impact of oil-and-gas wells in the spring. So we did after 2012 when the concentration of oil products approached the background data.

In the subsurface of elementary geochemical landscapes, the concentration of oil products drastically decreased in the transeluvial one in the period from 1.0 to 1.5 years after the cessation of drilling operations. A slow decrease in the content of oil products within the humus-eluviated horizon is due to the location within its boundaries of the former drilling site and temporary barn of sewage, that is, sources of hydrocarbon contamination. In the eluvial-humus horizon, the decrease in the concentration of the pollutant was less intense, as the processes of oil products desalination and decomposition were accompanied by the entering of new amounts of pollutants out of the upper horizons (Table). The obtained results of changes in the concentration of oil products over time can be useful for assessing the natural degradation of oil products in landscape conditions. Similar researches at this stage are not enough for a justified assessment of the natural degradation of these pollutants in the laboratory. At the same time, the obtained data should be used taking into the account the possible inflow of pollutants into the landscape from the localized sources within the territory of the former drilling site and temporary drilling barn that was not fully remediated.

Time after		Change in concentration of OP,%					
the cessa- tion of drill- ing opera-	Transsuperaqual elementary land- scapes silts	Transeluvial el scape	ementary land- es soils	Autonomous eluvial elemen- tary landscapes soils			
tions, years	0.1-0.2	0.1-0.2	0.3-0.5	0.1-0.2	0.3-0.5		
0.5	-31	-21	-1	+27	+60		
1.0	-42	-39	+5	-10	+191		
1.5	-58	-73	-18	-67	+116		
2.0	-57	-76	-5	-55	+57		
2.5	-76	-88	-28	-80	+42		
3.0	-81	-88	-45	-70	-29		
3.5	-89	-97	-77	-97	-100		
4.0	-90	-100	-73	-100	-100		
6.0	-98	-100	-95	-100	-100		
8.0	-99	-97	-96	-100	-89		

Table. Characteristics of the change in the content of oil products after the cessation of drilling operations within the Vilhivska oil searching area

The data obtained within Vilhivska research area were compared with the data obtained within the Pivdennostynavska research area, where the average content of oil products in groundwater decreased from 1.29 mg/dm<sup>3</sup> to 0.14 mg/dm<sup>3</sup> 2 years after the cessation of drilling operations, which is 10.9% of the initial content <sup>[12]</sup>.

The interesting results were obtained in Argentina. In the laboratory conditions, the soil from Patagonia that was dried, sifted, and artificially contaminated with crude oil lost 26.4% of oil products for 1 month. After that, the process of hydrocarbon degradation slowed down significantly. The experiment lasted 13 months, and during this time, the content of the oil products decreased by 45.5% (from 49.2 to 26.8 mg/g) <sup>[13]</sup>. Malaysian soils in natural conditions, contaminated with oil products in the amount of 550 mg/g, reduced the content of pollutant on average by 86% after 70 days. The same oil products under laboratory conditions during the same time degraded by 65% <sup>[14]</sup>. These results indicate that the degradation of oil products in laboratory conditions is slower compared to the field conditions; therefore, extrapolating the results of the studies from the laboratory to natural conditions is inapplicable. Also, one should be very cautious in case of transferring the results of the degradation of pollutants in different geological, soil, climatic, and other natural conditions.

The obtained results are unique considering the natural conditions, long duration of the study (9 years) and can be useful in predicting changes in the concentration of oil products in soils and designing environmental protection measures and civil protection measures. The results presented in the article develop the theory of geochemistry of technogenesis, the theory of geochemical landscapes, create a reliable experimental basis for improving the scientific methods of ecological and crisis monitoring.

#### 4. Conclusions

Due to the drilling of deep oil-and-gas wells, soils in the central part of the Boryslav-Pokuttya oil-and-gas bearing area are subjected to intense hydrocarbon contamination, increases the level of environmental hazards and creates potential threats of emergency situations.

After the completion of the man-made impact, soil pollution significantly decreases during the first 1-3 years. Reducing the contamination of the substrate with oil products depends on the depth. In the near-surface layers, it occurs faster: in soils, it reaches background data after 4-6 years; at great depths, near the occurrence of bedrock – after 7-9 years or more. This is due to the oil products infiltration from the land surface.

In summer, the intensity of oil products degradation increases due to increased temperature and better access to oxygen compared to the winter period.

In spring, during the snow melting, the average concentration of contaminants in the soil may increase due to their leaching and subsequent migration from pollution sources.

When the concentration of oil products approaches the background, monitoring studies within the technogenic impact of oil-and-gas wells are economically justified once a year in the spring.

#### References

- [1] Moghal MA, Saqi MI, Hameed A and Bugti MN. Subsurface geometry of Potwar sub-basin in relation to structuration end entrapment. Pakistan Journal of Hydrocarbon Research. 2007; 17: 61-72.
- [2] Okechukwu CA, Goodluck A, Mustapha A, Eganoba SO and Alani OK. Oil well sidetracking in mature fields: its potential for increasing recovery from Nigeria's mature fields. Pet Coal. 2017; 59(1): 38-46.
- [3] Yan C, Luo G and Ehlig-Economides CA. Systematic study of Bakken well performance over three well completion design eras. Abstracts of Papers; SPE/CSUR Unconventional Resources Conference – Canada, 30 September – 2 October 2014; Calgary, Alberta, Canada. doi:10.2118/171566-MS

- [4] Feyzullayev AA and Ibragimov VB Environmental Consequences of Long-Term Development of Petroleum Fields, Absheron p-la, Azerbaijan, Case History. Journal of Environmental Protection. 2014; 5: 1603-1610. doi:10.4236/jep.2014.517151
- [5] The History of the Oil Industry. Retrieved from http://www.sjvgeology.org/history/index.html.
- [6] Rusyn IB, Moroz OM, Karabyn VV and Kulachkovs'ki OR. Biodehradatsiia vuhlevodniv nafty drizhdzhamy rodu Candida. [Biodegradation of oil hydrocarbons by Candida yeast]. Mikrobiolohichnyi zhurnal. 2003; 65(6): 36-42 (in Ukrainian)
- [7] Karabyn V, Shtain B and Popovych V. Thermal regimes of spontaneous firing coal washing waste sites. News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical sciences. 2018; 3(429): 64-74.
- [8] Glazovskaya M.A. Geokhimicheskiye osnový tipologii i metodiki issledovaniy prirodnykh landshaftov. [Geochemical foundations of typology and methods of research of natural landscapes] Oykumena: Smolensk, 2002; p. 288. (in Russian).
- [9] Polchyna SM. Profilno-dyferentsiiovani ohleieni grunty Peredkarpattia: geneza, variabelnist, systematyka [Profile-differentiated gleyed soils Precarpathians: genesis, variability, taxonomy]. Chernivetskyi natsionalnyi universytet: Chernivtsi, 2014; p. 271. (in Ukrainian).
- [10] Soil Atlas of Europe, European Soil Bureau Network European Commission, Luxembourg. 2005. Retrieved from https://esdac.jrc.ec.europa.eu/content/soil-atlas-europe
- [11] Kanivets VI and Ilienko VI Marhantsevysto-zalizysti konkretsii v gruntakh rehionu Ukrainskykh Karpat [Manganese-glandular nodules in the soils of the region of the Ukrainian Carpathians]. Ahrokhimila i gruntoznavstvo. 1975; 28: 54-62. (in Ukrainian).
- [12] Karabyn VV, Kolodii VV, Yarontovskyi OH, Kozak YuI and Karabyn O.O. Shchodo dynamiky zabrudnennia gruntovykh vod Peredkarpattia u zoni tekhnohenezu rodovyshch nafty. [Concerning the dynamics of groundwater pollution of Precarpathians in the zone of technogenesis of oil fields] Pratsi naukovoho tovarystva imeni Shevchenka. Heolohichnyi zbirnyk. 2007; 11: 182-190. (in Ukrainian).
- [13] Peressutti SR, Alvarezb HM and Puccib OH. Dynamics of hydrocarbon-degrading bacteriocenosis ofan experimental oil pollution in Patagonian soil. International Biodeterioration & Biodegradation. 2003; 52: 21 – 30. doi:10.1002/abio.370200207
- [14] Suja F, Rahim F, Taha MR, Hambali N, Razali MR, Khalid A and Hamzah A. Effects of local microbial bioaugmentation and biostimulation on the bioremediation of total petroleum hydrocarbons (TPH) in crude oil contaminated soil based on laboratory and field observations. International Biodeterioration & Biodegradation. 2014; 90: 115-122.

To whom correspondence should be addressed: Dr. Vasyl Karabyn, Department of Environment Safety, Lviv State University of Life Safety, 35, Kleparivska St., Lviv, 79000, Ukraine

# Article

# **Open Access**

IMPROVING THE TECHNOLOGY OF PREPARING COAL FOR THE PRODUCTION OF BLAST-FURNACE COKE UNDER THE CONDITIONS OF MULTI-BASIN RAW MATE-RIAL BASE. MESSAGE 1. OPTIMIZING THE COMPOSITION OF COAL BATCH BY MEANS OF PETROGRAPHIC CHARACTERISTICS

V. P. Lyalyuk, D. A. Kassim, E. O. Shmeltser\*, I. A. Lyakhova

Kryvyi Rig Metallurgical Institute, Ukraine National Metallurgical Academy, 50006, Kryvyi Rig, Ukraine

Received September 27, 2018; Accepted December 21, 2018

#### Abstract

The optimality of coking batch may be assessed on the basis of the coefficient  $K_{opt}(vt)$ . A method is proposed for determining  $K_{opt}(vt)$  by means of petrographic analysis. This approach permits an ongoing assessment of the optimal composition of the coking batch and prediction of the coke's mechanical strength.

Keywords: coke; coal batch; optimal rank composition; petrographic analysis.

#### 1. Introduction

The coal raw material base of the coke production of PJSC ArcelorMittal Kryvyi Rih, like the majority of the coke enterprises of Ukraine, has a multi-basin character, and the share of domestic raw materials is about 20%. The increase in the share of imported coal (coal concentrates in Russia, Kazakhstan, and the United States, Canada) is associated both with a shortage of Ukrainian coal of suitable quality (low sulfur content,  $I_0 \leq 2.5$  basicity index), and with an increase in the quality requirements for coke to reduce its consumption in blast smelting, as well as in connection with the introduction of pulverized coal injection technology in blast furnace production.

Analysis of the qualitative characteristics of coal concentrates that make up the raw material base for coking an enterprise allows us to formulate its features and basic principles of formation: both now and in the future, the coal raw material base of the coke production will be multi-basin in nature; in the batch, along with coal concentrates from Ukraine, Russia and abroad, the own assets of the Karaganda basin in the amount of 25-30% will be used, which increases the ash content of the batch by 1% on average, the coke ash content by 12% or more. At the same time, the introduction of pulverized coal injection technology into blast furnaces necessitates the attraction or production of blast-furnace coke with high mechanical strength ( $M_{25}$ > 88%,  $M_{10}$  <7.5%), low reactivity CRI <30-35% and high hot strength (CSR> 55-60%) <sup>[1]</sup>.

Under the conditions of the formed multi-basin raw material base of coking, which predetermines the differences in the technological properties and material composition of imported and domestic coal concentrates, it is necessary to clarify and improve the basic technological methods of preparation for their use in coal mixtures. Achieving these characteristics of coke for blast furnace smelting conditions is possible with a comprehensive, scientifically based approach to improving the technology of preparing coal for coking, which consists in developing methods and technological measures aimed at optimizing the composition, properties, and degree of grinding of the batch, taking into account its petrographic characteristics.

### 2. Results and discussions

The aim of our research was an attempt to determine the criteria for optimizing the parameters of the batch to obtain coke of a given quality for modern blast furnace smelting.

Because the quality of the incoming coal is unstable and its supply is erratic, the rank composition of the batch will vary and will not always ensure the required coke quality. The correct choice of the rank composition is very important. For this purpose, it is expedient to use not only the yield of volatiles and clinkering properties of the coal but also petrographic analysis <sup>[2]</sup>.

Petrographic analysis is an effective method of determining the actual composition of coal mixtures. On that basis, the rank composition of coal blends and the uniformity of the vitrinite component may be determined. The vitrinite reflectograms of concentrates from enrichment facilities give a clear idea of the actual content of the declared rank in the given concentrate and are essential in assessing the concentrate's quality. The actual rank composition of a batch containing concentrates from different enrichment facilities must be determined on the basis of the petrographic characteristics—in particular, the reflectograms—of the batch <sup>[3]</sup>.

The vitrinite reflectance is the most reliable basis for quantitative metamorphic assessment of the coal. By petrographic analysis, we may establish the actual content of vitrinite components corresponding to a particular rank in commercial coal from mines, in concentrates from enrichment facilities, and in coking batch. Coal from Ukraine, Russia, Kazakhstan, and the United States differs sharply in technological properties and petrographic characteristics. Most Ukrainian enrichment facilities do not have a steady coal supply and consequently must enrich coal of two or more ranks. That results in mutual interference of the components and reduces the technological value of the concentrate produced <sup>[4]</sup>.

Accordingly, the earlier practice of batch formulation on the basis of the assigned rank of the concentrates, together with technical analysis and plastometric characteristics, does not permit correct assessment of the coal's technological value or prediction of the expected coke quality, as shown in <sup>[41</sup>. Reliable monitoring of the concentrates sent to the plant and the well-founded formulation of coking batch must take account of petrographic characteristics: the maceral composition, mean reflectance, and reflectogram of the vitrinite.

Of the extensive research in this area, we base our analysis on <sup>[5]</sup>. An optimal batch composition with 43% clinkering components and 57% lean components was proposed in <sup>[5]</sup>. In this composition, the coke group constitutes 37% of the lean components, while Zh coal (bituminous coal) constitutes 23% of the clinkering components. (These figures are assumed constant for any batch, crushing system, and coking conditions). Then, the optimality of the batch composition may be estimated on the basis of the coefficient K<sub>opt</sub> proposed in <sup>[5]</sup>. Using K<sub>opt</sub>, we may measure the discrepancy between the actual rank composition of the batch and the baseline (optimal) composition. The formula for K<sub>opt</sub> is as follows <sup>[5]</sup>

$$K_{opt} = 100(K_c \cdot K_{co} \cdot K_b), \%.$$

(1)

where  $K_c = [100 - (\Sigma CC - 43) \times 2]/100$  characterizes the optimality of the ratio of clinkering and lean components;  $K_{co} = [100 - (\Sigma CG - 37)]/100$  characterizes the optimality of the content of coke-group coal; and  $K_b = [100 - (\Sigma B - 23)]/100$  characterizes the optimality of the content of bituminous coal.

With the increase in  $K_{opt}$ , the coke is stronger, as indicated by the rise in  $M_{40}$  and  $M_{25}$ <sup>[5]</sup>. Note also that  $K_{opt}$  permits both ongoing and retrospective assessment of how optimal the batch composition is; and also permits prediction of the coke's mechanical strength. This method of optimization has performed well in the coke plant at OAO EVRAZ NTMK <sup>[6]</sup>.

The optimality of the batch composition at Ukrainian coke plants was also assessed on the basis of  $K_{opt}$  in <sup>[7]</sup>. The numerical factors 43, 37, and 23 in the formulas for  $K_c$ ,  $K_{co}$ , and  $K_b$  were retained for Ukrainian coke plants. (Note again that the coefficients are assumed constant for any enterprise, batch, crushing system, and coking conditions, which may seem unlikely). Analysis for Ukrainian coke plants between 2004 and 2006 shows that the mean  $K_{opt}$ 

value declines: from 77.4% in 2004 to 73% in 2005 and 66.9% in 2006. That may be attributed primarily to the decline in  $K_c$ —in other words, to the growing shortage of clinkering coal. Another finding is that the increase in  $K_{opt}$  is associated with a decrease in  $M_{10}$  and increase in  $M_{25}$ . In other words, the coke quality is enhanced, despite the decline in the absolute value of  $K_{opt}$ .

The coefficients of 43, 37, and 23 used in calculating  $K_c$ ,  $K_{co}$ , and  $K_b$  may be corrected in accordance with the characteristics of the coking coal available at a particular plant, according to <sup>[7]</sup>. (This casts doubt on the constancy of these coefficients in any coking conditions).

Detailed analysis for Ukrainian coke plants in 2010 and 2011 on the basis of  $K_{opt}$  yields the unexpected result that  $K_{opt}$  does not correspond to the quality of the coke. That contradicts the finding in <sup>[5]</sup>.

We may offer the following explanation of the findings. First, it is not correct to determine the rank composition of the batch in optimization on the basis of the suppliers' declarations. In addition, it is not correct to assume constant coefficients in the formulas for  $K_c$ ,  $K_{co}$ , and  $K_b$  when determining  $K_{opt}$  on the basis of petrographic and reflectogram analysis. Note also that all the all the coal ranks present in the batch according to petrographic analysis must be individually taken into account.

In this context, note the proposal in <sup>[8]</sup>: specifically, that ongoing and objective formulation of coking batch entails direct optimization of coke quality (such as the mechanical strength).

Hence, the coefficients in optimization must be found from information regarding the production of high-quality coke at the specific enterprises, in specific conditions.

We now propose the coefficient  $K_{opt(Vt)}$  on the basis of the proposal in <sup>[8]</sup> and the method in <sup>[5]</sup>  $K_{opt(Vt)} = 100(K_GK_{Zh}K_KK_{OS})$  (2)

Here  $K_G$  characterizes the optimality of the content of vitrinite components with reflectance 0.65-0.89% (G coal)

 $K_{G} = [100 - (\Sigma Vt_{Ro=0.65-0.89} - X_{g})]/100,$ 

 $K_{Zh}$  characterizes the optimality of the content of vitrinite components with reflectance 0.90-1.19% (Zh coal)

$$K_{Zh} = [100 - (\Sigma Vt_{Ro = 0.90-1.19} - X_{Zh})]/100,$$

 $K_{\rm K}$  characterizes the optimality of the content of vitrinite components with reflectance 1.20-1.39% (K coal) and  $K_{\rm OS}$  characterizes the optimality of the content of vitrinite components with reflectance 1.40-1.69% (OS coal).

 $K_{K} = [100 - (\Sigma V t_{Ro = 1.20 - 1.39} - X_{K})]/100,$   $K_{OS} = [100 - (\Sigma V t_{Ro = 1.40 - 1.69} - X_{OS})/100.$ (5)
(6)

In Eqs. (2)—(6), the coefficients  $X_G$ ,  $X_{Zh}$ ,  $X_K$ , and  $X_{OS}$  characterize the baseline content of the corresponding rank in the optimization of the batch's rank composition. The values of  $X_G$ ,  $X_{Zh}$ ,  $X_K$ , and  $X_{OS}$  are determined on the basis of petrographic analysis of the coal concentrates during a period in which high-quality coke is obtained at a specific coke plant. In our view, their values cannot be the same for all shops and plants.

The values of  $X_G$ ,  $X_{Zh}$ ,  $X_K$ , and  $X_{OS}$  must be corrected (recalculated) if the  $M_{25}$  values of the coke deteriorate by more than 1%, say. In addition, the absolute difference between the actual and optimal contents of the components is calculated in the formulas for  $K_G$ ,  $K_{Zh}$ ,  $K_K$ , and  $K_{OS}$  (disregarding the sign of the result), as in the method of <sup>[5]</sup>.

In accordance with the proposed method, we determine the values of  $X_G$ ,  $X_{Zh}$ ,  $X_K$ , and  $X_{OS}$  for the coke plant at PAO ArcelorMittal Krivoi Rog in a period with the production of highquality coke, for the coal then available <sup>[9]</sup>. We find that  $X_G = 14$ ,  $X_{Zh} = 65$ ,  $X_K = 14$ , and  $X_{OS} = 7$ . On the basis of Eqs. (2)-(6), we may then plot  $M_{25}$  as a function of  $K_{opt(Vt)}$  (Fig. 1).

(3)

(4)



Fig. 1. Dependence of coke strength M25 on Kopt(Vt)

#### 3. Conclusions

On the one hand, the relation between  $K_{opt(Vt)}$  and the coke strength is closer than for  $K_{opt}$ . On the other hand, we find that the coke quality increases with increase in  $K_{opt(Vt)}$ , and the absolute value of this coefficient reaches the level recommended in <sup>[5-6]</sup>.

Thus, our research again confirms the need for petrographic analysis in order to monitor the actual rank composition of the coking batch during optimization. In determining the optimization coefficient  $K_{opt(Vt)}$ , the baseline content of the various ranks in the coking batch must be established during a period in which high-quality coke is obtained at the specific coke plant. The baseline cannot be the same for all shops and plants.

#### Symbols

*CRI, CSR – coke reactivity index and coke strength after reaction, % Vt – vitrinite, %;* 

Ro – mean vitrinite reflection coefficient, %;

M10, M25 – indices of resistance of coke abrasion and crushability, respectively, %.

#### References

- [1] Romanyuk IV, Sikan II, Mukina NV, et al., Prospective development of the coal resource base of the Arcelor Mittal Krivoy Rog coke chemical production, Uglekhim. Zh., 2016; 3–4: 12–18.
- [2] Gainieva GR, and Boyarchikova RL. Reflectogram assessment of the coal reserves of OAO Zapadno-Sibirskii Metallurgicheskii Kombinat, Koks Khim., 2005; 5: 18–22
- [3] Chernyshov YuA, Ovchinnikova SA, Podlubnyi AV, et al., Assessing the properties of coal and complex batch at OAO Zaporozhkoks on the basis of petrographic characteristics and new coeffcients, Uglekhim. Zh., 2009; 1-2: 12–20.
- [4] Kaftan YuS, Drozdnik ID, Miroshnichenko DV, et al., Scientific principles for batch formulation using coal from different basins, Uglekhim. Zh., 2010; 3-4: 25–31.
- [5] Shtark PV, Stepanov YuV, Popova NK, and Vorsina, DV, Optimal composition of coal batch, Coke and Chemistry, 2007; 50(3): 45–49.
- [6] Popova NK, and Stepanov YuV. More on the optimization of batch composition, Coke and Chemistry, 2013; 56(5): 165–166.
- [7] Ulanovskii ML, and Likhenko AN. Assessing Ukrainian coking batch in terms of optimization of the rank composition, Coke and Chemistry, 2008, vol. 51, no. 7, pp. 256–259.
- [8] Stankevich AS, Kruglov VN, Vorsina DV, and Zolotukhin YuA. Model for optimization of coke quality on the basis of the chemical and petrographic characteristics and nonlinear programming, Koks Khim., 2000; 5: 21–29.
- [9] Lyalyuk VP, Kassim DA, Lyakhova IA, and Sokolova VP. Coke quality and optimization of the batch composition, Coke and Chemistry, 2012; 55(12): 448–452.

To whom correspondence should be addressed: Dr. E. O. Shmeltser, Kryvyi Rig Metallurgical Institute, Ukraine National Metallurgical Academy, 50006, Kryvyi Rig, Ukraine, <u>shmelka0402@gmail.com</u>

# Article

**Open Access** 

IMPROVING THE TECHNOLOGY OF PREPARING COAL FOR THE PRODUCTION OF BLAST-FURNACE COKE UNDER THE CONDITIONS OF MULTI-BASIN RAW MATE-RIAL BASE. MESSAGE 2. OPTIMIZING THE DEGREE OF CRUSHING BY MEANS OF PETROGRAPHIC CHARACTERISTICS OF THE BATCH COMPONENTS

V. P. Lyalyuk, E. O. Shmeltser\*, D. A. Kassim, I. A. Lyakhova

Kryvyi Rig Metallurgical Institute, Ukraine National Metallurgical Academy, 50006, Kryvyi Rig, Ukraine

Received October 17, 2018; Accepted December 21, 2018

#### Abstract

Our research in the coal-preparation shop of the coke plant at ArcelorMittal Krivoi Rog shows that coal crushing is not only associated with the distribution of the macerals over the size classes but also with change in composition of the coal. Thus, with increase in the degree of crushing from 55.5 to 96.2%, the vitrinite content in the batch declines from 70 to 63%, while the total content of fusinized components increases from 29 to 35%. Therefore, the change in microcomponent composition on intensity of grinding the coking batch must be studied in order to explain the coking process and to optimize batch preparation.

*Keywords:* coal; crushing; maceral composition; vitrinite; fusinized components.

#### 1. Introduction

Before coking, the coal batch is crushed so as to ensure the required degree of crushing (in terms of the content of the primary < 3 mm class), the required content of the auxiliary < 0.5 mm class, the optimal granulometric composition, and the maximum packing density of the coal batch. That improves the clinkering and coking properties of the coal and ultimately the quality of the coke. In addition, the consistency of the coke properties depends on the mixing of the coal batch after crushing [1–6].

At the same time, the crushing of coal does not simply change the coal's grain size. Coke quality depends on the monitoring and adjustment of the distribution of the petrographic components over the size classes and the changes in maceral composition as a result of crushing. That will also affect the clinkering and coking properties of the coal.

Consequently, the literature provides considerable practical information on those topics. As yet, however, we lack theoretical principles explaining the decrease in vitrinite content (Vt) with an increase in the degree of crushing and the increase in the total content of lean (fusinized) components ( $\Sigma FC$ ).

#### 2. Results and discussions

The petrographic analysis is essential to the production of high-quality coke when using petrographically nonuniform coal and in expanding the enrichment of coals of different rank. That entails the introduction of characteristics based on the petrographic analysis in the theory and practice of coking-batch crushing.

As an example, we may consider the petrographic assessment of the technological value of coking batch on the basis of characteristics developed at the Ukrainian Coal-Chemistry Institute (UCCI)<sup>[7-8]</sup>.

Thus, the quantity of vitrinite components corresponding to intermediate metamorphic stages, as recalculated for the coal's organic mass, is expressed by the clinkering characteristic  $C_{\rm b}$  of the batch  $^{[7-8]}$ 

(1)

$$C_b = \frac{\sum (0,90 \div 1,39) \cdot V_t}{100}$$

where  $\Sigma(0.90-1.39)$  is the content of vitrinite components with reflectance in the range 0.9-1.39%; Vt is the concentration of vitrinite-group macerals, %.

A second coking characteristic  $K_b$  of the batch is calculated from the formula [7-8]

$$K_{b} = \frac{\left(\Sigma(0,90 \div 1,39) \cdot Vt/100\right) + L}{\Sigma FC + \Sigma(\ge 1,70) \cdot Vt/100}.$$
(2)

where  $\Sigma(0.90-1.39)$  is the content of vitrinite components with reflectance in the range 0.9– 1.39%; Vt is the concentration of vitrinite-group macerals, %; L is the concentration of liptinite-group macerals, %;  $\Sigma FC$  is the sum of fusinized macerals (I + 2/3Sv), %;  $\Sigma(>1.70)$ Vt/100 is the content of vitrinite components with reflectance of 1.70% or more.

On the basis of  $C_b$  and  $K_b$ , we may obtain a general quantitative estimate of the batch's petrographic characteristics, including the maceral composition and the results of reflectogram analysis. With the increase in  $C_b$ , the strength of the coke produced will be higher. In turn, with an increase in  $K_b$ , the probability of wear-resistant and relatively uncrushable coke will increase, other conditions being equal <sup>[7]</sup>.

In order to improve the preparation of coal batch for coking, we must optimize the degree of crushing (the content of the < 3 mm class), taking account of the petrographic characteristics of the batch components.

On the basis of petrographic analysis and the UCCI method we recommend determine the optimal size class of the batch (%) as a function of its actual rank composition <sup>[9]</sup>

$$k = \frac{75 \cdot Vt \cdot \frac{\sum(0,9-1,39)}{100} + 90 \cdot Vt \cdot \frac{\sum(0,5-0,89) + \sum(1,4-2,6)}{100} + 90 \cdot \sum FC}{100},$$
 (3)

where  $\Sigma(0.5-2.6)$  is the content of the vitrinite components with reflectance in the range 0.5-2.6%, corresponding to different coal ranks; 75 is the recommended degree of crushing of Zh and K coal, %; 90 is the recommended degree of crushing of G, OS, and T coal, %;  $\Sigma FC$  – sum of fusinized components (I + 2/3Sv), %.

Thus, the correction of the degree of coal blends crushing permitting the maintenance of coke quality consistent with blast-furnace requirements (minimum strength  $M_{25}$ =90%,  $M_{10}$ =6%).

The next step in our research is to consider the changes in maceral composition as a result of crushing.

The coking properties of the coal batch (especially in the case of petrographically nonuniform coal) depend considerably on the distribution of the coal components over the size class, as noted in <sup>[10]</sup>. This is especially important in developing methods for batch preparation and in selecting the optimal degree of crushing. The clinkering properties of each coal grain depend on its petrographic composition and size. For the same batch, the clinkering properties will improve when the distribution of the coal over the size classes is modified by the selective crushing of the batch, instead of the traditional methods (undifferentiated crushing of the whole batch or separate crushing of each component). In the case of undifferentiated crushing, increase in the degree of crushing always results in significant differences between the large and small classes in terms of their properties, on account of the expulsion of the relatively soft vitrinite from the coal grains: the ash content of the large classes increases, while their clinkering properties are degraded.

Without a change in the composition of the batch, its coking properties may be considerably improved by establishing a more uniform distribution of its components over the size classes,

as noted in <sup>[11]</sup>. This is possible by the appropriate crushing of the coal batch, group crushing of the components, and careful grouping of the available coal.

The change in micro-component composition on crushing the coking batch must be studied in order to explain the coking process and to optimize batch preparation. The group that is most difficult to crush is the liptinites, which are concentrated in large classes. Vitrinites, conversely, are more brittle and concentrated in smaller classes. The microcomponent distribution also depends on the level of metamorphic development. The crushing of vitrinite is easiest for coal of moderate metamorphic development (coke coal). The resistance to crushing is greatest for vitrinite in long-flame coal and anthracite <sup>[12]</sup>. Coal with 50–80% vitrinite (with the same  $R_o$ ) is less strong than coal with a smaller vitrinite content, as noted in <sup>[13]</sup>.

At the same time, mineral impurities such as calcite and pyrite may increase the strength of the coal if they are present in the organic mass—in other words, if they are syngenetic. (They fill the pores of fusinite, telinite, etc.) If calcite and pyrite are found in cracks (if they are epigenetic), the strength of the coal is not increased <sup>[14]</sup>. Research shows that the <4 and >4 mm classes have different petrographic composition. For instance, the vitrinite content is greater in the <4 mm class than in the >4 mm class <sup>[15]</sup>.

Many studies also indicate that coal crushing is not only associated with the distribution of the macerals over the size classes but also with the change in the composition of the coal.

The change in the composition of gas (G) coal with an increase in the content of the < 3 mm class from 35 to 91% was studied in <sup>[16]</sup>. With 35.4% of the < 3 mm class, the vitrinite content is 76.9%; with 57.1% of the < 3 mm class, the vitrinite content is only 72.1%. With 90.8% of the < 3 mm class, the vitrinite content falls to 64.9%. Thus, the vitrinite content is 12% different for 35.4% and 90.8% crushing. The liptinite content declines correspondingly from an initial value of 13.3% to 14.2, 17.3, and 22.7%, respectively.

The change in the petrographic composition of the batch is accompanied by deterioration of the clinkering properties. For example, the plastic-layer thickness y is 17 mm when the content of the <3 mm class is 35.4% and 12% when the degree of crushing is 90.8%. The Rog index declines from 57.7 to 38.2.

Research in the coal-preparation shop of the coke plant at ArcelorMittal Krivoi Rog also shows that the petrographic composition of the batch changes on crushing. Table 1 presents the change in the vitrinite content and the total content of fusinized components before and after crushing of the batch sent to coke batteries 1-6.

It follows from Table 1 that crushing of the batch changes its composition. However, the change in the vitrinite content on crushing may be attributed to the errors of the method. According to State Standard GOST 9414.3-93 (the ISO 7403-3-84 standard), the consistency of the method is 5.1% when the vitrinite content in the sample is 80%.

	Vitrini	∑FC	, %	
Sample	before	after	before	after
	crushing	crushing	crushing	crushing
		Batteries 1-3		
1	75	70	23	27
2	75	68	23	30
3	74	72	24	27
4	74	64	24	32
5	74	65	24	32
		Battery 4		
1	75	68	23	29
2	74	69	24	28
3	74	62	24	36
4	74	66	24	31
5	74	63	24	34
		Batteries 5-6		

Table 1. Petrographic indices of coal batch

1	75	68	23	30
2	75	65	23	33
3	75	64	23	33
4	74	63	23	34
5	74	73	24	25
6	75	67	23	31

At the same time, it is evident from these results and from literature data that this error is exceeded in many cases; values of 7-12% may be obtained.

To confirm the change in the petrographic composition of coking batch on crushing, we also conduct a direct experiment. Batch is taken from the crushers in the coal-preparation shop, carefully homogenized, and split into thirds. One part is used as the uncrushed baseline, with 55.5% of the < 3 mm class; the other two parts are passed through a laboratory mill to obtain 75.5 and 96.2% of the <3 mm class, respectively (Table 2).

Table 2. Granulometric composition of batch

	Granulometric composition of batch by size class, (mm)									
Sample	>6	6-3	3-0,5	≤0,5	≤3 mm					
1	32,8	11,7	27,1	28,4	55,5					
2	5,0	19,5	43,8	32,7	75,5					
3	0,2	3,6	52,9	43,3	96,2					

Table 3 present the petrographic composition of the three samples. The experiment indicates that, with an increase in the degree of crushing from 55.5 to 96.2%, the vitrinite content falls from 70 to 63% ( $\Delta = 7\%$ ), while the content of fusinized components increases from 29 to 35%, with deterioration in the clinkering and coking properties of the coal batch.

T . I. I		the second se	
I ania K	Patroarannic indicas of t	Three campies with	different deares of critching
Table J.			
			· · · · · · · · · · · · · · · · · · ·

		Sample	
Characteristic	1	2	3
Content of 0-3 mm class, %	55,5	75,5	96,2
Vitrinit Vt, %	70	66	63
ΣFC, %	29	33	35

Many such examples may be presented, but what is the underlying mechanism? We know from the literature that the disintegration of coal depends on its microstructure and molecular structure. Note that the coal fractures along the boundary between microlayers of lithotypes, so that the coal is divided between the vitrinite group and the inertinite group [17-18].

The crushing of coal not only reduces the particle size and increases the specific surface but also changes its structure, as shown in <sup>[19]</sup>. In addition, the molecular interactions are disrupted, and chemical bonds in the organic macromolecules will be broken <sup>[20]</sup>.

In crushing, coal does not simply disintegrate but becomes chemical active, as noted in <sup>[21]</sup>. Changes in the pore structure facilitate oxidation. Quantitative data for peroxides in the fractions of G coal indicate that, for technological applications, coal should not be crushed beyond 0.5 mm, because smaller particles are much more rapidly oxidized <sup>[22]</sup>.

In crushing, the molecular structure of the coal is broken down <sup>[18]</sup>. In particular, the length of the chemical chains is reduced, while the compounds become more aromatic. The main structural changes due to stress occur not only in the framework of molecules and macromolecules but also at their periphery—that is, in the space between and above the molecules. Note the difference in strength not only of carbon-hydrogen bonds but also of carbon-carbon and carbon-oxygen bonds. The structural strength of the micro-components in the coal will depend on the number of such bonds in the molecules and macromolecules and on their relative positions.

The relation between the degree of crushing and the structural changes (in terms of the atomic ratio C/H) was established in <sup>[19]</sup>. For example, on crushing coal, C/H tends to decline in the early stages; later on, it increases somewhat. On crushing, the interplane distance increases, while the height of the stacks of carbon layers declines. This indicates disruption of the coal structure such that disordered carbon appears

We may speak of a vitrinite macromolecule with a specific spatial position. It consists of repeating structural units, corresponding to a set of condensed aromatic nuclei with different numbers of rings (mainly 2-8 rings)<sup>[23]</sup>.

Analysis of the IR and NMR spectra for the crushing products of G coal indicates destruction of the arylalkyl ester bonds and the ester bonds within the aliphatic structures, together with rupture of the ester bonds with the aromatic rings and the formation of phenol groups <sup>[24]</sup>.

#### 3. Conclusions

In order to improve the clinkering and coking properties of the coal and ultimately the quality of the coke, we must optimize the degree of crushing (the content of the < 3 mm class), taking account of the petrographic characteristics of the batch components.

Experimental data from many sources indicate that, in crushing, the distribution of the petrographic micro-components over the size classes is modified. We may also assume that, with an increase in the degree of crushing, the petrographic composition of the coal batch is changed: the vitrinite content falls.

For coal with 50-85% vitrinite, which is less strong than coal with smaller vitrinite content, crushing is probably accompanied by disruption of the molecular interactions and rupture of the chemical bonds in the organic macromolecules. That leads to the partial destruction of the vitrinite structure, which is brittle, especially in the intermediate stages of metamorphism ( $R_0 = 0.9-1.39\%$ ).

Further study of this topic is required. More precise and comprehensive experiments must be conducted in order to explain the influence of crushing coal composition. Thus, the theory and technology of coal crushing still require the focused attention of coking specialists.

#### Symbols

Vt – vitrinite, %; Sv – semivitrinite, %; I – inetinite, %; L – liptinite, %; ΣFC – sum of fusinized components, %; Ro – mean vitrinite reflection coefficient, %; M10, M25 – indices of resistance of coke abrasion and crushability, respectively, %;

#### References

- [1] Lyalyuk VP, Uchitel' AD, Lyakhova IA, Kassim DA, and Zaitsev GL. Preparation of coking batch. Coke and Chemistry, 2011; 54(8). 271–286.
- [2] Lyalyuk VP, Sokolova VP, Lyakhova IA, and Kassim DA. Ensuring stable quality of blast-furnace coke. Coke and Chemistry, 2012; 55(8): 304–308.
- [3] Lyalyuk VP, Kassim DA, Lyakhova IA, and Sokolova VP. Coke quality and optimization of batch composition. Coke and Chemistry, 2012; 55(12). 448-452.
- [4] Lyalyuk VP, Sokolova VP, Lyakhova IA, and Kassim DA. Quality fluctuations of coking coal. Coke and Chemistry, 2013; 56(1): 1-6.
- [5] Lyalyuk VP, Shmeltser KÖ, Lyakhova IA, and Kassim DA. Changes in granulometric composition of blast-furnace coke. Coke and Chemistry, 2013; 56(12): 456-460.
- [6] Lyalyuk VP, Shmeltser EO, Lyakhova IA, and Kassim DA. Influence of the batch properties and coking technology on the granulometric composition of coke. Coke and Chemistry, 2014; 57(10): 398-404.

- [7] Chernyshov YuA, Ovchinnikova SA, Podlubnyi AV, et al., Assessing the properties of coal and complex batch at OAO Zaporozhkoks on the basis of petrographic characteristics and new coefficients. Uglekhim. Zh., 2009; (1/2): 12-20.
- [8] Spravochnik koksokhimika. T. 1. Ugli dlya koksovaniya. Obogashchenie uglei. Podgotovka uglei k koksovaniyu (Handbook of Coke Chemistry, Vol. 1: Coking Coal, Coal Enrichment and Preparation for Coking), Borisov LN, and Shapoval YuG. Eds., Kharkov: Izd. Dom Inzhek, 2010.
- [9] Lyalyuk VP, Lyakhova IA, Kassim DA, Shmeltser EO. et al., Ukranian Patent 85803, 2013.
- [10] Fomin AP, Konyakhin AP, and Martynyuk II. Specific distribution of coal material by classes of coal charge. Koks Khim., 1981; (8): 2-4.
- [11] Aleksandrova LP, Nagornyi YuS, and Gulyaev VM. Re-distribution of the components of material composition of coals by the size classes. Koks Khim., 1992; (10): 5-6.
- [12] Koshina M, and Maglicheva A. Change of macrocomponent composition during the grinding of coal. Khim. Tverd. Topliva, 1980; (4): 12-18.
- [13] Temeeva LA. Relationship between the coal strength properties with petrographic characteristics. Khim. Tverd. Topliva, 1979; (4): 102-105.
- [14] Bykadorova VI, Matveeva II, and Polferov KYa. Influence of petrographic composition on the grind- ability of coals. Khim. Tverd. Topliva, 1970; (4): 28-33.
- [15] Korobchanskii IE, Kuznetsov MD, Eidel'man EYa. et al., Analysis of selective crushing of some coal of the Donetsk basin. Koks Khim, 1956; (6): 8-13.
- [16] Kuznetsov MD, and Lyannaya ZG. Composition and properties of large coal classes from the Donetsk basin. Koks Khim, 1960; (5): 10-13.
- [17] Mitsenko GP. Microstructure and composition of microlithotypes of coals of working layers of the Donetsk basin. Khim. Tverd. Topliva, 1991, (5): 3-6.
- [18] Ivanov VP. Structural features of coals and their mechanical destruction. Koks Khim., 2008; (9): 24-27.
- [19] Khrenkova TM, Lebedev VV, Goldenko NL, and Golovina GS. Change type of coals during grinding. Khim. Tverd. Topliva, 1975; (1): 11-17.
- [20] Lebedev VV, Khrenkova TM, Chubarova MA. et al., Change of coal properties during dispersion. Khim. Tverd. Topliva, 1977; (6): 11-16.
- [21] Lebedev VV, Golovina GS, and Cheredkova KI. Change of coal porosity during vibratory grinding. Khim. Tverd. Topliva, 1978; (5): 43-44.
- [22] Kamneva AI, Gukha Sh, and Smiryagina NA. Influence of the grinding degree on the formation of peroxide compounds in the air oxidation of coal. Khim. Tverd. Topliva, 1969; (5): 115-116.
- [23] <u>http://studopedia.ru/2 123646 osHoBnie-predstavleniya-o-himicheskoy-strukture-ugley.html</u>
- [24] Khrenkova TM, and Goldenko NL. Analysis of mechanical destruction products of gas coal used in hydrogenation. Khim. Tverd. Topliva, 1978; (5): 44-45.

To whom correspondence should be addressed: Dr. E. O. Shmeltser, Kryvyi Rig Metallurgical Institute, Ukraine National Metallurgical Academy, 50006, Kryvyi Rig, Ukraine, <u>shmelka0402@gmail.com</u>

# Article

**Open Access** 

MINIMIZING EVAPORATION OF LIGHT HYDROCARBONS FOR IRAQI GASOLINE BY USING D-GLU-CITOL FATTY ACID ESTERS AS REDUCED PRESSURE AGENTS, SYNTHESIS AND CHARACTERIZA-TION

Abdullah Hussein Kshash, Ali Sami Ismail\*

Department of Chemistry, Education College for Pure Science, University of Anbar, Ramadi – Iraq

Received September 24, 2018; Accepted December 21, 2018

#### Abstract

The study involved synthesis of [1,6-Di-O-(4-Alkanoyloxybenzoyl)-D-glucitol by reaction of 4-alkanoyloxy benzoyl chloride with D-glucitol in 2:1 molar ratio in pyridine as a solvent, all the reactions monitored by TLC and the structures were characterized using FTIR technique. Synthesized compounds possibility of reducing pressure were estimated by lowering vapor pressure for concentrations (1-10 mg L<sup>-1</sup>) at various temperatures (37.8, 40, 43 and 45°C). Saturated vapor pressure (Reid vapor pressure) and surface tension showed successful attempt for using synthesized -D-Glucitol fatty acid esters as agents for reducing gasoline pressure at various concentrations and temperatures. These compounds were reduced the surface tension as average 3 mN/m for Benzoic acid and D-glucitol fatty acid ester compounds, while reduced vapor pressure as average 18.8 kPa for Benzoic acid fatty acid ester and 25 kPa for D-glucitol fatty acid ester compounds respectively.

Keywords: D-glucitol fatty acid ester; Benzoic acid fatty acid ester; gasoline pressure; Reid vapor pressure.

#### 1. Introduction

Accumulating the nonpolar segment, commonly called"the tail"and the other polar segment called "the head" in same molecule provides requirements of amphiphilic molecules (Surfactant) such as sugar fatty acid esters (SFAEs). These compounds can be produced by using either chemically <sup>[1]</sup> or enzymatically <sup>[2-8]</sup>. These compounds featured nonionic surfactants and used in foods, pharmaceutical and cosmetics because they are odorless, tasteless, biodegradable, nontoxic and nonirritant <sup>[9-11]</sup>. Some of sugar fatty acid esters (SFAEs) are insecticidal and miticidal <sup>[12]</sup>. Physical properties of them were varying by sugar group and number of carbon atoms in alkyl chain <sup>[13]</sup>. Surfactant have wide variety applications involving wetting, dispersing, foaming, detergency and emulsification agents <sup>[14]</sup>. Due to the different segments for surface active compounds, they are lined up to form aggregates called micelles at concentration called critical micelle concentration (CMC) which may be formed in either polar or nonpolar solvents. In the nonpolar solvent, reversed or inverted micelles formed, and with the same nonpolar solvent normal micelles formed, and the hydrophobic segment, while in polar solvent normal micelles formed, and the hydrophobic segment shielded from solvent by hydrophobic segment <sup>[15]</sup> (see Figure 1).

The properties of surfactant agents such as surface tension and conductivity were changed with the length of hydrophobic tail and concentration of CMC <sup>[16-18]</sup>. All countries suffering from losing of gasoline and light hydrocarbons via evaporating which caused environmentally and economic problems. For example, In Russia 500-600 thousands tons of oil were lost by evaporation yearly <sup>[19-21]</sup>. It is known that the temperature of weather in Iraq up to 45°C during the summer. This makes fuel station owners in Iraq sufferers from evaporation of gasoline during storage, refueling and transport then increasing polluter in the environment, so refinery most recompense fuel station owners by additional quantity of gasoline rather than evaporated, this causes of the economic problem. The purpose of this paper is synthesis of 4hydroxy benzoic acid and -D-glucitol fatty acid esters derivatives, as reducing pressure agents, therefore the reduction of gasoline vapor pressure then reduces evaporation for a healthy environment and reduces economic losses.



Figure 1. Normal and reverse Micelle

### 2. Materials and methods

#### 2.1. Materials

D-glucitol, 4-hydroxy benzoic acid, myristic acid, palmitic acid, stearic acid and thionyl chloride Sigma-Aldrich Chemical Co. were used without further purification, Solvents Scharlau Chemical Co. Surface tension was performed at 25°C by capillary tube method, melting point was measured on JENWAY apparatus, FTIR spectra were recorded as Attenuated total reflection (ATR) on Bruker-Tensor 27 Spectrometer, UV-Vis spectra were record by UV/visible Jenway spectrophotometer Model 6800, solvent THF.

#### 2.2. Methods

#### 2.2.1. Procedure for synthesis

#### i. Alkanoyloxy benzoic acid(A<sub>14</sub>, A<sub>16</sub> and A<sub>18</sub>)

To two necks 100 mL RB flask contains 30 mL dry THF and (14.5 mmol) of 4-hydroxy benzoic acid and few drops of  $Et_3N$  was added (14.5 mmol) of appropriate acid chloride mixed with 10 mL dry THF through dropping funnel at 0°C under N<sub>2</sub> gas flow, the mixture was stirred at RT overnight, then poured on crush ice with stirring after 30 min. Filtered, washed with distilled water (50 mL), dried and recrystallized from dichloromethane.

# ii. 4-Alkanoyloxy benzoyl chloride (B<sub>14</sub>, B<sub>16</sub> and A<sub>18</sub>)

In 100 mL RB flask contains 20 mL dry THF and (5 mmol) of 4-alkanoyloxy benzoic acid ( $A_{14}$ ,  $A_{16}$  and  $A_{18}$ ) was added (10 mmol) of thionyl chloride, the mixture refluxed for 2 hr. in water bath at 75 °C, then distilled under reduce pressure to remove the solvent and excess of thionyl chloride to give the desired acid chlorides.

# iii. 1,6-Di-O-(4-Alkanoyloxybenzoyl)-D-Glucitol (C<sub>14</sub>, C<sub>16</sub> and C<sub>18</sub>)

To two necks 100 mL RB flask immersed in ice contains 50 mL dry pyridine and (3 mmol) of D-glucitol was added drop by drop (6 mmol) of appropriate 4-Alkanoyloxy Benzoyl chloride ( $B_{14}$ ,  $B_{16}$  and  $B_{18}$ ) through dropping funnel under  $N_2$  gas flow, the mixture was stirred at RT overnight, then acidified with 10 ml of 25% HCl then poured on crush ice with stirring, obtained product was filtered, washed with 5% HCl then successive with distilled water.

# 2.2.2. Characterization of 4-Alkanoyloxy Benzoic Acid (A14, A16 and A18)

FTIR, UV/visible and some data of physical properties for (4-Alkanoyloxy benzoic acid) are listed below.

# i. Myristyloxy Benzoic Acid [A<sub>14</sub>]

White solid, yield 87%; mp 97 °C. IR (ATR, v cm<sup>-1</sup>): 2500-3446 (O-H Carbixylic acid), 3026 (C-H aromatic), 2917, 2844 (C-H aliphatic), 1694 (C=O), 1581, 1514 (C=C aromatic), 721 (bending C-H aliphatic). UV/visible (THF) nm: 253  $\Pi \rightarrow \Pi^*$ (rings), TLC: R<sub>f</sub> =0.61 (toluene: methanol)(8:2).

# ii. Palmitoyloxy Benzoic Acid [A<sub>16</sub>]

White solid, yield 85%; mp 58 °C. IR (ATR, v cm<sup>-1</sup>): 2500-3400 (O-H Carbixylic acid), 3028 (C-H aromatic), 2913, 2847 (C-H aliphatic), 1694 (C=O), 1608, 1503 (C=C aromatic), 717 (bending C-H aliphatic). UV/visible (THF) nm: 251  $\pi \rightarrow \pi^*$ (rings), TLC: R<sub>f</sub> =0.59 (toluene: methanol)(8:2).

### iii. Stearoyloxy Benzoic Acid [A<sub>18</sub>]

White solid, yield 81%; mp 55 °C. IR (ATR, v cm<sup>-1</sup>): 2500-3400 (O-H Carbixylic acid), 3026 (C-H aromatic), 2914, 2847 (C-H aliphatic), 1697 (C=O), 1569, 1499 (C=C aromatic), 723 (bending C-H aliphatic). UV/visible (THF) nm: 253  $\Pi \rightarrow \Pi^*$ (rings), TLC:  $R_f = 0.60$  (toluene: methanol) (8:2).

# 2.2.3. FTIR data for (4-Alkanoyloxy benzoyl chloride) are listed below

# i. Myristyloxy Benzoyl Chloride [B<sub>14</sub>]

Yellow liquid, yield 90%, d. 0.879 gm/mL. IR (ATR, v cm<sup>-1</sup>): 3048 (C-H aromatic), 2925 (C-H aliphatic), 1797 (C=O), 1602, 1515 (C=C aromatic), 722 (bending C-H aliphatic).

# ii. Palmitoyloxy Benzoyl Chloride [B16]

Yellow liquid, yield 90%, d. 0.889 gm/mL. IR (ATR, v cm<sup>-1</sup>): 3047 (C-H aromatic), 2922 (C-H aliphatic), 1797 (C=O), 1601, 1510 (C=C aromatic), 721 (bending C-H aliphatic).

# iii. Stearoyloxy Benzoyl Chloride [B18]

Yellow liquid, yield 87%, d. 0.966 gm/mL. IR (ATR, v cm<sup>-1</sup>): 3047 (C-H aromatic), 2922 (C-H aliphatic), 1799 (C=O), 1601, 1511 (C=C aromatic), 721 (bending C-H aliphatic).

# 2.2.4. Characterization of (1, 6-Di-O-(4-Alkanoyloxy benzoyl)-D- Glucitol) $(C_{14}, C_{16}$ and $C_{18}$ )

The following characterization data for D-Glucitol fatty acid esters.

# i. (1,6-Di-O-(4-Myristyloxy benzoyl)-D- Glucitol),[C14]

White gum, 71%. IR (ATR, v cm<sup>-1</sup>): 3329 (O-H), 3028 (C-H aromatic), 2920 (C-H aliphatic), 1731 (C=O), 1606, 1499 (C=C aromatic), 721 (bending C-H aliphatic). UV/visible (THF) nm: 251  $\Pi \rightarrow \Pi^*$  (rings). TLC: R<sub>f</sub> =0.87 (Benzene: methanol)(9:1).

# ii. (1,6-Di-O-(4-Palmitoyloxy benzoyl)-D- Glucitol),[C<sub>16</sub>]

White gum, 76%. IR (ATR, v cm<sup>-1</sup>): 3325 (O-H), 3029 (C-H aromatic), 2916 (C-H aliphatic), 1734 (C=O), 1616, 1528 (C=C aromatic), 722 (bending C-H aliphatic). UV/visible (THF) nm: 247  $\Pi \rightarrow \Pi^*$  (rings). TLC: R<sub>f</sub> =0.87 (Benzene: methanol)(9:1).

# iii. (1,6-Di-O-(4-Stearoyloxy benzoyl)-D-Glucitol),[C<sub>18</sub>]

White gum, 69%. IR (ATR, v cm<sup>-1</sup>): 3346 (O-H), 3026 (C-H aromatic), 2914 (C-H aliphatic), 1735 (C=O), 1616, 1528 (C=C aromatic), 722 (bending C-H aliphatic). UV/visible (THF) nm: 252  $\Pi \rightarrow \Pi^*$  (rings). TLC: R<sub>f</sub> =0.87 (Benzene: methanol)(9:1).

# 3. Result and discussion

The desired compounds were synthesized according to the route illustrated in scheme 1. The scheme shows initial exothermic esterification reactions for phenolic hydroxyl; therefore, the reactions were carried out in an ice bath, followed by conversion of acids to their chlorides by reaction of acids with thionyl chloride. Finally, esterification reaction of group sorbitol was carried out by using acid chlorides and pyridine as a solvent, all esterification reactions of sorbitol were taking place in ice bath due to absorbing of emitted heat and prevent reactions on inner hydroxyl groups. The repulsion between non-bonding electrons on oxygen atoms for hydroxyl groups with electronic cloud of  $\pi$  orbitals for aromatic rings assist to orients esterifi-

cation reactions towards only positions 1 and 6, due to effect of repulsion, which occur between two hydroxyl groups, while esterification reaction using inner (2,3,4 and 5 hydroxyl groups) gave the repulsion which will occurs between four hydroxyl groups in addition steric bulky for groups.



i )dry THF, N<sub>2</sub>, adding at 0  $^{\circ}$ C, Stirring overnight at RT. ii)dry THF, SOCl<sub>2</sub>, Reflux 2hr.at 75  $^{\circ}$ C iii)py.glucitol, adding at 0  $^{\circ}$ C, Stirring overnight at RT, n= (16,14,12)

Scheme 1. Synthetic route of surfactant compounds

#### 3.1. Surface tension measurements

Surface tension measurements consider as important way for studying aggregation behavior of nonionic surfactants <sup>[22]</sup>. Surface tension for six synthesized surfactants was evaluated for concentrations (1 - 10 mg L<sup>-1</sup>) at 25 °C, results are listed in (table 1).

mg L <sup>-1</sup>	A14	<b>A</b> 16	A18	C14	C 16	C18
0	22.1637	22.1637	22.1637	22.1637	22.1637	22.1637
1	20.2294	20.5015	19.9641	20.4101	20.6038	20.6101
2	19.8708	19.9242	19.8655	20.8060	20.7369	19.7026
3	19.8908	19.9027	19.6682	20.0250	19.9740	19.9990
4	19.8681	20.1116	19.6664	18.5892	19.4010	18.9892
5	19.6812	20.2918	19.6297	19.7090	20.0871	19.7090
6	18.7827	20.0533	19.5987	19.4741	20.0512	19.7741
7	19.1843	19.3393	18.9991	20.1664	20.5899	20.3664
8	19.3553	20.2490	19.7076	20.2140	20.5690	20.1140
9	19.9396	20.2420	19.6664	19.8567	20.2391	20.1567
10	19.7615	20.2917	19.4629	20.0249	20.6165	20.0249

Table 1. Surface tension mN/m for synthesized compounds.

The values in Table 1, indicate that all synthesized compounds having surface active properties due to their ability to decrease surface tension. Moreover the dependence of Surface tension on surfactant concentration (Figure 2 and 3)



Figure 2. Dependence of surface tension on the surfactant concentration (B14, B16 and B18)



Figure 3. Dependence of surface tension on the surfactant concentration (C14, C16 and C18)

The graphs in (Figure 2 and Figure 3) indicate that concentrations (6 and 7 mg  $L^{-1}$  for  $B_x$  compounds) and (4 mg  $L^{-1}$  for  $C_x$  compounds) respectively most active concentration to reduce surface tension.





This concentration called critical aggregation concentration CAC, subsequently addition concentration leads to rising of surface tension values, this behavior can be explained by (Figure 4), before CAC stage, surfactant concentration insufficient to form aggregation to binding with gasoline molecule, at CAC be available enough by binding sites for gasoline molecule with formed aggregations, at concentration more than CAC hydrophobic tail for addend surfactant compete gasoline molecule to binding with formed aggregation, then decreasing aggregation ability to attract gasoline molecule on surface – weather interface.

#### 3.2. Saturated vapor pressure

Saturated vapor pressure (Reid Vapor Pressure RVP) was evaluated by preparation of ten concentrations  $(1 - 10 \text{ mg L}^{-1})$  for every synthesized compound at (37.8, 40, 43 and 45°C) as simulation to different temperature of air in Iraq and compared with free gasoline.

### 3.2.1. Saturated vapor pressure for ( B14, B16 and B18) compounds

Table 2 and Figures (5, 6 and 7) show results of saturated vapor pressure (RVP) for surfactants (4-alkanoyloxy benzoic acid) were investigated.

		Concentration mg L <sup>-1</sup>											
		0	1	2	3	4	5	6	7	8	9	10	٥C
		59.1	58.5	58.6	55.4	55.3	53.1	56.9	54.9	53.3	49.9	54.0	37.8
	D.,	62.3	63.8	61.8	55.7	53.9	53.8	57.8	57.4	52.9	52.0	55.6	40
	D14	67.7	68.1	66.2	61.9	56.4	57.1	58.6	55.1	55.4	52.3	57.3	43
		70.5	69.2	67.0	60.5	60.1	56.1	58.5	57.0	57.8	54.4	59.2	45
		59.1	56.8	54.8	51.9	53.2	52.2	53.8	55.9	54.8	50.2	55.7	37.8
np.	Bec	62.3	59.1	56.5	52.7	52.2	51.6	52.9	51.8	51.4	51.1	57.1	40
Cor	<b>D</b> 16	67.7	55.9	54.8	54.2	55.2	55.3	55.1	54.9	52.8	51.8	58.5	43
		70.5	64.9	63.5	57.1	54.7	55.5	55.2	55.9	55.1	52.9	58.9	45
		59.1	56.1	41.1	39.8	44.9	40.5	35.4	36.3	33.9	30.1	38.3	37.8
	<b>B</b> <sub>40</sub>	62.3	61.7	54.5	44.6	44.3	46.5	47.8	46.9	41.1	33.9	46.9	40
	D18	67.7	49.7	45.1	50.1	49.9	44.2	50.0	50.9	51.0	35.6	45.1	43
		70.5	68.8	64.8	46.9	53.2	50.2	53.8	55.9	56.0	38.9	48.6	45

Table 2. Saturated Vapor Pressure (kPa) for B14, B16 and B18 compounds



Figure 5. Dependence of saturated vapor pressure on B14 concentration



Figure 6. Dependence of saturated vapor pressure on B<sub>16</sub> concentration



Figure 7. Dependence of saturated vapor pressure on B18 concentration

Results of saturated vapor pressure of compounds ( $B_{14}$ ,  $B_{16}$  and  $B_{18}$ ) show that addend 9 mg L<sup>-1</sup> most active concentration due to minimize vapor pressure in comparison with free gasoline, this behavior can be explained by mole fraction *xi* and *Pi* saturated vapor pressure of the hydrocarbon on gasoline surface, when surface layer contains concentration of surfactant, the concentration of gasoline reduced therein, then the mole fraction *xi* of gasoline reduced, in accordance with vapor pressure  $P=\sum Pixi$ , reduces the saturated vapor pressure according to Raoult-Dalton's law.

#### 3.2.2. Saturated vapor pressure for (C14, C16 and C18) compounds

At different concentrations  $(1 - 10 \text{ mg L}^{-1})$  and temperatures (37.8, 40, 43 and 45°C) saturated vapor pressure (RVP) for (1,6-Di-O-(4-alkanoyloxy benzoyl)-D-Glucitol) as surfactant was investigated, results are listed in table 3 and graphs (Figure 8, Figure 9 and Figure 10).

Saturated vapor pressure results for D-glucitol fatty acid esters ( $C_{14}$ ,  $C_{16}$  and  $C_{18}$ ) shows that addend 4 mg L<sup>-1</sup> of ( $C_{16}$  and  $C_{18}$ ) and 7 mg L<sup>-1</sup> of ( $C_{14}$ ) minimize vapor pressure, and when comparing this results with active concentration for ( $B_{14}$ ,  $B_{16}$  and  $B_{18}$ ) compounds, its found that required quantity of  $C_x$  less than  $B_x$  compounds, this is due to the large size of -D-glucitol fatty acid esters molecule, which reduces the number of molecules needed to form the aggregations required to lowing the pressure and it contains two hydrocarbon chains in addition to its ability to form four hydrogen bonding between two molecules.

	Concentration mg L <sup>-1</sup>												
		0	1	2	3	4	5	6	7	8	9	10	°C
		59.1	69.9	67.3	51.2	49.6	46.1	48.2	44.0	45.6	51.2	50.3	37.8
	C 14	62.3	75.5	70.0	49.2	56.1	48.7	48.1	38.9	42.9	55.9	50.1	40
	C 14	67.7	78.0	66.9	55.0	52.1	51.1	60.1	48.3	53.9	62.4	54.1	43
		70.5	72.3	66.9	60.6	61.9	52.9	61.8	51.3	54.2	53.4	51.9	45
		59.1	59.5	54.4	38.1	34.1	35.2	34.9	39.7	42.3	37.9	36.8	37.8
du	<b>C</b>	62.3	59.1	45.2	46.5	37.7	39.9	38.7	49.1	53.2	50.9	50.0	40
۲ ک	C 16	67.7	53.3	43.1	49.2	39.4	45.2	48.1	45.9	51.1	48.7	47.1	43
0		70.5	62.4	59.3	52.8	40.5	53.7	53.1	57.1	55.1	54.8	51.2	45
		59.1	50.1	42.5	42.6	36.2	40.1	41.0	40.5	42.2	40.6	40.6	37.8
	C 10	62.3	45.8	48.1	38.9	33.7	37.9	42.6	40.2	36.1	44.6	42.1	40
	C 18	67.7	63.9	44.9	45.9	37.1	43.8	42.7	42.3	41.8	40.7	45.7	43
		70.5	53.2	51.8	48.1	38.1	48.1	45.1	45.3	46.9	44.1	52.8	45

Table 3. Saturated Vapor Pressure (kPa) for C14, C16 and C18 compounds



Figure 8. Dependence of saturated vapor pressure on C14 concentration



Figure 9. Dependence of saturated vapor pressure on C<sub>16</sub> concentration



Figure 10. Dependence of saturated vapor pressure on C 18 concentration

#### 4. Conclusions

Compounds 4-hydroxy benzoic acid and -D-Glucitol fatty acid esters have been successfully synthesized and characterized by FTIR. Their potential as surface active agents compounds have been proved by reducing surface tension and saturated vapor pressure of Iraqi gasoline at more than one temperature, making their use possible to reduce the evaporation of gasoline and thereby reduce pollutants in the environment as well as reducing economic losses.

#### References

- [1] Ferrer M, Cruces MA, Plou FJ, Pastor E, Fuentes G, Bernabe M et al. Chemical versus enzymatic catalysis for the regioselective synthesis of sucrose esters of fatty acids. Studies in Surface Science and Catalysis. 2000; 130: 509–514. <u>https://doi.org/10.1016/S0167-2991(00)81008-3</u>
- [2] Neta NS, Teixeira JA, Rodrigues LR. Sugar ester surfactants: Enzymatic synthesis and applications in food industry. Crit. Rev. Food. Sci. Nutr. 2015; 55: 595–610. https://doi.org/10.1080/10408398.2012.667461
- [3] Chang SW, Shaw J F. Biocatalysis for the production of carbohydrate esters, New Biotechnology 2009; 26: 109–116. <u>https://doi.org/10.1016/j.nbt. 2009.07.003</u>
- [4] Singh M, Singh S, Singh RS, Chisti Y, Banerjee UC. Transesterification of primary and secondary alcohols using Pseudomonas aeruginosa lipase. Bioresource Technology 2008; 99(7): 2116–2120. <u>https://doi.org/10.1016/j.biortech.2007.05.041</u>
- [5] Cauglia F, Canepa P. The enzymatic synthesis of glucosylmyristate as a reaction model for general considerations on sugar esters production, Bioresource Technology 2008; 99(10): 4065–4072. <u>https://doi.org/10.1016/j.biortech.2007.01.036</u>
- [6] Karmee SK. Lipase catalyzed synthesis of ester based surfactants from biomass derivatives, Biofuels, Bioproducts and Biorefining 2008; 2(2): 144–154. <u>https://doi.org/10.1002/bbb.60</u>
- [7] Hernandez FJ, Delos AP, Lozano LJ, Godinez C. Biocatalytic ester synthesis in ionic liquid media, Journal of Chemical Technology and Biotechnology 2010; 85: 1423–1435. https://doi.org/10.1002/jctb.2453
- [8] Yan Y, Bornscheuer UT, Stadler G, Lutz-Wahl S, Reuss M, Schmid RD. Production of sugar fatty acid esters by enzymatic esterification in a stirred-tank membrane reactor: optimization of parameters by response surface methodology, Journal of the American Oil Chemists Society 2001; 78(2): 147–153. <u>https://doi.org/10.1007/s11746-001-0235-x</u>
- [9] Ferrer M, Soliveri J, Plou FJ, Lopez-Cortes N, Reyes-Duarte D, Christensen M et al. Synthesis of sugar esters in solvent mixtures by lipases from Thermomyces lanuginosus and Candida antarctica B, and their antimicrobial properties, Enzyme and Microbial Technology 2005; 36(4): 391–398. <u>https://doi.org/10.1016/j.enzmictec.2004.02.009</u>
- [10] Queneau Y, Chambert S, Besset C, Cheaib R. Recent progress in the synthesis of carbohydrate-based amphiphilic materials: the examples of sucrose and isomaltulose, Carbohydrate Research 2008; 343(12):1999–2009.<u>https://doi.org/10.1016/j.carres.2008.02.008</u>
- [11] Puterka GJ, Farone W, Palmer T, Barrington A. Structure-function relationships affecting the insecticidal and miticidal activity of sugar esters, Journal of Economic Entomology 2003; 96(3): 636–644. <u>https://doi.org/10.1093/jee/96.3.636</u>
- [12] Herrington TM, Midmore BR, Sahi SS. Sucrose Esters as Emulsion Stabilisers, in Microemulsions and Emulsions in Foods, ACS Symposium Series 448, edited by M. El-Nokaly and D. Cornell, American Chemical Society, Washington, DC. 1991; chapter 7: pp 82-102.
- [13] Hatice G. The Basic Theory. Chemistry and Technology of Surfactants.1<sup>st</sup> Ed; Richard, JF. Blackwell Publishing Ltd. State Avenue, Ames, Iowa 50014-8300, USA 2006; pp. 42- 52.
- [14] Hoffman H, Ulbright W. Thermodynamic Data for Biochemistry and Biotechnology. Springer-Verlag, Berlin 1986: pp 297.
- [15] Kadam Y, Yerramilli U, Bahadur AP. Micelles from PEO-PPO-PEO block copolymer as monocontainers for solubilization of a poorly water soluble drug hydrochlorothiazide, J. Colloid Surf. B: Biointerface 2011; 83(1): 49- 57. <u>https://doi.org/10.1016/j.colsurfb.2010.10.041</u>
- [16] Lankveld JMG, Lyklema J. Adsorption of Polyvinyl Alcohol on the Paraffin-Water Interface. I. Interfacial tension as a function of time and concentration, J. Colloid Interf. Sci. 1972; 41(3): 454- 465.<u>https://doi.org/10.1016/0021-9797(72)90369-4</u>
- [17] Change SA, Gray DG. The Surface Tension of Aqueous Hydroxypropyl Cellulose Solutions, J. Colloid Interf. Sci. 1978; 67(2): 255- 265. <u>https://doi.org/10.1016/0021-9797(78)90010-3</u>
- [18] Persson B, Nilsson S, Bergman R. Dynamic Surface Tension of Dilute Aqueous Solutions of Nonionic Cellulose Derivatives in Relation to Other Macromolecular Characterization Parameters, J. Colloid. Interf. Sci. 1999; 218(2): 433- 441. <u>https://doi.org/10.1006/jcis.1999.6449</u>
- [19] Hilpert M, Adria BM, Ni J, Rule AM, Nachman KE. Hydrocarbon Release During Fuel Storage and Transfer at Gas Stations: Environmental and Health Effects, Curr. Envir. Health. 2015; 2: 412–422.https://doi.org/10.1007/s40572-015-0074-8
- [20] Farhan MM, Korzun NV. Reduction of losses of light hydrocarbons from oil and gasoline, News of Higher Educational Establishments, Oil and gas. 2011; 6: 95 98.
- [21] Farhan MM, Al-jumialy MM, Al-muhammadi AD, Ismail AS. Development of a new method for reducing the loss of light hydrocarbons at breather value of oil tanks, Energy Procedia 2017; 141: 471- 478. <u>https://doi.org/10.1016/j.egypro.2017.11.061</u>
- [22] Nizri G, Lagerge S, Kamyshny A, Major DT, Magdassi S. Polymer-surfactant interactions: Binding mechanism of sodium dodecyl sulfate to poly (diallyldimethylammonium chloride), J. Colloid Interf. Sci. 2008; 320(1): 74-81. <u>https://doi.org/10.1016/j.jcis.2008.01.016</u>

To whom correspondence should be addressed: Dr. Ali Sami Ismail, Department of Chemistry, Education College for Pure Science, University of Anbar, Ramadi – Iraq

## Article

## **Open Access**

CALCULATION METHOD FOR PREDICTION OF THE CETANE INDEX OF BLEN DED DIESEL FUELS

Maria V. Kirgina\*, Ilya A. Bogdanov, Andrey A. Altynov, Nataliya S. Belinskaya

National Research Tomsk Polytechnic University, Russia

Received October 1, 2018; Accepted December 21, 2018

#### Abstract

The article considers modern calculation methods for determining the cetane index of diesel fuels. The most accurate calculation method was established. The non-additivity of the cetane index and the fractional composition of diesel fuels was experimentally proven. The method for calculating the cetane index of blended diesel fuels was developed based on the true boiling points. The method takes into account the non-additivity of the cetane index.

Keywords: diesel fuel; calculation method; cetane index; fractional composition; true boiling point.

#### 1. Introduction

Over the last years, a rapid increase in the number of motor transport equipped with diesel engines has been observed all over the world. Majority of the industrially developed countriesimporters of petroleum products are focused on the quality of diesel fuels and are bent on reduction of harmful emissions. Thus, strict control and improvement of the diesel fuel quality, produced these days, is one of the most crucial tasks.

The key quality indicators of diesel fuels, which are strictly imposed by requirements, include cetane index, flash point, density, kinematic viscosity and low-temperature properties (cloud point, cold filter plugging point, pour point).

The most important characteristic of diesel fuel when used in internal combustion engines is the cetane index. The optimal operation of modern engines is provided by diesel fuels with cetane index ranged from 45 to 55 points. In case of using the diesel fuel with the cetane index of less than 45 points, the ignition delay (the time between the injection and ignition of fuel) and the rate of pressure rise in the combustion chamber increase sharply resulting in enhancement of engine wear. When diesel fuel has the cetane index of more than 55 points, the combustion efficiency decreases, the smoke opacity increases, and fuel consumption in creases.

The essence of the experimental method for determination of cetane index is as follows: the cetane index of diesel fuel is determined by comparing its combustion characteristics in the test engine with the characteristics of blends of control fuels with a known cetane index under standard operating conditions. However, the experimental determination of the cetane index is a multi-stage and labor-intensive process, which requires certain skills, special equipment, as well as time and money costs. For these reasons, the selection of the most accurate calculation method and development of a new calculation method for prediction of cetane index are relevant tasks <sup>[1-5]</sup>.

# **2.** An overview of correlations for the quantitative prediction of the cetane index and selection of the most accurate calculation method

The cetane index (CI) of diesel fuels can be calculated using a number of correlations <sup>[6]</sup>. According to the formula presented in the international standard ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four-variable equation" <sup>[7]</sup>, the calculation is performed according to the following equation with four variables:

$$CI_{ISO} = 45.2 + 0.0892 \cdot T_{10N} + (0.131 + 0.901B) \cdot T_{50N} + + (0.0523 - 0.42B) \cdot T_{90N} + [0.00049 \cdot (T_{10N}^2 - T_{90N}^2)] + 107B + 60B^2 T_{10N} = T_{10\%} - 215 T_{50N} = T_{50\%} - 260 T_{90N} = T_{90\%} - 310 B = [\exp(-0.0035 \cdot D_N)] - 1 D_N = D - 850$$
(1)

 $T_{10\%}$ ,  $T_{50\%}$ ,  $T_{90\%}$  are the boiling points of 10 % vol., 50 % vol., and 90 % vol. fraction, °C; D is the density at 15°C.

Also, the cetane index of diesel fuels can be calculated by the formula presented in the National State Standard 27768-88 "Diesel fuel. Determination of cetane index by calculation method" <sup>[8]</sup>. The method consists in measuring the density of diesel fuel at the temperature of 15°C and the average boiling point of the 50% vol. fraction of diesel fuel. In this method the cetane index is calculated by the equation:

$$CI_{NS} = 454.74 - 1641.416 \cdot \rho_4^{15} + 774.74 \cdot (\rho_4^{15})^2 - 0.554 \cdot t + 97.803 \cdot (\lg t)^2$$
(2)

 $\rho_4^{15}$  is density at 15°C measured according to the National State Standard 3900-85 "Petroleum and petroleum products. Methods for determination of density", g/sm<sup>3</sup>; *t* is the boiling point of 50% vol. fraction corrected for the normal barometric pressure of 101.3 kPa, °C; *t* is measured according to the National State Standard 2177-99 "Petroleum products. Methods for determination of distillation characteristics".

To calculate the cetane index of oil fractions, the following equation, presented in the standard ASTM D976 "Standard test method for calculated cetane index of distillate fuels", can also be used <sup>[9]</sup>:

$$CI_{ASTM} = 0.49083 + 1.06577 \cdot x - 0.0010552 \cdot x^{2}$$

$$x = 97.833 \cdot (\log(T_{50\% F}))^{2} + 2.2088 \cdot API \cdot \log(T_{50\% F}) +$$

$$+0.01247 \cdot API^{2} - 423.51 \cdot \log(T_{50\% F}) - 4.7807 \cdot API + 419.59$$

$$API = \frac{141.5}{\rho_{4}^{15}} - 131.5$$
(3)

 $T_{50\%F}$  is the boiling point of 50 % vol. fraction, F; API is the relative specific gravity.

Using the data obtained by the experimental measurements at industrial production of diesel fuels, the cetane index was calculated by equations (1) – (3) ( $CI_{ISO}$ ,  $CI_{NS}$ ,  $CI_{ASTM}$ ) to determine the most accurate calculation method. The results of the calculation were compared with experimentally measured cetane index of diesel fuels ( $CI_{exp.}$ ) and the calculation errors ( $\Delta_{ISO}$ ,  $\Delta_{NS}$ ,  $\Delta_{ASTM}$ ) were determined. The results of the calculations are given in Table 1.

No.	T <sub>10%</sub>	T <sub>50%</sub>	T <sub>90%</sub>	Density at 15°C	CI <sub>exp.</sub>	$CI_{ISO}$	CI <sub>NS</sub>	CIASTM	$\Delta_{ISO}$	$\Delta_{NS}$	$\Delta_{ASTM}$
		°C		kg/m³				points			
1	187	222	266	826.0	43.30	43.31	42.97	43.52	0.01	0.33	0.22
2	194	223	265	825.6	44.10	44.08	43.46	44.00	0.02	0.64	0.10
3	198	234	278	831.6	45.00	44.96	44.87	45.07	0.04	0.13	0.07
4	201	237	283	831.5	46.10	46.06	45.81	46.02	0.04	0.29	0.08
5	192	229	285	823.3	47.10	47.08	46.28	46.80	0.02	0.82	0.30
6	221	285	339	857.4	47.20	47.17	48.42	49.48	0.03	1.22	2.28
7	228	283	337	856.0	48.10	48.12	48.50	49.49	0.02	0.40	1.39
8	228	287	341	856.2	48.60	48.62	49.15	50.45	0.02	0.55	1.85

Table 1. Results of calculating the cetane index of diesel fuel by different methods

No.	T <sub>10%</sub>	T <sub>50%</sub>	T <sub>90%</sub>	Density at 15°C	CI <sub>exp.</sub>	$CI_{ISO}$	CI <sub>NS</sub>	$CI_{ASTM}$	$\Delta_{ISO}$	$\Delta_{NS}$	$\Delta_{ASTM}$
9	231	283	339	853.9	49.30	49.31	49.17	50.28	0.01	0.13	0.98
10	261	305	340	865.7	50.30	50.32	49.03	51.39	0.02	1.27	1.09
11	262	312	338	866.3	50.70	50.67	49.77	52.85	0.03	0.93	2.15
12	260	299	345	862.1	51.40	51.36	49.26	51.25	0.04	2.14	0.15
13	271	315	346	868.1	51.70	51.73	49.60	52.89	0.03	2.10	1.19
14	269	314	350	866.2	52.30	52.36	50.05	53.36	0.06	2.25	1.06
15	272	314	355	865.9	53.10	53.08	50.14	53.47	0.02	2.96	0.37
16	268	312	355	863.1	53.50	53.55	50.74	54.04	0.05	2.76	0.54
17	280	320	353	867.2	54.10	54.12	50.45	54.40	0.02	3.65	0.30
							avera	age error	0.03	1.33	0.83

According to the data in Table 1, the most accurate calculation method for determining the cetane index is the method presented in ISO 4264 since the average error of this method is 0.03 points, while the average errors of the methods presented in the National State Standard 27768-88 and ASTM D976 are 1.33 and 0.83 points, respectively. The method presented in the ISO 4264 standard is used for further calculations.

#### 3. Non-additivity of the cetane index and the fractional composition of diesel fuels

In this work, the cetane indices of the components of diesel fuels were calculated according to the equation ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four-variable equation" using the data from Russian industrial enterprise <sup>[10]</sup>. The results of the calculation are presented in Table 2.

Component	T10%	T50% oC	Т90%	Density at 15°C kg/m <sup>3</sup>	CIISO
Straight-run diesel fraction	176	198	256	801.3	45.9
Kerosene fraction	159	180	211	787.4	43.6
Hydrotreated diesel fraction	258	292	336	844.9	57.4
Dewaxed diesel fraction	208	243	283	835.0	46.3

Table 2. Calculated cetane indices of commercial diesel fuels components

Further, the calculations of cetane indices of commercial diesel fuels blends, were performed. Cetane indices for mixtures were also determined experimentally. The calculation was performed according to the rule of additivity, assuming that each of the components contributes to the total cetane index of the blend in proportion to its mass fraction in this blend:

$$CI_{mix.} = \sum_{i=1}^{n} CI_i v_i$$

(4)

 $CI_{mix.}$  is the cetane index of the blend, points;  $CI_i$  is the cetane index of  $i^{th}$  component of the blend, points;  $v_i$  is the mass fraction of  $i^{th}$  component in the blend, % wt.

Table 3 shows the ratios of the blending components of diesel fuel (blending recipes), the cetane indices of the blends determined experimentally ( $CI_{mix.exp.}$ ), cetane indices of the blends calculated according to the rule of additivity ( $CI_{mix.add.}$ ), as well as the error ( $\Delta_{add.}$ ) and the average calculation error ( $\Delta_{add.av.}$ ) of the cetane index of the blends determined by the rule of additivity.

As a result, the difference between the cetane index of the blend, determined experimentally, and the cetane index of the blend, calculated according to the rule of additivity, varies from 1 to 3 points. This fact evidences the non-additivity of the cetane index of diesel fuels. Thus, there is the necessity to develop methods for calculating the cetane indices of blended diesel fuels, taking into account the non-additivity.

	Blends							
Components	1	2	3	4				
	vi, % wt.							
Straight-run diesel fraction	0.40	0.40	0.37	0.40				
Kerosene fraction	0.12	0.00	0.00	0.00				
Hydrotreated diesel fraction	0.30	0.35	0.40	0.50				
Dewaxed diesel fraction	0.18	0.25	0.23	0.10				
CImix.exp.	47	49	48	50				
CImix.add.	49	50	51	52				
$\Delta$ add.	2	1	3	2				
$\Delta$ add.av.			2					

Table 3. Calculated cetane indexes of blended diesel fuels

Calculation of the cetane index of blended diesel fuel, taking into account the non-additivity, is possible by using the fractional composition of blend. However, when solving the problems of production planning (the development of blending recipes), the blend is not yet exist, and it is impossible to determine its fractional composition. At the same time, the fractional composition of the blending components is usually known. A further stage of the study was to establish whether the fractional composition of diesel fuel is subject to the rule of additivity.

For this purpose, 4 samples of commercial diesel fuel were taken from fuel station located in Russia. Each sample was assigned a numerical cipher from 1 to 4. For all 4 samples, the fractional composition was determined experimentally (Table 4).

No	IBP	T10%	T20%	T30%	T40%	T50%	T60%	T70%	T80%	T90%		
NO.		°C										
1	142	177	203	225	244	263	281	301	322	353		
2	172	198	214	231	246	260	275	291	311	339		
3	130	202	225	242	260	275	294	314	334	331		
4	162	214	239	256	268	278	290	304	318	336		

Table 4. Fractional composition of diesel fuels

Using the 4 samples of commercial diesel fuel, the blends were prepared according to the recipes presented in Table 5. Each prepared blend was assigned a numerical number from 1 to 9.

No of the		Compos	sition, %	
blend	1	2	3	4
1	50	20	30	-
2	50	50	-	-
3	70	30	-	-
4	80	20	-	-
5	-	33.3	33.3	33.4
6	-	50	30	20
7	-	50	20	30
8	_	30	50	20
9	-	20	30	50

Table 5. Blending recipes of commercial diesel fuels

Based on the fractional composition, presented in Table 4, and the blending ratios of diesel fuel, presented in Table 5, the fractional composition of blends 1-9 was calculated by the rule of additivity. The calculation results were compared with the experimentally determined fractional composition of blends 1-9 (Table 6).

As a result, the fractional composition of the blended diesel fuels is also a non-additive value, the average calculation error by the rule of additivity varies from 2 to 9°C.

			Experim	entally o	letermin	ed fraction	onal com	position		
No.	IBP	<b>T</b> 10%	<b>T</b> 20%	<b>T</b> 30%	<i>T</i> 40%	<b>T</b> 50%	<b>T</b> 60%	<b>T</b> 70%	<b>T</b> 80%	<b>T</b> 90%
					0	С				
1	147	186	207	231	250	266	282	303	325	339
2	139	184	204	221	240	256	270	290	310	326
3	147	185	205	223	240	259	276	294	314	344
4	140	180	203	222	240	258	276	295	318	346
5	155	201	219	244	257	271	285	301	319	320
6	168	202	222	237	254	268	283	300	319	344
7	167	205	221	239	254	268	283	300	318	342
8	167	207	226	244	259	274	289	306	329	348
9	166	210	226	249	262	275	289	305	324	344
		Fraction	al compo	osition ca	lculated	accordin	ig to the	rule of a	dditivity	
No.	IBP	<i>T</i> 10%	<b>T</b> 20%	<b>T</b> 30%	<i>T</i> 40%	<b>T</b> 50%	<b>T</b> 60%	<b>T</b> 70%	<b>T</b> 80%	<b>T</b> 90%
					0	С				
1	144.4	188.7	211.8	231.3	249.2	266.0	283.7	302.9	323.4	343.6
2	157.0	187.5	208.5	228.0	245.0	261.5	278.0	296.0	316.5	346.0
3	151.0	183.3	206.3	226.8	244.6	262.1	279.2	298.0	318.7	348.8
4	148.0	181.2	205.2	226.2	244.4	262.4	279.8	299.0	319.8	350.2
5	153.1	202.6	223.7	240.6	255.4	268.3	283.5	300.0	317.8	332.0
6	157.4	202.4	222.3	239.3	254.6	268.1	283.7	300.5	319.3	336.0
7	160.6	203.6	223.7	240.7	255.4	268.4	283.3	299.5	317.7	336.5
8	149.0	203.2	224.5	241.5	257.4	271.1	287.5	305.1	323.9	334.4
9	154.4	207.2	229.8	246.8	261.2	273.5	288.2	304.4	321.4	335.1
					Δa	dd.				
No.	IBP	<b>T</b> 10%	<b>T</b> 20%	<b>T</b> 30%	<i>T</i> 40%	<b>T</b> 50%	<b>T</b> 60%	<b>T</b> 70%	<b>T</b> 80%	<b>T</b> 90%
					0	С				
1	2.6	2.7	4.8	0.3	0.8	0.0	1.7	0.1	1.6	4.6
2	18.0	3.5	4.5	7.0	5.0	5.5	8.0	6.0	6.5	20.0
3	4.0	1.7	1.3	3.8	4.6	3.1	3.2	4.0	4.7	4.8
4	8.0	1.2	2.2	4.2	4.4	4.4	3.8	4.0	1.8	4.2
5	1.9	1.6	4.7	3.4	1.6	2.7	1.5	1.0	1.2	12.0
6	10.6	0.4	0.3	2.3	0.6	0.1	0.7	0.5	0.3	8.0
7	6.4	1.4	2.7	1.7	1.4	0.4	0.3	0.5	0.3	5.5
8	18.0	3.8	1.5	2.5	1.6	2.9	1.5	0.9	5.1	13.6
9	11.6	2.8	3.8	2.2	0.8	1.5	0.8	0.6	2.6	8.9
∆av.	9.0	2.1	2.9	3.0	2.3	2.3	2.4	2.0	2.7	9.1

Table 6. Comparison of the fractional composition calculated according to the rule of additivity with experimentally determined fractional composition

## 4. Calculation method for prediction of the cetane index of blended diesel fuels taking into account non-additivity

As the fractional composition of diesel fuel does not subject the rule of additivity, the developed calculation method uses the true boiling points of the fractions.

Data obtained by atmospheric distillation of petroleum fractions, as a rule, do not represent the actual boiling points of the components in the fraction. Therefore, technologists are more

interested in the true boiling points (TBP) of the components in the petroleum product. TBP is obtained by distillation of petroleum products using a tray distillation column with 15-100 theoretical plates with a relatively high reflux ratio (1-5 or higher). A high degree of fractionation in these columns gives accurate separation of the components of the mixture. However, the lack of unified equipment and the complexity of the procedure itself are significant drawbacks of the laboratory measurement of the TBP. The determination of the TBP is more complex procedure than the determination of the fractional composition in terms of time and money. However, there are calculation methods for converting the fractional composition (FC) to the true boiling point [11]:

$$TBP = a(FC)^b$$

(5)

*TBP* is true boiling point, °K; *FC* is fractional composition, °K; *a*, *b* are empirical coefficients. The values of coefficients *a* and *b* are presented in Table 7.

<i>FC</i> , % vol.	а	Ь	<i>FC</i> , % vol.	а	b
0	2.9747	0.8466	70	8.2873	0.6871
10	1.4459	0.9511	90	10.6266	0.6529
30	0.8506	1.0315	100	7.9952	0.6949
50	3.2680	0.8274			

Table 7. Coefficients for converting the fractional composition to the true boiling point

Using equation (5), TBP was calculated for the components of diesel fuels produced at one of the Russian refineries (Table 2). Using the obtained correlations, the initial boiling point (0%) and the end boiling points (100%) of fractions were determined (Table 8).

Table 8. TBP of diesel fuel components

Commencent	FC				ТВР				
Component	10%	50%	90%	0%	10%	50%	90%	100%	
Straight-run diesel fraction	449	471	529	423	433	473	541	559	
Kerosene fraction	432	453	484	405	415	455	495	505	
Hydrotreated diesel fraction	531	565	609	507	520	569	624	638	
Dewaxed diesel fraction	481	516	556	454	467	519	569	582	

In view of the absence of information on the initial and the end boiling points of fractions, the correlations of distillation yield of the fraction versus the boiling point were founded. These correlations were used to obtain necessary data (Figures 1-8).



Figure 1. Distillation yield of straight-run diesel fraction versus initial boiling point dewaxed diesel fraction versus end boiling point



Figure 2. Distillation yield of straight-run diesel fraction versus end boiling point versus end boiling point



Figure 3. Distillation yield of kerosene fraction fraction versus initial boiling point of dewaxed diesel fraction versus end boiling point



Figure 5. Distillation yield of hydrotreated diesel fraction versus initial boiling point



Figure 7. Distillation yield of dewaxed diesel fraction versus initial boiling point



Figure 4. Distillation yield of kerosene fraction versus end boiling point



Figure 6. Distillation yield of hydrotreated diesel fraction versus end boiling point



Figure 8. Distillation yield of dewaxed diesel fraction versus end boiling point

Using the data presented in Table 8, the distillation yields of fractions were calculated at the temperature from the initial boiling point to the end boiling point in increments of 1°K.

To calculate the cetane index of the blended diesel fuel, the key component of the blend are determined, i.e. the component whose proportion in the blending recipe is greatest. Further, the true boiling point of 90 % vol. fraction of the key component are determined (Table 8). Then, at the temperature obtained from the correlations, presented in Figures 1-8, the distillation yields of the remaining components involved in blending ( $\mu_i$ ) are determined. Then the obtained values are multiplied by the volume content of the components in the blend ( $v_i$ ) and the obtained values are normalized ( $X_i$ ). The obtained values ( $Y_i$ ) represent the proportion of each component contributes to the cetane index of the blend.

Let's consider an example of calculation of the cetane index of the blended diesel fuel, produced according to the blending receipt No. 1, presented in Table 3.

The key component of diesel fuel produced according to the blending receipt No. 1 is straight-run diesel fraction. The true boiling point of 90 % vol. fraction of this component is

541 °K (Table 8). From the correlations presented in Figures 3-8, we determine that at the temperature of 541 °K, 27 % vol. hydrotreated diesel fraction, 67.5 % vol. dewaxed diesel fraction, and 100 % vol. kerosene fraction are distilled.

The values of  $X_i$  are determined as follows:

 $X_{i} = \mu_{i} \cdot \nu_{i}$ Thus, we obtain:  $X_{1}=0.4.0.9=0.360$ ;  $X_{2}=0.1.1=0.120$ ;  $X_{3}=0.3.0.27=0.081$ ;  $X_{4}=0.18.0.675=0.122$ ; Then we normalize the values of  $X_{i}$ :  $Y_{i} = X_{i} / \sum_{i=1}^{n} X_{i}$ Thus, we obtain:  $Y_{1}=0.527$ ;  $Y_{2}=0.176$ ;  $Y_{3}=0.119$ ;  $Y_{4}=0.179$ (6)
(7)

The cetane idex is calculated according to the rule of additivity. Using the developed calculation method, the cetane indices of the blended diesel fuels ( $CI_{mix.met.}$ ) were calculated for the four blending recipes presented in Table 3 (Table 9).

Table 9. Calculated cetane indices using the developed method

Component	Vi	$\mu_i$	$X_i$	$Y_i$	$CI_{ISO}$	CI <sub>mix.met.</sub>
	R	eceipt No	. 1			
Straight-run diesel fraction	0.40	0.900	0.360	0.527	45.9	
Kerosene fraction	0.12	1.000	0.120	0.176	43.6	47
Hydrotreated diesel fraction	0.30	0.270	0.081	0.119	57.4	47
Dewaxed diesel fraction	0.18	0.675	0.122	0.179	46.3	
	R	eceipt No	. 2			
Straight-run diesel fraction	0.40	0.900	0.360	0.578	45.9	
Hydrotreated diesel fraction	0.35	0.270	0.095	0.152	57.4	48
Dewaxed diesel fraction	0.25	0.675	0.169	0.271	46.3	
	R	eceipt No	. 3			
Straight-run diesel fraction	0.37	1.000	0.370	0.380	45.9	
Hydrotreated diesel fraction	0.40	0.900	0.360	0.370	57.4	50
Dewaxed diesel fraction	0.23	1.000	0.230	0.240	46.3	
	R	eceipt No	. 4			
Straight-run diesel fraction	0.40	0.900	0.360	0.640	45.9	
Hydrotreated diesel fraction	0.50	0.270	0.135	0.240	57.4	49
Dewaxed diesel fraction	0.10	0.675	0.0675	0.120	46.3	

Calculated values were compared with experimentally determined cetane indices of blends, as well as with cetane indices of blends, calculated according to the rule of additivity (Table 10).

Receipt	CImix.exp.	CImix.add.	CImix.met.	$\Delta$ add.	∆met.
1	47	49	47	2	0
2	49	50	48	1	1
3	48	51	50	3	2
4	50	52	49	2	1
			<b>∆</b> av.	2	1

Thus, the developed method allows calculating the cetane index of blended diesel fuels with an average error ( $\Delta_{met.}$ ) not exceeding 1 point, while the calculation according to the rule of additivity has an average error of 2 points.

#### 5. Conclusion

1. Based on the experimental data, it was established that the most accurate method for calculating the cetane index of diesel fuel is the method proposed by the ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four-variable equation". This method can be used for the successful quantitative prediction of cetane indices of diesel fractions. 2. Using the industrial blending recipes for the production of diesel fuels, it was shown that the cetane index of blended diesel fuels is non-additive value. The average deviation from the calculation according to the rule of additivity is 2 points.

3. On the basis of laboratory studies, it was established that the fractional composition of the blended diesel fuels does not subject the rule of additivity. The average error of calculation by the rule of additivity varies from 2 to 9 °C.

4. The developed calculation method for prediction of the cetane index of the blended diesel fuels is based on the true boiling points of blending components. The method takes into account non-additivity of the cetane index. The absolute error of calculating the cetane index according to the developed method does not exceed 1 point.

#### Acknowlegements

The work was performed within the framework of the state task №10.13268.2018/8.9.

#### List of symbols

CI – cetane index, points;

*T*10% – boiling point of 10%vol. fraction, °C;

T50% – boiling point of 50%vol. fraction, °C;

T90% – boiling point of 90%vol. fraction, °C;

 $D - density at 15 \,^{\circ}C, \, kg/m^3;$ 

 $\rho_4^{15}$  – density at 15 °C, g/sm<sup>3</sup>;

t – boiling point of 50 % vol. fraction corrected for the normal barometric pressure of 101.3 kPa, °C.  $T_{50\%F}$  – boiling point of 50 % vol. fraction, °F;

API – relative specific gravity;

*CIIso – cetane index proposed by the ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four-variable equation", points;* 

*CINS* – *cetane index proposed by the National State Standard* 27768-88 "*Diesel fuel. Determination of cetane index by calculation method*", *points;* 

CIASTM – cetane index proposed by the ASTM D976 "Standard test method for calculated cetane index of distillate fuels", points;

Clexp. - cetane index determined experimentally, points;

 $\Delta$ <sub>ISO</sub> – calculation error of cetane index according to the ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four-variable equation", points;

 $\Delta NS$  – calculation error of cetane index according to the National State Standard 27768-88 "Diesel fuel. Determination of cetane index by calculation method", points;

 $\Delta$ ASTM – calculation error of cetane index according to the ASTM D976 "Standard test method for calculated cetane index of distillate fuels", points;

CImix. - cetane index of the blend, points;

*CIi* – cetane index of *i*<sup>th</sup> component of the blend, points;

*vi* – mass fraction of *i*<sup>th</sup> component in the blend, % wt.;

*CImix.exp.* – *cetane index of the blend determined experimentally, points;* 

CImix.add. - cetane index of the blend calculated according to the rule of additivity, points;

 $\Delta_{add.}$  – calculation error of the cetane index by the rule of additivity, points;

 $\Delta_{add.av.}$  – average calculation error of the cetane index by the rule of additivity, points;

TBP – true boiling point, °K;

FC – fractional composition, °K;

a, b – empirical coefficients for calculation of true boiling point;

 $\mu_i$  – distillation yield of i<sup>th</sup> component at true boiling point of 90 % vol. fraction of the key component, % vol.;

 $X_i$  – coefficient for converting the content of i<sup>th</sup> component in the blend used to calculate cetane index taking into account non-additivity;

*Yi* – proportion of each component contributes to the cetane index of the blend;

CImix.met. - cetane index of the blend, calculated according to the developed method, points;

 $\Delta_{met.}$  – calculation error of cetane index of the blend according to the developed method, points.

#### References

- [1] Krutz E, Polonowski CJ. The Influence of Fuel Cetane Number on Catalyst Light-Off Operation in a Modern Diesel Engine. Int. J. Fuels Lubr. 2017; 10(3).
- [2] Stratiev D, Shishkova I, Nedelchev A, Kirilov K, Nikolaychuk E, Ivanov A, Sharafutdinov I, Veli A, Mitkova M, Tsaneva T, Petkova N, Sharpe R, Yordanov D, Belchev Z, Nenov S, Rudnev N, Atanassova V, Sotirova E, Sotirov S, Atanassov K. Investigation of Relationships between Petroleum Properties and Their Impact on Crude Oil Compatibility. Energy Fuels. 2015; 29(12): 7836-7854.
- [3] Borugadda VB, Goud VV. Improved low-temperature properties of chemically modified high free fatty acid castor oil-methyl esters: Blending and optimization study. J. Energy Eng. 2016; 142(1).
- [4] Zhang H, Fu W, Guo Y, Ling F, Gao B, Cheng Z. Determination of Diesel Cetane Number by Air Flow Control. Pet. Process. Petrochem. 2017; 48(8): 90-93.
- [5] Smolenskii EA, Bavykin VM, Ryzhov AN, Slovokhotova OL, Chuvaeva IV, Lapidus AL. Cetane numbers of hydrocarbons: calculations using optimal topological indices. Russ. Chem. Bull. 2008; 57(3): 461-467.
- [6] Altynov AA, Bogdanov IA, Kirgina MV, Sakhnevich BV. Proceedings 2016 11th International Forum on Strategic Technology, IFOST 2016. 2016; 615-618.
- [7] ISO 4264:2007 "Petroleum products Calculation of cetane index of middle-distillate fuels by the four-variable equation" [Electronic source]. Access: https://www.iso.org.
- [8] National State Standard 27768-88 "Diesel fuel. Determination of cetane index by calculation method" [Electronic source]. Access: http://vsegost.com.
- [9] ASTM D976 «Standard test method for calculated cetane index of distillate fuels».
- [10] Belinskaya NS, Ivanchina ED, Ivashkina EN, Sejtenova G. Studying Patterns of Synthesis of Low Freezing Distillates from Atmospheric Gasoil by Means of Mathematical Modelling. Curr. Org. Synth. 2017; 14(3): 365-371.
- [11] Riazi MR. Characterization and properties of petroleum fractions. 1 st ed., p. cm. ASTM manual series: MNL50. ASTM stock number: MNL50. 2005. p. 427.

To whom correspondence should be addressed: Dr. Maria V. Kirgina, Division for Chemical Engineering, School of Earth Sciences & Engineering, National Research Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; e-mail: mkirgina@tpu.ru

## Article

**Open Access** 

FEASIBILITY STUDIES OF JET FUELS USING AS A LOW-TEMPERATURE ADDITIVE TO STRAIGHT-RUN DIESEL FUELS

Maria V. Kirgina\*, Ilya A. Bogdanov, Andrey A. Altynov, Nikolay S. Krinitsyn

National Research Tomsk Polytechnic University, Russia

Received November 21, 2018; Accepted January 11, 2019

#### Abstract

The article considers the feasibility of using jet fuel as a low-temperature additive for diesel fuels. The main physicochemical properties and operational characteristics of straight-run diesel fuel sample, jet fuel sample, and their blends have been experimentally determined. It has been established that the use of jet fuel as a low-temperature additive allows producing summer diesel fuel brands. Moreover, it has been established that the use of jet fuel in combination with a depressant-dispersant additive allows producing interseasonal diesel fuel.

Keywords: diesel fuel; jet fuel; blend; low-temperature properties; cetane index; additive.

#### 1. Introduction

Diesel fuel (DT), today, is one of the most common types of motor fuel, in addition to passenger cars, diesel fuel is used on small crafts and electric power generators.

To ensure reliable and environmentally friendly operation of a diesel engine, it is necessary to have high-quality diesel fuel of a certain composition, which is characterized by specified physicochemical properties and operational characteristics. On the Russian Federation territory, the production of diesel fuels is regulated by the government, according to the following requirements documents USS 305-2013 "Diesel fuel. Specifications" <sup>[1]</sup> and the Technical Regulations of the Customs Union TRTS 013 2011 "Requirements to automobile and aviation gasoline, diesel and ship fuel, jet engine fuel and furnace oil" <sup>[2]</sup>, which has the highest priority in the field of turnover and production motor fuels. Meanwhile, the use of diesel fuel is limited in areas with a cold climate, in the northern and Arctic territories. This is due to contained in diesel fuel paraffin hydrocarbons, which forms crystals at low temperatures and adversely affects the operation of the engine.

There are various ways to improve the low-temperature properties of diesel fuels. The catalytic dewaxing process can significantly improve the pour point of diesel fuels, but this method is applicable only in large industries. It is worth noting that motor fuels in remote, northern areas, as a rule, are produced at local medium and small enterprises.

The most common and effective way to improve the low-temperature properties of diesel fuel is the use of depressant and dispersant additives, as well as additive substances, characterized by good low-temperature properties.

One of the possible additives for improves the low-temperature properties of diesel fuel is jet fuel <sup>[3-10]</sup>. Jet fuel (JF) is characterized by exceptional low-temperature properties, so according to the USS 10227-2013 "Jet fuels. Specifications" <sup>[11]</sup>, which regulates the production of jet fuels in the Russian Federation, the freezing point of jet fuel must be, not higher than 60°C.

However, jet fuels as an additive to improve the low-temperature properties of diesel fuel is used sparingly. This is due to the negative impact of jet fuel on other operational characteristics of diesel fuel, in particular – on the flammability of the blend, characterized by a cetane index. Thus, the purpose of this work is to study the physicochemical properties and operational characteristics of diesel and jet fuels, as well as look into the possibility of using jet fuels as a low-temperature additive to straight-run diesel fuels.

#### 2. Object and methods of research

The objects of research in the work were: a sample of straight-run diesel fuel obtained from one of the Western Siberia fields of the Russian Federation, and a sample of jet fuel, granted by LLC "Tomsk Airport."

Using the described above petroleum products, blends have been prepared. The percentage in blends of jet and diesel fuels is presented in Table 1. The numerical codes from 1 to 3 have been assigned to blends, in order of increasing percentage of their jet fuel.

Table 1.	Recipes of blends	of jet and	diesel fuel
----------	-------------------	------------	-------------

Pland	Content, %vol.			
Dienu	Jet fuel	Diesel fuel		
Blend 1	5	95		
Blend 2	10	90		
Blend 3	20	80		

For the studied samples of jet fuel and diesel fuel, the following physicochemical properties and operational characteristics were determined: fractional composition, density, viscosity, sulfur content, low-temperature properties (cold filter plugging point, pour point), and also cetane index was calculated.

The determination was carried out according to the test methods presented below. Depending on the origin, jet fuel and diesel fuel can have various fractional composition and wide boiling ranges.

The test method presented in ISO 3405:2011 "Petroleum products. Determination of distillation characteristics at atmospheric pressure" <sup>[12]</sup> was used to determining the fractional composition of jet and diesel fuel samples.

The summary of this test method is as follows: 100 cm<sup>3</sup> of the test sample is distillated under conditions consistent with the nature of the product and conducted continuous observations of the thermometer readings and the volume of condensate.

The density of the fuel is the most important physicochemical property of the fuel that allows one to indirectly judge particular operational characteristics. For the jet fuel, density is an indicator that determines the flying range. Therefore, attempts are being made to obtain fuels with the highest possible density <sup>[13]</sup>. The determination of the density of the studied oil products in work was carried out using a hydrometer. Studies were conducted according to the requirements presented in the ISO 3675:1998 "Crude petroleum and liquid petroleum products. Laboratory determination of density. Hydrometer method" <sup>[14]</sup>.

The summary of this test method for determining the density is as follows: a hydrometer is immersed in a cylinder filled with the studied oil product after that researcher takes readings the scale of the hydrometer.

The viscosity of the fuel, as a rule, determine the dispersibility of the fuel, its pumpability in the fuel system and the wear of the pump plungers. The lower the viscosity, the better the fuel is atomized and the higher the dispersion of the microdroplets. The pumpability of the fuel also improves with a decrease its viscosity <sup>[15]</sup>.

The kinematic viscosity of jet fuel and diesel fuel samples of was determined by the method presented in ISO 3104:1994 "Petroleum products. Transparent and opaque liquids. Determination of kinematic viscosity and calculation of dynamic viscosity" <sup>[16]</sup>.

The summary of this test method of determination the kinematic viscosity is as follows: the time (in seconds) the expiration of a certain volume of liquid in the capillary of a glass viscometer under the influence of gravity at a constant temperature of 20°C is measured.

One of the most strictly regulated environmental indicators of fuel quality is the sulfur content. This is due to the fact that sulfur in its pure form and sulfur-containing compounds

in the composition of petroleum products are extremely toxic impurities, characterized by corrosivity, which reduces the service life of the metal engine parts.

Determination of sulfur content in the studied samples was carried out according to the method presented in the ASTM D4294-16 "Standard test method for sulfur in petroleum and petroleum products by energy dispersive X-ray fluorescence spectrometry" <sup>[17]</sup>.

The summary of this test method for determining the total sulfur content in petroleum and petroleum products is as follows: a sample is placed in a beam of rays emitted by an x-ray tube. The resulting excited characteristic X-ray radiation is measured and compared the received pulse counter signal with the signals obtained when testing pre-prepared calibration samples. In results, it is obtained the total sulfur content in % wt. or mg/kg.

The most important operational characteristics of diesel and jet fuels, which allow concluding that it is possible to use fuel at reduced temperature, for example, at altitude, in winter and arctic conditions are their low-temperature properties.

The pour point of jet and diesel fuel of samples was determined by the method presented in ISO 3013:1997 "Petroleum products. Determination of the freezing point of aviation fuels" <sup>[18]</sup>.

The summary of the method for determining the pour point is to place the tube with the test sample in a cryostat with a coolant (ethanol) and cool it to the expected pour point. At this temperature, the tube with the oil product is tilted at an angle of 45°, and the level of the liquid is monitored. Thus, it is found the temperature at which the level of the sample in a test tube, tilted at an angle of 45°, remains stationary for a certain time. This temperature is the pour point of the sample.

The cold filter plugging point (CFPP) of the jet and diesel fuel samples was determined according to the method presented in ASTM D6371-17 "Standard test method for cold filter plugging point of diesel and heating fuels" <sup>[19]</sup>. The summary of the method is as follows: the fuel sample is cooled, pumped over a standardized wire mesh filter under controlled vacuum, and it is filled the pipette up to the mark. Continuing to cool the fuel, this procedure is repeated at intervals of 1°C. The test is continued to a temperature at which the number of paraffin crystals released from the solution slows down the flow of fuel so that the pipette filling time exceeds 60 seconds. The temperature at which the fuel was last filtered is taken as the cold filter plugging point of the fuel.

The calculation of the cetane index of jet and diesel fuel samples was carried out according to the method presented in the ISO 4264 "Petroleum products – Calculation of cetane index of middle-distillate fuels by the four variable equation" <sup>[20]</sup>, since it was established <sup>[21]</sup> that this method of calculation is the most accurate:

$$CI = 45.2 + 0.0892 \cdot T_{10N} + (0.131 + 0.901B) \cdot T_{50N} +$$

$$+(0.0523 - 0.42B) \cdot T_{90N} + [0.00049 \cdot (T_{10N}^2 - T_{90N}^2)] + 107B + 60B^2;$$

$$T_{10N} = T_{10\%} - 215; \ T_{50N} = T_{50\%} - 260; \ T_{90N} = T_{90\%} - 310;$$

$$B = [\exp(-0.0035 \cdot D_N)] - 1; \ D_N = D - 850$$
(1)

where *CI* is a cetane index, points;  $T_{10\%}$ ,  $T_{50\%}$ ,  $T_{90\%}$  are boiling temperatures of 10 vol. %, 50 vol. % and 90 vol. % of diesel fraction, respectively, °C; *D* is a density of diesel fuel at 15°C, kg/m<sup>3</sup>.

#### 3. Results

#### 3.1. Physicochemical properties and operational characteristics of straight-run diesel fuel

Using the described test methods, the physicochemical properties and operational characteristics of straight-run diesel fuel sample were determined. The results are presented in Table 2.

N⁰	Parameter	Value
1	Density at 15°C, kg/m <sup>3</sup>	842.3
2	Kinematic viscosity at 20°C, mm <sup>2</sup> /s	4.424
3	Content of total sulfur, % wt.	0.242
4	Fractional composition, °C:	
	initial boiling point	151
	10 % vol. boils at a temperature	183
	50 % vol. boils at a temperature	271
	90 % vol. boils at a temperature	359
	95 % vol. boils at a temperature	360
5	Cetane index, points	50,6
6	Pour point,°C	-18
7	Cold filter plugging point,°C	-3

Table 2. The results of determination the characteristics of straight-run diesel fuel sample

## 3.2. Physicochemical properties and operational characteristics of jet fuel

Using the described test methods, the physicochemical properties and operational characteristics of jet fuel sample were determined. The results are presented in Table 3.

Table 3. The results of determination the characteristics of jet fuel sample

N⁰	Parameter	Value
1	Density at 20°C, kg/m <sup>3</sup>	792.0
2	Kinematic viscosity at 20°C, mm <sup>2</sup> /s	1.508
3	Content of total sulfur, % wt.	0.034
4	Fractional composition, °C :	
	initial boiling point	140
	10 % vol. boils at a temperature	154
	50 % vol. boils at a temperature	185
	90 % vol. boils at a temperature	215
	98 % vol. boils at a temperature	226
5	Freezing point, C	-65

It should be noted that the sample of jet fuel is not frozen at the maximum freezing temperature of the cryostat ( $-80^{\circ}$ C).

#### 3.3. Physicochemical properties and operational characteristics of straight-run diesel fuel and jet fuel blends

For the prepared blends, using the described methods, physicochemical properties, and operational characteristics were also determined. The results are presented in Table 4.

Table 4. The results of determination the characteristics of straight-run diesel fuel and jet fuel blends

N⁰	Parameter	Blend 1	Blend 2	Blend 3
1	Density at 15°C, kg/m <sup>3</sup>	838.3	837.3	834.3
2	Kinematic viscosity at 20°C, mm <sup>2</sup> /s	4.087	3.437	3.137
3	Content of total sulfur, % wt.	0.218	0.217	0.197
4	Fractional composition, °C:			
	initial boiling point	147	146	145
	10 % vol. boils at a temperature	182	179	176
	50 % vol. boils at a temperature	258	255	246
	90 % vol. boils at a temperature	344	340	338
	95 % vol. boils at a temperature	360	358	356
5	Cetane index, points	49.1	48.7	47.4
6	Pour point,°C	-35.0	-35.3	-36.0
7	Cold filter plugging point, C	-4	-4	-5

From the results which are presented in Table 4, it follows that with increase the part of jet fuel in the blend, the values of such characteristics as cetane index, density, sulfur content,

and kinematic viscosity decreases, and also the fractional composition is lightened. At the same time, the addition of jet fuel to straight-run diesel fuel improves its low-temperature characteristics.

#### 4. Results and discussion

#### 4.1. Conformity assessment of the straight-run diesel fuel characteristics to the requirements of standards

Comparison of the straight-run diesel fuel sample characteristics with the requirements <sup>[1]</sup>, regulating the production of diesel fuels in the Russian Federation, is presented in Table 5. According to <sup>[1]</sup>, diesel fuel is classified into 4 brands, depending on its characteristics: S - summer, IS - interseasonal, W - winter, A - arctic.

Table 5. Conformity assessment of the straight-run diesel fuel sample characteristics to the requirements [1]

NIO	Baramotor	DF	DF brand			
IN-	Falameter	test sample	S	IS	W	А
1	Cetane index, points, min.	48.4		4	45.0	
2	Density at 15°C, kg/m <sup>3</sup> , max.	842.3	863	3.4	843.4	833.5
3	Kinematic viscosity at 20°C, mm <sup>2</sup> /s	4.424	3.0-	6.0	1.8-5.0	1.5-4.0
4	Fractional composition, C, max.:					
	50 % vol. boils at a temperature	271		280		255
	95 % vol. boils at a temperature	360			360	
6	Cold filter plugging point,°C, max.	-3	-5	-15	-35	-45
7	Content of total sulfur, % wt., max.	0.242			0.2	

As can be seen from Table 5, the investigated diesel fuel meets the requirements of <sup>[1]</sup> for all brands in such characteristics as the cetane index and boiling point 95 % vol. Based on characteristics such as density, viscosity and boiling point of 50 % vol. investigated diesel fuel can be classified to S, IS, and W brands. However, based on such characteristics as the content of sulfur and CFPP, the investigated diesel fuel does not meet the requirements of any brand, and according to <sup>[1]</sup> cannot be realized on the territory of the Russian Federation.

# 4.2. Conformity assessment of the jet fuel characteristics to the requirements of standards

Comparison of the jet fuel sample characteristics with the requirements <sup>[11]</sup>, regulating the production of jet fuel in the Russian Federation, is presented in Table 6.

N⁰	Parameter	RT	TS-1	RT	
		test sample	brand	brand	
1	Density at 20 °C, kg/m <sup>3</sup> , min.	792.0	775.0		
	Fractional composition, °C max.:				
	initial boiling point	140	150	135-155	
-	10 % vol. boils at a temperature	154	165	175	
Z	50 % vol. boils at a temperature	185	195	225	
	90 % vol. boils at a temperature	215	230	270	
	98 % vol. boils at a temperature	226	250	280	
3	Freezing point, °C, max.	-65	-60		
4	Content of total sulfur, % wt., max.	0.034	0.1		
5	Kinematic viscosity at 20 °C, mm <sup>2</sup> /s, min	1.508	1	.25	

Table 6. Conformity assessment of the jet fuel sample characteristics to the requirements <sup>[11]</sup>

As can be seen from Table 6, the investigated jet fuel sample meets all the requirements of <sup>[11]</sup>, for the TS-1 and the RT brands. The results of investigations allow us to conclude that the test sample of jet fuel provided by LLC "Airport TOMSK" is characterized by high quality.

#### 4.3. Conformity assessment of the straight-run diesel fuel and jet fuel blends characteristics to the requirements of standards

Comparison of the blends characteristics, which have been prepared of straight-run diesel fuel and jet fuel for investigation, with the requirements <sup>[1]</sup>, regulating the production of diesel fuels in the Russian Federation, is presented in Table 7.

Table 7. Conformity assessment of the straight-run diesel fuel and jet fuel blends characteristics to the requirements <sup>[1]</sup>

NO	Darameter	Pland 1	1 Blend 2	Pland 2	DF brand			
IN-	Parameter	Dieliu I		Biellu 3	S	IS	W	А
1	Cetane index, points, min.	47.6	47.3	46.6		4	5.0	
2	Density at 15°C, kg/m³, max.	838.3	837.3	834.3	86	3.4	843.4	833.5
3	Kinematic viscosity at 20°C, mm²/s	4.087	3.437	3.137	3.0-	6.0	1.8-5.0	1.5-4.0
4	Fractional composition, °C, ma	ix.:						
	50 % vol. boils at a temperature	258	255	246		280		255
	95 % vol. boils at a temperature	360	358	356		3	60	
6	Cold filter plugging point,°C, max.	-4	-4	-5	-5	-15	-35	-45
7	Content of total sulfur, % wt., max	0.218	0.217	0.197		(	).2	

From the results which are presented in Table 7 it can be seen that the addition of 20 % vol. jet fuel to diesel fuel allows to reduce the CFPP by  $2^{\circ}C$  (up to  $-5^{\circ}C$ ), which meets the requirements <sup>[1]</sup> for CFPP to brand of diesel fuel S, and allows realize this fuel in the Russian Federation.

It should be noted that adding even 20 % vol. jet fuel to diesel fuel, the cetane index of blend meets the requirements of <sup>[1]</sup>, which suggests that adding jet fuel to diesel fuel does not significantly much reduce the flammability.

Further still, the adding of 20 % vol. jet fuel to blend allows: to reduce the sulfur content to the required level, and bring in line with requirements for A diesel fuel brand, such characteristics as viscosity and boiling point of 50 % vol.

At the next stage of the work, the authors investigated the possibility of producing interseasonal diesel fuel brand (IS), applying the integrated use of an additive (jet fuel) and a depressant-dispersant additive (Diesel Flie $\beta$  Fit).

For this purpose, a depressant-dispersant additive for diesel fuel "Diesel Flie $\beta$ -Fit", manufactured by LIQUI MOLY, was added to the blend of diesel and jet fuels number 3, at a concentration recommended by the manufacturer (0.3 mL of additive per 100 mL of fuel). For the obtained blend (blend number 3.1), CFPP was determined (using the same test method <sup>[19]</sup>). The obtained results showed that the addition of low-temperature additives simultaneously with 20 % vol. jet fuel allows you to reduce CFPP of straight-run diesel fuel by 20 °C (up to - 23°C), which meets the requirements of CFPP, to the brand IS diesel fuel brand <sup>[11]</sup>.

The results indicate the feasibility of using jet fuel (including in combination with depressant-dispersant additives) as an additive, which improves low-temperature properties of straight-run diesel fuels.

## 5. Conclusion

The physicochemical properties and operational characteristics of jet fuel sample (fractional composition, density, viscosity, sulfur content, low-temperature properties) have been investigated. It has been established that the analyzed jet fuel in its properties meets all the requirements of <sup>[11]</sup>, both for the TS-1 and for the RT brands. It is shown that the sample of jet fuel, provided by LLC "Airport TOMSK", is characterized by high quality.

The physicochemical properties and operational characteristics of straight-run diesel fuel sample have been investigated. It was established that the test sample of straight-run diesel fuel meets the requirements of <sup>[1]</sup> for all brands in such characteristics as cetane index, density and boiling point of 95 % vol.; for brands S, IS and W only by viscosity and boiling point of 50 % vol. At the same time, it was established that such characteristics as the content of sulfur and CFPP of analyzed straight-run diesel fuel does not meet the requirements of any diesel fuel brads and cannot be realized on the Russian Federation territory.

The physicochemical properties and operational characteristics of blends of jet and diesel fuels have been investigated. It is shown that with an increase the content of jet fuel in the blend, the cetane index, density, viscosity and sulfur content of diesel fuel decrease, the fractional composition is lightened, CFPP becomes more negative. It is established that addition of 20 % vol. jet fuel to diesel fuel allows to reduce the sulfur content in the blend to 0.197 % wt., CFPP to 2°C (up to -5°C); the addition of a depressant-dispersant additive to-gether with 20 % vol. jet fuel to diesel fuel allows to reduce the CFPP to 20°C (up to -23°C).

It is shown that the addition of jet fuel to straight-run diesel fuel makes it possible to obtain commercial diesel fuel brand S, together with a depressant-dispersant additive – commercial diesel fuel brand IS. It has been established that it is reasonable to use jet fuel (including in together with depressant-dispersant additives) in as a low-temperature additive to straight-run diesel fuels.

#### Acknowledgements

This work was supported by the Ministry of Education and Science of Russian Federation, a basic part of the state task "Science", project 2.5760.2017/8.9.

#### List of symbols

DF	diesel fuel;	CI	cetane index, points;
JF	jet fuel;	T10%	boiling point of 10 % vol. fraction, °C;
CFPP	cold filter plugging point;	T50%	boiling point of 50 % vol. fraction, °C;
S	summer diesel fuel brand;	T90%	boiling point of 90 % vol. fraction, °C;
IS	interseasonal diesel fuel brand;	D	density at 15°C, kg/m <sup>3</sup> ;
W	winter diesel fuel brand;	RT	jet fuel brand;
Α	arctic diesel fuel brand;	TS-1	jet fuel brand.

#### References

- [1] USS 305-2013 "Diesel fuel. Specifications".
- [2] Technical Regulations of the Customs Union TR TS 013 2011 "Requirements to automobile and aviation gasoline, diesel and ship fuel, jet engine fuel and furnace oil".
- [3] Lim YK, Kim JY, Kim JR, Ha JH. Appl. Chem. Eng. 2017; 28 (4): 460-466.
- [4] Li J, Yang G, Yoneyama Y, Vitidsant T, Tsubaki N. Fuel, 2016; 171: 159-166.
- [5] Ghamari M, Ratner A. Fuel, 2016; 178: 63-70.
- [6] Li X, Huang X, Liu H. Combust. Flame, 2018; 188: 262-272.
- [7] Petrukhina NN, Maksimov A.A. Pet. Chem, 2018; 58 (5): 347-374.
- [8] Yang J, Xin Z, He QS, Corscadden K, Niu H. Fuel. 2019; 237: 916-936.
- [9] Kapilan N, Baykov BD. Pet. Coal, 2014; 56 (1): 79-86.
- [10] Belinskaya NS, Ivanchina ED, Ivashkina EN, Sejtenova G. Curr. Org. Synth., 2017; 14(3): 365-371.
- [11] USS 10227-2013 "Jet fuels. Specifications".
- [12] ISO 3405:2011 "Petroleum products. Determination of distillation characteristics at atmospheric pressure".

- [13] Akhmetov SA, Serikov TP, Kuzeev IR, Baiazitov MI. Technology and equipment of the refining of oil and gas, Nedra Publ.: Saint-Petersburg, 2006; p. 868.
- [14] ISO 3675:1998 "Crude petroleum and liquid petroleum products. Laboratory determination of density. Hydrometer method".
- [15] Manovyan AK. Technology of natural energy producing material processing, Chemistry KolosS: Moscow, 2004; p. 455.
- [16] ISO 3104:1994 "Petroleum products. Transparent and opaque liquids. Determination of kinematic viscosity and calculation of dynamic viscosity".
- [17] ASTM D4294-16 "Standard test method for sulfur in petroleum and petroleum products by energy dispersive X-ray fluorescence spectrometry".
- [18] ISO 3013:1997 "Petroleum products. Determination of the freezing point of aviation fuels".
- [19] ASTM D6371-17 "Standard test method for cold filter plugging point of diesel and heating fuels".
- [20] ISO 4264 "Petroleum products Calculation of cetane index of middle-distillate fuels by the four variable equation".
- [21] Altynov AA, Bogdanov IA, Kirgina MV, Sakhnevich BV. "Determination of operational characteristics of diesel fuel: A study on computational methods", Proceedings-2016 11th International Forum on Strategic Technology, IFOST 2016, Novosibirsk, pp. 615-618, June, 2016.

To whom correspondence should be addressed: Dr. Maria V. Kirgina, Division for Chemical Engineering, School of Earth Sciences & Engineering, National Research Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; e-mail: <u>mkirgina@tpu.ru</u>

# Article

COMPOSITIONAL STUDY OF OIL AND GAS DRILLING WASTES IN AN ONSHORE NIGER DELTA FIELD, NIGERIA

Chiazor J. Egbuachor<sup>1</sup>\*, and Kingsley K. Nwozor<sup>2</sup>

<sup>1</sup> Belushi World Class (Oil and Gas) Ltd, Port Harcourt, Nigeria

<sup>2</sup> Department of Geology, Chukuuemeka Odumegwu Ojukwu University, Uli, Nigeria

Received November 21, 2018; Accepted January 11, 2019

#### Abstract

Hostilities often arise between oil companies and host communities in the Niger Delta region of Nigeria due to environmental challenges instigated by drilling activities, especially the poor handling of drilling wastes. The bulk of the wastes, dominated by waste drilling fluids and lithological cuttings are those generated in the course of drilling oil and gas wells. In their raw state, the waste materials constitute a considerable hazard to the environment as the concentration of the physico-chemical properties grossly violate the acceptable regulatory standard. With improved local awareness, modern technology, and efficient regulatory monitoring, oil field waste disposal and management practices have improved over the years. However, gaps in the waste management chain often lead to spillages and improper disposal which compromises environmental quality and safety. As a result, the corporate integrity of oil companies suffers greatly with the implication of costly litigations and violent reactions from the host communities and other stakeholders. This case study examines the constituents of spent materials at a typical drilling site in an onshore oilfield located in the Niger Delta. The results show that many of the constituent physico-chemical parameters are significantly above the recommended limits. As such, the materials pose significant environmental hazards and therefore need to be safely handled and properly treated before disposal into the natural environment.

Keywords: drilling wastes; Niger Delta; environmental pollution; physico-chemical properties.

#### 1. Introduction

Drilling activities have been established in the Niger Delta region since 1951 when the first generation of exploration wells was spudded in Owerri area, in the northern fringes of the region. Subsequent commercial discoveries created a thriving national economy that is almost entirely dependent on petroleum resources. The phenomenal rise in exploration and production activities generates various types of wastes at each stage of the operation, and these have different physico-chemical compositions. Thus, the presence of vast loads of solid and fluidized wastes has given rise to environmental pressures especially in the onshore areas where most of the infrastructure are sited close to human settlements, farmlands and communal water sources (e.g., ponds, creeks, streams, and rivers). As a result of this, the human population that is dependent on the natural environment for sustenance is exposed to significant health and socioeconomic risks <sup>[1]</sup>.

The major sources of oil field waste materials are drilling wastewater, rock cuttings, muds, and well treatment discharges. Drilling operations make use of drilling fluids (mixtures of various liquids and weighting agents, like barite) to wet and soften the geological formations, circulate and cool the drilling bit, stabilise the wellbore by controlling formation pressures and flush out drilled rock cuttings to the surface. Hence, spent drilling fluids may contain oil, gas, heavy metals and other toxic additives of the original mud mix as well as the geochemical members of the penetrated rock sequences. In many instances, produced water is channelled into water bodies with little or no treatment. Another contributor to environmental stress is the enormous quantities of solid matter in the form of mud and rock cuttings produced during drilling. Often, these are dumped in open land spaces and mud pits, reworked into cheap local construction and fill materials, or disposed into flood channels, natural water systems, and river banks. With the introduction of these sediments into the environment, toxic leachates from sediment particles can considerably compromise the environment. Although the Department of Petroleum Resources (DPR) is empowered by law to regulate and monitor compliance with environmental standards in the Nigerian oil and gas industry, unfortunately, lack of reliable data makes it difficult to assess the extent of risks posed to the ecosystem of the operational areas by drilling industry effluents. Therefore, there is a need for field-based monitoring and laboratory analysis to assess the composition and potential environmental effects of drilling wastes in order to devise an efficient management strategy.

## 2. Study area

This case study was conducted in the Greater Ughelli Depobelt (Figure 1) in the northwestern margin of the Niger Delta sedimentary basin where a well was drilled for hydrocarbon exploration.



Figure 1. Map of Niger Delta showing the study area (red box) and the major depobelts in the basin

The study area is a flat-lying coastal sedimentary terrain dominated by sandy lowlands. It is drained by a network of streams and rivers whose flow rate is relatively slow due mainly to the flat terrain and close proximity to the sea. These natural water systems run as the tributaries of major rivers (e.g., Warri, Forcados and Niger) that have access to the Atlantic Ocean. Typical of many wells in the area, the candidate well penetrated Tertiary sediments of the Greater Ughelli depobelt. The regional stratigraphy consists of Akata, Agbada, Benin formations, and surficial deltaic plain sands. A detailed discussion of the regional stratigraphy of the Niger Delta is provided in Nwajide<sup>[2]</sup>. The unconsolidated sand units of the deltaic plain sand and Benin Formation constitute prolific aquifers. Because these aquifers are shallow (usually less than 50 m), it is easy for groundwater to be abstracted through hand dug wells and boreholes. The sandy overburden and unconfined nature of the aquifer system make the risks of groundwater pollution quite high.

## 3. Materials and method

The study involved field measurements and laboratory analysis. Tests done in the field included pH, total dissolved solids, turbidity, and temperature. Laboratory analysis was carried

out for total suspended solids, chemical and biological oxygen demand, and salinity. Fifteen samples of effluent drilling materials were taken from five different mud pits at the rig site over a three-week period. The weekly sampling approach made it possible for samples from different depths along the well path to be obtained as drilling was going on. The samples were grouped as A to E according to the mud pits and sub-numbered 1 to 3 indicating the week of the sampling (see Table 1). The labelled samples were cautiously transported in ice packs and stored at 4°C before the laboratory analysis for physico-chemical characteristics. The handling and storage of samples followed the ASTM 3856 <sup>[3]</sup> recommended standard laboratory practices. The results obtained were compared with the Department of Petroleum Resources Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (DPR EGASPIN).

## 4. Analytical procedure

A suite of best-practice analytical procedures was followed because of the need to test for specific parameters. For the Total Suspended Solids (TSS), the non-filterable residue was extracted from the sample using 0.45µm standard filter paper and then dried to a constant weight at temperatures that ranged from 103°C to 105°C. Samples were analysed for Chemical Oxygen Demand (COD) by digestion in a Hach reactor, and the values read on the automatic display while the Biological Oxygen Demand (BOD) was obtained with the Warburg and Sierp manometric method. The argentiometric method was used to determine the level of concentration of chlorides (salinity) in the samples. The method involves titration in silver nitrate. Also, residual chlorine in samples was determined with the Hach method by reacting hypochlorides with nitrogen, N-diethyl-p-phenylenediamine to get a red colour which is directly interpreted and displayed as values by the digital system

#### 5. Results and discussion

Having prepared the samples for the analysis of parameters of interest as previously discussed, the results of the analysis and recommended limits of each of the parameters as stipulated by DPR, the oil industry regulatory agency are presented in Table 1 and subsequently discussed.

Sample locations	Parameters	pН	Temp (°C)	Turbidity (NTU)	TDS (mg/L)	TSS (mg/L)	BOD (mg/L)	COD (mg/L)	salinity (mg/L)	Ratio BOD:COD
	DPR limit	8.5	25	10	2000	30	10	10	600	0.8
A1		6.67	29.7	57.1	107.2	73.15	16.03	90.2	44.1	5.6
A2		7.1	29.2	90.1	299.6	101.2	34.07	120.25	205.4	3.5
A3		6.97	29.3	63.1	229.48	78.1	110.2	448.94	115.24	4.1
B1		8.18	29.9	17.03	84.17	19	21.04	130.27	32.06	6.2
B2		10.5	29.1	70.14	1804.7	22	76.15	444.93	1315.75	5.8
B3		7.38	29.13	11	2405	12	94.2	681.42	1778.72	7.2
C1		6.51	30.5	32.06	74	21.04	47.1	230.5	28.05	4.9
C2		7.88	29.03	19.03	235.4	26.05	59.12	305.64	141.3	5.2
C3		8.49	29.13	17.03	42	23.04	17.03	45.1	27.05	2.6
D1		6.97	29.93	7.01	107.22	29.06	12.02	43.1	44.1	3.6
D2		7.38	28.93	8.01	90.1	10	9.02	30.06	48.1	3.3
D3		6.57	29.13	8	86.1	16.03	64.13	240.5	39.1	3.8
E1		7.2	29.8	36.07	142.2	47.1	34.07	91.2	62.13	2.7
E2		6.9	28.9	88.18	193.4	100.2	41.1	107.22	89.18	2.6
E3		7.38	29.4	258.5	289.6	323.6	156.32	515.07	80.16	3.3

Table 1. Results of physico-chemical analysis of drilling waste samples used in the study.

## 5.1. Odour

Odour is mainly attributed to the emissions of volatile organic materials and sulphur compounds <sup>[4]</sup>. The guideline by DPR specifies that drill site wastes should have no objectionable odour. However, all the samples in the study had odour considered to be objectionable. As a first pass test, an undesirable smell is in itself a pollutant. The wastes, therefore, need to be treated before disposal so that the odour would not circulate further and cause discomfort (such as dizziness, nausea, insomnia, headaches and loss of appetite) to the local populace, degrade air quality, or introduce deleterious materials into the ecosystem especially natural sources of domestic water.

#### 5.2. pH

This is a measure of the acidic or basic (alkaline) nature of a solution and is determined by the concentration of hydrogen ions. The pH of the medium is an important factor that controls neutralization, precipitation, coagulation and other biological processes <sup>[5]</sup>. Acceptable limits of pH are 6.0 - 9.0 and 6.5 - 8.5 for FMEnv and DPR respectively. Out-of-limit pH values would impair the natural ecosystem chemical balance as it affects the coagulation of substances and can adversely impact on aquatic life <sup>[5]</sup>. This is because most organic matter and bacteria thrive best at the neutral or slightly alkaline environment. The pH was measured in the field using a digital pH meter. The results (Figure 2A) ranged from 6.5 to 10.5. A value of 10.5 as obtained in location B2 is significantly above the regulatory standards.



Figure 2. Comparison of pH, temperature, turbidity and total dissolved solids of effluent wastewater at different locations (blue bars) with DPR approved limits (red bar)

## 5.3. Temperature (°C)

Temperature is one of the major drivers of the interaction of waste materials and the natural environment. It directly affects the reactivity, degradability, and concentration of other physico-chemical parameters. For instance, its impact on the rates of biological processes affects the performance of activated sludge systems <sup>[6]</sup>. In general, microbial activity increases with increasing temperature until an optimum value is attained, beyond which a decline in microbial activity occurs <sup>[7]</sup>. Also, the solubility of substances increases with increasing temperature <sup>[8]</sup>. However, thermal pollution is a problem as it impedes oxygen dissolution and will, therefore, impact negatively on the quality of natural water bodies such as streams and ponds. The DPR approved temperature limit for effluent fluids is 25°C. As shown in Figure 2B, the samples investigated in this study had temperature values of 29.1°C to 30.5°C. These values considerably exceeded the DPR recommended limit <sup>[11]</sup>.

## 5.4. Turbidity

Turbidity is a measure of the clarity of the fluid under optical inspection. Variations in clarity is an indication of the presence of particles (such as silt and clay-sized sediments, organic matter like algae and plankton) in the fluid. According to Chen *et al.* <sup>[9]</sup>, variations in turbidity helps in understanding the distribution of total suspended solids or sediments (TSS), which by extension would reflect processes like coastal erosion and mobilization of chemicals or pollutants. Turbidity is therefore considered in environmental monitoring because it is a measure of water quality. Excess levels of turbidity can lead to eutrophication challenges in natural water systems <sup>[10]</sup>, the unaesthetic appearance of water, and can expose the populace to gastro-intestinal health risks. Turbidity is usually measured with a nephelometer and expressed in Nephelometric Turbidity Units (NTU). While the DPR allowable limit of turbidity is 10 NTU, results in this analysis revealed values of between 7.0 NTU and 258 NTU. The distribution (Figure 2A) shows that turbidity was consistently higher than DPR recommended limits in all the locations (A, B, C, and E) except in D.

## 5.5. Total dissolved solids (TDS)

Total dissolved solids describe the presence of inorganic salts (e.g., calcium, magnesium, sodium, chlorides, sulfate, and carbonate) and some organic matter in the solution. The method of determining TDS was the measurement of specific conductivity with a conductivity probe that detects the presence of ions in water. Conductivity measurements were converted into TDS values by means of a factor that calibrated for the samples. Figure 2D shows that the minimum recorded value of TDS is 42 mg/l while the maximum is 2405 mg/L. The values of 2405 mg/L recorded in B3 sample is above the DPR recommended limit of 2000 mg/l. Nall and Sedlak <sup>[12]</sup> noted that elevated levels of TDS could result in scales and corrosion of industrial cooling towers and piping fixtures. High TDS effluents can cause changes in the levels of salinity and ion concentrations thereby constituting a significant hazard of toxicity and mortality to flora and fauna in discharge areas.

## 5.6. Total suspended solids (TSS)

This is a measure of particles in the fluid that would not pass through the 2.0  $\mu$ m filter. If allowed, these particles settle as sediments. Spent drilling mud and rock cuttings can be carried by storm water into water bodies causing elevated values of TSS. Higher values of TSS may increase the temperature of the fluid as the particles absorb light and heat with the implication of decreasing the amount of dissolved oxygen <sup>[13-14]</sup>. DPR recommended limit for TSS is 30 mg/l. However, results of the analysis (Figure 3A) indicated values of between 10 mg/l and 324 mg/l. Out of the 15 samples analysed, 9 were found to be within the acceptable limits. The recorded maximum value of 324 mg/l in E3 is more than ten times above the acceptable limit. Such a high amount of sediment load if unchecked would affect coagulation and filtration and also lead to siltation of natural water systems.



Figure 3. Comparison of TSS, BOD, COD, and salinity of effluent wastewater at different locations (blue bars) with DPR approved limits (red bar).

## 5.7. Biological oxygen demand (BOD)

Microorganisms (e.g., bacteria) need oxygen for the decomposition of organic wastes. The amount of oxygen consumed by these waste-decomposing bacteria is the biological oxygen demand <sup>[15]</sup>. Where there are large quantities of organic waste to be broken down, oxygen demand will also be high because a greater population of bacteria will be involved <sup>[16]</sup>. High amounts of BOD will be interpreted in many cases as evidence of pollution from organic materials. In this wise, the DPR approved limit of BODs is 10 mg/L. For the effluent wastewater samples analysed in the study, the concentration values of BODs (as shown in Figure 3B) widely varied and range from 9 mg/L to 156 mg/L. Only the D2 sample with a value of 9 mg/l is within the DPR recommended limit. On the basis of the recorded BOD results of the other 14 samples, the effluents pose significant pollution hazard to the environment.

## 5.8. Chemical oxygen demand (COD)

As an index of pollution, the chemical oxygen demand measures the amount of dissolved oxygen consumed in the chemical oxidation of organic matter to carbon dioxide and water under specific analytical conditions. This helps in the assessment of wastes for biologically-resistant organic components and toxins. The inference is that higher amounts of COD is an indication of higher levels of oxidizable organic material in the sample and will, therefore, deplete the levels of dissolved oxygen. For the effluent wastewater samples that were analysed in this study, the values of COD ranged from 30 mg/l to 681 mg/L (see Figure 3C). This contravenes the DPR approved limit of 10 mg/L.

## 5.9. Ratio of BOD to COD

By comparing the values of BOD to COD, the biological degradability of wastes can be assessed <sup>[17]</sup>. This ratio-based survey indicates the proportion of the total organic matter that can be decomposed by biological processes <sup>[18]</sup>. In a study aimed at achieving safe and sustainable treatment options for organic matter in the environment, Samudro and Mangkoedihardjo, <sup>[19]</sup> zoned BOD/COD ratios into toxic, biodegradable and acceptable or stable. Highly biodegradable wastes have BOD to COD ratios of not less than 0.8 <sup>[20-21]</sup>. In Figure 4A, data in this study show that BODs are lower in value than the corresponding CODs for the same sample. A plot of the BOD to COD ratio (Figure 4B) indicates that the values are in excess of 0.8. This suggests that the wastes are biodegradable.



Figure 4. Comparison of BOD and COD data. As expected, in (A), BOD values (green plot) trend lower than the corresponding COD (red plot). The resulting ratios of BOD to COD plotted in (B) are considerably above 0.8 limits (red bar). The inference is that the wastes are highly polluted and biodegradable.

## 5.10. Salinity



Figure 5. Variation of salinity in effluent wastewater. Except in samples B2 and B3, the values are generally low and in compliance with regulatory standards

One of the characteristics of coastal environments is the ability of aquatic species to tolerate adverse conditions including high salinity <sup>[22-23]</sup>. As a result of this, many industrial processes exploit marine ecosystems as natural receptacles of wastes of all sorts including those with elevated concentrations of salt. In the tested samples, values of salinity (as chloride) ranged from 27 mg/L to 1779 mg/L (Figure 5). The results in B2 and B3 are abnormally high and above the DPR approved limit of 600mg/L. Considering that 15 samples were analysed and 13 of these were in compliance with the DPR limits, the salinity of the drilling wastes does not constitute a significant threat to the environment.

However, chronic salt stress can severely degrade the environment <sup>[24-25]</sup>. In particular, salinity adversely impacts on biological degradation processes due to reduced microbial activities. It also inhibits the growth and production of biomass by wetland plants and equally affects the assimilation of nitrogen and phosphorus <sup>[26-28]</sup>. High levels of salt concentration in the environment can affect and deteriorate the quality of freshwater.

#### 6. Summary and conclusion

The study shows the physico-chemical characteristics of effluent materials from drilling operations in the oil field under consideration and the environmental significance of the parameters. The wastes, in most cases, are additives in drilling muds as well as in-situ reservoir properties that were flushed to the surface by the circulating drilling fluids. Although some of the identified chemical components can be naturally degraded by microorganisms in the environment, they, however, constitute significant risk if the quantity is in excess of what the natural process can easily decompose, a baseline being the respective DPR approved limits. As shown in the table of values (Table 1), the waste materials require treatment before disposal, as most of the tested parameters such as pH, temperature, turbidity, BOD and COD have values that are above the acceptable regulatory limit. At such high concentrations, the risk of pollution is significantly high. Therefore, the waste materials need to be treated before disposal into the natural environment.

#### References

- [1] Solomon UU. The state of solid waste management in Nigeria. Waste Management Journal; 2009; 29: 2787 2790.
- [2] Nwajide CS. Geology of Nigeria's Sedimentary Basins. CSS Press, Lagos, Nigeria; 2013: 347-548.
- [3] ASTM D3856 11. Standard Guide for Management Systems in Laboratories Engaged in Analysis of Water; 2015; 11 (01).
- [4] Estrada JM, Bart Kraakman NJR, Muñoz R, Lebrero R. A comparative analysis of odour treatment technologies in wastewater treatment plants. Environmental Science Technology; 2011; 45 (3): 1100-1106.
- [5] Lijklema L. Factors Affecting pH Change in Alkaline Waste Water Treatment I, Water Research Pergamon Press; 1969; 3:913-930.
- [6] Grady CP, Daigger GT, and Lim HC. Biological Wastewater Treatment. 2nd ed. New York: Marcel Dekker; 1999; 407–408.
- [7] International Water Association. Advanced Biological Treatment Processes for Industrial Wastewaters. London: IWA Publishing; 2006: 32–33.
- [8] El-Otify AM. Evaluation of the physicochemical and chlorophyll-a conditions of a subtropical aquaculture in Lake Nasser area, Egypt. Beni-Suef University Journal of Basic and Applied Sciences; 2015; 4:327–37.
- [9] Chen Z, Hu C, and Muller-Karger F. Monitoring turbidity in Tampa Bay using MODIS / Aqua 250-m imagery. Remote Sensing of Environment; 2006; 109:207–220.
- [10] Johansson JOR. Historical overview of Tampa Bay water quality and seagrass: Issues and trends. In H. Greening (Ed.), Seagrass management: It's not just nutrients! Tampa Bay Estuary Program symposium proceedings, 22–24 August, 2000; St. Petersburg.
- [11] DPR. Environmental Guidelines and Standards for the Petroleum Industry in Nigeria. Lagos. Department of Petroleum Resources. Ministry of Petroleum Resources. 1991.
- [12] Nall DH and Sedlak R. Total Dissolved Solids in Reclaimed Water. Ashrae Journal; 2013: 28-38.
- [13] Ademoroti CMA. Standard method for water and Effluents Analysis. Foludex press Ltd, Ibadan; 1996; 22-112.
- [14] Singh SN, Srivastava G, Bhatt A. Physicochemical Determination of Pollutants in wastewater in Dheradun. Current World Environment; 2012; 7 (1):133-138.
- [15] HMSO. 5 Day Biochemical Oxygen Demand (BOD5) with Dissolved Oxygen in Water, Amendments Second Edition. Methods for the Examination of Waters and Associated Materials; HMSO, London, 1998.
- [16] Okoh AI, Babalola GO and Bakare MK. Microbial densities and physico-chemical quality of some crude oil flow stations' saver pit effluents in the Niger Delta areas of Nigeria. Sci. Total Environ; 1996; 30:73-8.
- [17] Lee AH and Nikraz H. BOD:COD Ratio as an Indicator for Pollutants Leaching from Landfill. Journal of Clean Energy Technologies; 2014; 2 (3): 263-266.
- [18] Dhall P, Siddiqi TO, Ahmad A, Kumar R and Kumar A. Restructuring BOD:COD Ratio of Dairy Milk Industrial Wastewaters in BOD Analysis by Formulating a Specific Microbial Seed. The Scientific World Journal; 2012; Article ID 105712.

- [19] Samudro G and Mangkoedihardjo S. Review on BOD, COD and BOD/COD Ratio: A Triangle Zone for Toxic, Biodegradable and Stable Levels. International Journal of Academic Research; 2010; 2 (4):235-239.
- [20] Kumar A, Dhall P and Kuma R. Redefining BOD:COD ratio of pulp mill industrial wastewaters in BOD analysis by formulating a specific microbial seed. International Biodeterioration & Biodegradation; 2010; 64:197-202.
- [21] Sharma A, Kumar A, Kumar R, Gangal SV, Gangal V, Makhijani SD. Assessment of biodegradability of organic acids by a defined microbial mixture. Bulletin of Environmental Contamination and Toxicology; 1996; 57:34-40.
- [22] Clough BF, Boto KG, Attiwill PM. Mangroves and sewage: a revaluation. In: Teas, H.J. (Ed.), In: Biology and Ecology of Mangrove Tasks for Vegetation Science Series; Dr. W. Junk Publishers, Lancaster; 1983; 8:151–162.
- [23] Takemura T, Hanagata N, Sugihara K, Baba S, Karube I, Dubinsky Z. Physiological and biochemical responses to salt stress in the mangrove, Bruguiera gymnorhiza. Aquatic Botany 2000; 68:15–28.
- [24] Kargi F and Dincer AR. Effect of salt concentration on biological treatment of saline wastewater by fed-batch operation. Enzyme and Microbial Technology; 1996; 19 (7): 529–37.
- [25] Yan Wu Y, Tam NFY, and Wong MH. (2008). Effects of salinity on treatment of municipal wastewater by constructed mangrove wetland microcosms. Marine Pollution 2008; 57:727–734.
- [26] Brown JJ, Glenn EP, Fitzsimmons KM, Smith SE. Halophytes for the treatment of saline aquaculture. Aquaculture; 1999; 175:225–268.
- [27] Conner WH, Mcleod KW, McCarron JK. Flooding and salinity effects on growths and survival of four common forested wetland species. Wetlands Ecology and Management; 1977; 5:99–109.
- [28] Parida AK and Das AB. Effects of NaCl stress on nitrogen and phosphorus metabolism in a true mangrove Bruguiera parviflora grown under hydroponic culture. Journal of Plant Physiology; 2003; 161:921–928.
- [29] Ajao EA. and Anurigwo S. Land based sources of pollution in the Niger Delta, Nigeria. Ambio journal of the human environment; 2002; 31 (5): 442 445.
- [30] Belluck DA, Benjamin SL, Dawson T. Groundwater contamination by atrazine and its metabolites: risk assessment, policy and legal implications. In Pesticide transformation products: Fate and significance in the Environment; Somasundaram, L., Coats, JR., Eds.; American Chemical Society: Washington, D. C; 1991; 165–76.
- [31] Caldwell DH, and Langelier WF. Manometric Measurement of the Biochemical Oxygen Demand of Sewage. Sewage Works Journal; 1948; 20 (2): 202-218.
- [32] Federal Ministry of Environment National Guidelines and Standards for Water Quality in Nigeria, 1995.
- [33] HACH Water Analysis Handbook, 3rd edition, HACH Company, Loveland, Colorado, USA, 1997.
- [34] vlab.amrita.edu. Determination of pH of Waste Water Sample, 2012.

To whom correspondence should be addressed: Chiazor J. Egbuachor, Belushi World Class (Oil and Gas) Ltd, Port Harcourt, Nigeria

# Article

## **Open Access**

IMPLEMENTATIONS OF MICROBIAL TECHNOLOGY EXTEND LONGEVITY OF OIL FIELDS

Chang Hong Gao

American University of Ras Al Khaimah, UAE

Received November 13, 2018; Accepted January 11, 2019

#### Abstract

Microbially enhanced oil recovery (MEOR) is a unique technique, which involves the injection of live organisms and/or nutrients into underground reservoirs to improve oil production and longevity of the field. Even though MEOR remains a relatively marginal technology, field trials of MEOR have been active in North America and Asia. This paper reports 16 MEOR field projects since 2000. According to the field cases surveyed, around 70% of treated wells demonstrated positive responses. Besides, all of the projects were profitable. Traditionally, high temperature and high salinity have prohibited field applications of MEOR. Among the field cases in this survey, MEOR has been tried in low-permeability formations, high-salinity reservoirs, high-temperature reservoirs, and heavy-oil fields. MEOR proved effective for challenging reservoir conditions with careful selection of microbes and proper project execution.

Keywords: Microbe; Biosurfactant; Petroleum; Case study.

#### 1. Introduction

It is estimated that more than 50% of original oil remains underground at field abandonment. Scientists and engineers have developed a few methods to improve oil production and field longevity. Routine water and gas injection are being carried out in the oilfields worldwide. Besides, enhanced oil recovery (EOR) methods are often employed to produce the residual oil that is difficult to mobilize. Commercial EOR methods include steam injection, polymer injection, and  $CO_2$  injection [1-2].

Microbial enhanced oil recovery (MEOR) is a unique technique. In MEOR operations, live microorganisms and/or nutrients are injected into oil-bearing reservoirs. Bacteria and their metabolic products, such as biosurfactants and biopolymers mobilize the oil in the reservoir <sup>[3]</sup>. If favorable bacteria already reside in reservoirs, it is feasible to inject nutrients only. MEOR method has many distinguishable advantages. Natural products are usually harmless and environment-friendly. MEOR can be carried out in the field without major modification of present water injection facility. Besides, MEOR does not require high energy consumption <sup>[4]</sup>.

However, MEOR did not gain widely-spread field applications worldwide. Some factors limited its field implementations. (1) Bacteria cannot survive under very high temperature. Therefore, MEOR is usually excluded from high-temperature reservoirs. (2) High salinity restricts the growth of microbes. In reality, many reservoirs contain high-salinity formation water. (3) The heavy components in crude oil, such as asphaltene and bitumen are toxic to microbes. (4) After microbes are injected into the reservoir, they have to compete with endogenous bacteria for prosperity. But sometimes the exogenous bacteria cannot win the battle. (5) Various chemicals are injected into the reservoir, including but not limited to acids, polymers, and surfactants. These chemicals may negatively impact microbial activities in the reservoir<sup>[5]</sup>.

#### 2. MEOR mechanisms

Certain bacteria are able to produce surfactants, polymers, gases, and solvents that contribute to the mobilization of oil in the reservoir. Many experimental studies were devoted to the understanding of MEOR mechanisms. The proposed MEOR mechanisms include a reduction in interfacial tension (IFT), permeability modification (or selective plugging), reduction in oil viscosity, alteration of wettability, and biodegradation <sup>[6]</sup>. This paper focuses on field applications of MEOR, rather than its mechanisms. Detailed descriptions of MEOR mechanisms can be found in the literature <sup>[7-8]</sup>.

Certain bacteria produce biosurfactants that reduce oil-water interfacial tension <sup>[4,9-10]</sup>. The residual oil is held in porous rocks by capillary pressure, which is proportional to the interfacial tension (IFT) between oil and water. When IFT is reduced to a much lower value, residual oil begins to flow <sup>[11-12]</sup>. It was reported IFT reduced from 60 to 0.0012 N/m due to microbial metabolism <sup>[13]</sup>.

A porous rock contains pores of various sizes. When undergoing water flooding, larger pores receive most of the injected water, while residual oil remains in small pores without being swept. When bacteria flow in reservoir rocks, they also tend to enter large pores. The bacteria themselves, or the biopolymers they generate, can plug the high-permeability zones with large pores, thus forcing injected water to sweep the oil in low-permeability zones <sup>[8]</sup>.

Certain bacteria produce gas, organic acids and solvents in the reservoir <sup>[14]</sup>. Gas (such as methane and carbon dioxide) and solvents can dissolve in crude oil and reduce crude oil viscosity. It was observed that microbes could reduce heavy oil viscosity by more than 50% in the laboratory <sup>[11]</sup>. Lower oil viscosity leads to improved mobility ratio and oil recovery. In an experimental study, it was observed microbes produced large quantities of gas <sup>[15]</sup>. In reality, the produced gas can also increase the reservoir pressure, which leads to a higher production rate. Besides, some bacteria are able to degrade crude oil, especially the paraffin contents in crude oil <sup>[12]</sup>. When applied to the reservoir, bacteria can remove the paraffin deposit in the near wellbore region, thus improving permeability and production rate <sup>[16]</sup>.

#### 3. Field cases

Bacteria can be injected through either production well (also known as producer) or water injection well (also known as an injector). Most MEOR projects can be classified as huff and puff or microbial flooding, according to the methods of injection. For huff and puff operation, bacteria are injected into the reservoir through production wells. The wells are then shut in for some days before production resumes. For microbial flooding, bacteria reach reservoir through injection wells, then work their way to production wells. This section reviews MEOR field cases with relatively complete information.

## 3.1. North American fields

Five fields in Canada and USA operated by Husky Energy received an injection of nutrients only to activate indigenous microbes <sup>[12]</sup>. The reservoirs were of rather different rock and fluid properties, as seen in Table 1.

Reservoir	Devonian, Alberta, Canada	Sparky, Alberta, Canada	Upper Topanga, California, USA	Hauser, California, USA	Sparky C, Alberta, Canada
Oil specific gravity	0.82	0.96	0.95	0.91	0.93
Depth (m)	1,056	600	1,585	1,650	661
Temperature (°C)	49	25	74	93	26
Porosity (%)	14-16	16	26	18-30	30
Permeability (md)	300	700	100-1000	10-100	600
Salinity (ppm TDS)	142,600	80,642	35,000	18,900	70,000
Watercut (%)	98	95	85	85	88

Table 1. Properties of the reservoirs that received a nutrient injection

The Sparky field and Upper Topanga field produced relatively heavy oil, while the highsalinity Devonian field produced relatively light oil. From 2007 to late 2010, 35 producers and 30 injectors at the 5 fields received treatments, while 80% of wells showed positive responses. The producers saw a 205% increase in oil production combined. The field cases demonstrated MEOR was effective in treating both light and heavy oil reservoirs. Besides, MEOR was applied to high-temperature Hauser field with excellent results.

## 3.2. Mangunjaya field, Indonesia

The Mangunjaya field operated by Pertamina has been producing for 80 years, and oil recovery reached 40%, while water-cut reached 78% <sup>[18]</sup>. Water-cut is defined as the fraction of the volume of water in the produced liquid. The reservoir parameters are given in Table 2. In 2015, microbial huff and puff were conducted for two producing wells MJ-122 and MJ-155. The wells were first flushed with brine, then injected with microbes and nutrients, followed by a post flush with brine. Afterwards, the wells were shut in for 7 days. Three months after the treatments, water-cut dropped from 95% to around 50%, while the liquid production increase by 17%.

Table 2	Decenvoir	naramotore	of Mangur	viava field
I able Z.	Reservoir	Darameters		liava lielu

Oil Viscosity (cP)	2.5	Reservoir pressure (MPa)	7
Porosity (%)	27.5	Reservoir temperature (°C)	50
Permeability (md)	120	Rock Type	Sandstone
Oil Saturation (%)	55	Pay zone thickness (m)	61
Reservoir depth (m)	170-365		

## 3.3. Daqing field, China

The Daqing field operated by CNPC was discovered in 1959. Implementation of water injection and polymer flooding injection lead to good recovery factor. The field produces relatively light oil under moderate reservoir temperature. The favorable reservoir conditions make the field a good candidate for MEOR. Microbial huff and puff were conducted on 518 wells in 10 blocks at Daqing, which leads to 63,386 tonnes of incremental oil production <sup>[19]</sup>.

Bohetai block is a tight (i.e., low-permeability) reservoir with permeability ranging from 1 to 50 md. In 2002, huff and puff operations were conducted for thirteen production wells with a mixture of five different strains <sup>[20]</sup>. After injection, wells were shut in for 7 days. After production resumed, the viscosity of produced fluid dropped from 101 cP before the treatment to 57 cP afterwards, the wax content reduced by 1-5%, while the oil-water interfacial tension reduced by 40%. Ten wells responded positively to treatment. Water-cut of the block dropped from 61% to 44%. It was estimated 2,138 tonnes of extra oil were produced. The well with the highest permeability yielded the best output. The daily oil rate increased from 0.4 tonnes before the treatment to 5.2 tonnes afterwards. In 2003, four wells were chosen for the second round of bacterial huff and puff, while the results were still excellent.

After the successful trials at Bohetai block, Chao50 block received a bacterial injection from June 2004 to February 2005 <sup>[21]</sup>. It is a tight reservoir with the properties presented in Table 3.

Table 3.	Parameters	of	Chao50	block

Area of block (km <sup>2</sup> )	2.25	Average porosity	0.17	
OOIP (tonnes)	1,667,000	Average permeability (md)	25	
Reservoir depth (m)	989	Dead oil viscosity (cP)	94.3	
Reservoir thickness (m)	7.9 to 9.5	Water-cut	95%	
Reservoir temperature (°C)	55			

Traditionally, MEOR was recommended to permeability higher than 50 md. However the average permeability was only 25 md for this reservoir. The block involved 10 producers and 2 injectors. *Brevibacillus brevis* and *Bacillus cereus* were chosen for injection <sup>[22]</sup>. Their sizes were around  $0.8 \times 1.4$  micron and  $0.4 \times 1.0$  micron, respectively. The average pore throat size was 2.3 micron. Therefore, microbes were able to move through the pores. This assumption was supported by high concentrations of microbes in the produced fluid.

After injection of 250 tonnes of bacterial fluid, seven producers responded positively to microbial injection. Liquid output increased from 957 tonnes/month before the treatment to 1,456 tonnes/month. Monthly oil production climbed from 361 to 843 tonnes, while water-cut dropped from 95% to 38.6%. It was estimated that 13,600 tonnes of incremental oil were produced. Oil parameters also improved. The oil viscosity dropped by 20% to 76 c P. The paraffin content dropped by 5% to 7.6%. The interfacial tension dropped by 14% to 0.04 N/m It was observed the producers that were located near the injectors demonstrated better results. This trial proved MEOR could be effective even for very tight formation. After the successful trail, microbial EOR spread to 60 wells in the block, while 43 wells saw positive feedback with 9,175 tonnes of additional oil production.

## 3.4. Shengli field, China

Shengli field operated by Sinopec was discovered in 1961. The field features complex geologies and diversified reservoir characteristics. The field has produced more than one billion tonnes of oil so far. Water flooding, polymer flooding, and steam flooding are common practices in the field. MEOR also attracted much attention at Shengli. Microbial huff and puff have been conducted on 1640 wells, which contributed to 219,000 tonnes of additional oil production <sup>[23]</sup>. Some typical MEOR field cases at Shengli are introduced here.

The Luo801 block was producing heavy oil, as shown in Table 4. Rock expansion and solution gas resulted in an oil recovery of only 11%. After the liberation of solution gas, the oil became more viscous. In 1994, the viscosity of produced oil from well-805 was 189 cP. In 1998, oil viscosity climbed to 725 cP. The oil production from the block decreased from 472 to 200 tonnes/day. The pilot started in 1998 <sup>[24]</sup> when bacteria were injected through 4 injectors that are connected to 11 producers. Before the treatments, daily oil production from the block was 200 tonnes. After bacterial flooding, oil production climbed to more than 300 tonnes/day. It was estimated that around 43,500 tonnes of extra oil were produced.

Table 4. Parameters of Luo801 block

Area of the block (km <sup>2</sup> )	1.6	Reservoir temperature (ºC)	80
Reservoir depths (m)	1,680 to 1,800	Salinity of formation water (mg/L)	9,794
Porosity	0.281	Pour point of oil ( <sup>e</sup> C)	26 to 38
Permeability (md)	215.2	Density of oil (g/mL)	0.932

Zhan3 block has received water injection since 1989. Oil recovery reached only 25% after 22 years of water injection, while the water-cut was as high as 92%. The block contains 13 producers and 5 injectors. The reservoir parameters are given in Table 5. Three production wells received a nutrient injection, but no bacteria was introduced <sup>[25]</sup>. The wells were shut in for one week before production resumed. Wells saw an increase in oil production (3.4 to 10.4 tonnes/day), and a decrease in water-cut (93% to 88%). The successful pilot leads to expanded trials at the field. Till December 2014, totally 5,997 tonnes of nutrients has been injected, resulting in 27,000 tonnes of additional oil output <sup>[23]</sup>.

Table 5. Parameters of Zhan3 block

Area of block (km <sup>2</sup> )	1.5
OOIP (tonnes)	2,820,000
Reservoir depth (m)	1,240 - 1,360
Reservoir temperature (°C)	63
Porosity	0.30
Permeability (md)	800 - 1,000
Oil API gravity	11.8
Dead oil viscosity (cP)	1,885
Salinity of formation water (mg/L)	8,900

## 3.5. Xinjiang field, China

The Xinjiang field is located in west China and operated by CNPC. Fourteen wells at Xinjiang field received bacterial treatments from September 2007 to August 2008 <sup>[26]</sup>. The block produced heavy oil with reservoir parameters given in Table 6. Laboratory work demonstrated the selected microbes could emulsify heavy oil and significantly reduce oil viscosity. For the field trial, the wells were first treated with steam to remove wax and debris. After bacterial fluid was injected, the wells were shut in for 2-3 days before resuming production. Twelve wells showed positive responses, producing 1,535 tonnes of extra oil totally.

Table 6. Reservoir data for a trial block in Xinjiang

Wells depths (m)	92 to 610
Reservoir temperature (°C)	15 to 29
Porosity (%)	20.5 to 25
Permeability (md)	334 to 676
Dead oil viscosity at 50°C (cP)	228 to 1,135

In 2014, the 7-Zhong block was selected for nutrient injection, without receiving exogenous bacteria. The block involves 4 injectors and 11 producers. The block's OOIP was 719,000 tonnes, and oil recovery reached 41% before the treatment. The nutrient contained sugar, sodium nitrate, and ammonium phosphate. Nutrient injection lasted 1.5 years, with total injection volume equivalent to 0.1 PV <sup>[27]</sup>. Three months after the treatments started, all 11 wells showed positive feedback, while the number of bacteria in the produced water escalated to  $10^8/mL$ . Total oil production climbed from 14 tonnes/day before the treatment to 41 tonnes/day afterwards. Water-cut dropped from 90% to 81%. Additional oil production was estimated at 21513 tonnes <sup>[28]</sup>.

## 3.6. Liaohe field, China

The Liaohe field is located in Northeast China, operated by CNPC. Prior to implementation of MEOR at Liaohe field, laboratory work was conducted on two bacterial strains. It was discovered that the strains produced surfactants that could emulsify heavy oil. The bacteria grew best under 37 to 55°C. Field trial started in September 2005, when thirteen producers on Jin45 and Qian12 blocks in Liaohe field began to receive bacteria injection <sup>[29]</sup>. Prior to bacterial treatments, the blocks had been steamflooded for more than ten years, but the effect of steam already weakened. The wells produced heavy oil with a viscosity of over 5,000 cP at the surface. The wells were injected with bacteria then shut in for 7 to 9 days. After the wells were back on, the production rates soon began to rise. Till February 2006, twelve wells showed positive response and produced 2,511 tonnes of additional oil after the treatments. The trial proved MEOR was more cost-effective than steamflooding for the treated wells. For well Jin-45, producing one tonne of oil with steamflooding cost 863 CNY, while with bacteria the cost was only 339 CNY.

Average porosity	20.5%
Average permeability (md)	725
Reservoir depth (m)	1,410-1,650
Reservoir temperature (°C)	48
Oil saturation before treatment	60%

The Leng43 block at Liaohe field produces very heavy oil. The crude oil density was 0.97 g/mL, and its viscosity was between 9,620 and 43,000 cp at 50°C. The salinity of formation was relatively low at 5,435 mg/L. The reservoir parameters are given in Table 7. Five producers were selected for microbial huff and puff <sup>[30]</sup>. Before the treatment, the five wells had received a steam injection, but with poor production. The wells first received nutrient fluid through the casing-tubing annulus, followed by a mixture of bacteria and nutrient, finally a

slug of nutrient. The wells were then shut in for 7 days. After production resumed, four wells saw increases in oil production and decrease in water-cut by 10%. Additional 530 tonnes of oil was produced. For the fifth well, its liquid production increased significantly, but the oil rate was almost the same as before.

Jing35 block is a shallow heavy oil reservoir. The low reservoir temperature hinders the flow of heavy oil. As a result, the recovery factor was only 4.3% till 2012. Three cycles of microbial huff and puff were conducted on 6 production wells in 2013. Three bacteria strains were selected: *Geobacillus stearothermophilus, Geobacillus thermodenitrificans*, and *Pseudomonas aeruginosa.* Till June 2014, 5 out of 6 production wells reported increases in production, with 1,344 tonnes of incremental oil accumulatively. The effects of microbial treatments lasted more than 10 months <sup>[31]</sup>.

## 3.7. Baolige field, China

The Baolige field, located in Inner Mongolia and operated by CNPC, occupied 20.8 km<sup>2</sup> where 78 injectors and 169 producers were spaced. The field parameters are favorable for implementation of MEOR, as seen in Table 8. A large-scale MEOR project was started in May 2012. Nutrients and two strained were injected into the reservoir through injection wells. After 60 days, field oil production increased from 820 t/day to 920 t/day, while water-cut dropped from 78.5% to 65.8%. Beside, oil viscosity reduced from 188 cp to 80 cp. The field received 4 cycles of injection totally, followed by routine water flooding. Around 85% of all production wells reported higher production rates after microbial treatments. The oil production stabilized around 900 t/day till early 2016. By estimation, additional oil production reached 210,000 tonnes accumulatively <sup>[32]</sup>. In order to enhance microbial activities, nutrients and bacteria were added to produced water at water treatment facilities, before the produced water was re-injected into the reservoir <sup>[33]</sup>.

Table 8. Reservoir data of Baolige field

Area of block (km <sup>2</sup> )	20.8
OOIP (tonnes)	35 million
Reservoir temperature (°C)	50
Porosity	0.18
Permeability (md)	144
Dead oil viscosity (cP)	188

#### 4. Summary and discussions

This case study verifies the proposed MEOR mechanisms. Most field cases reported increases in injection pressure soon after bacteria injection. This can be attributed to the plugging of pore throats by microbes, production of biopolymers, or production of gases. It was also observed that the injection pressure began to decline at a certain stage of the projects. This is possibly because the surfactants produced by bacteria reduced interfacial tension between oil and water, which was also observed at the surface. Besides, the viscosity of produced oil decreased for many projects. After microbial treatments, many wells' paraffin issues also eased. This proved that the bacteria degraded crude oil to some extent. However, most projects did not experience a significant increase in gas production.

However, MEOR indeed involves more uncertainties than steam flood or polymer flood. In the past, most MEOR field cases were conducted for reservoir temperatures below 60°C<sup>[34]</sup>, because most bacteria cannot prosper at high temperatures. Besides, the high salinity in deep oil and gas reservoirs impacts bacterial growth negatively. Moreover, injected bacteria have to compete with the endogenous microbes in the reservoir. If the injected slug is not adequate, microbes cannot prosper. Thus, the effect of MEOR is compromised.

The field cases in this survey are summarized in Table 9. Commercial MEOR projects were carried out at Daqing field, and Baolige field, where the reservoir temperature was mild and the salinity was moderate. However, MEOR has been tried in more challenging reservoirs, i.e.,

high temperature, high salinity, low permeability, and heavy oil. For some field cases, reservoir temperature reached  $93^{\circ}$ C, salinity as high as 142,600 ppm, oil viscosity as high as 43,000 cp at the surface, and reservoir permeability as low as 25 md. Nevertheless, MEOR achieved good successes under such challenging conditions. Moreover, all of the projects proved profitable.

Table 9. Summary of MEOR field cases

Project	Reservoir features	Success rate
Five fields in Canada	Four fields with heavy oil	80%
and USA	One field with high salinity	
	One field with high temperature	
Mangunjaya	Low temperature;	100%
	Low Pressure	
Bohetai	Tight reservoir	77%
Chao50	Tight reservoir	70%
Luo801	Heavy oil;	Not reported
	Moderate permeability and salinity;	
Zhan3	Heavy oil; High permeability;	33%
	Moderate salinity;	
Xinjiang	Low temperature;	86%
	Moderate permeability;	
7-Zhong	Large injection volume	100%
Jin15 and Qian12	Heavy oil	92%
Leng-43	Heavy oil	80%
Jing-35	Heavy oil	83%
Baolige	Favorable reservoir conditions;	85%
	Large-scale field application;	

According to the field experiences, the criteria for MEOR applications can be extended with proper selection of bacteria and project execution. First of all, the selected strains must be able to prosper under the reservoir conditions. Then they mobilize oil by producing biosurfactants or degrading crude oil. This step requires a lot of efforts on identification, incubation, and evaluation of strains in the laboratory. Second, the injected slug should be adequate, so that the exogenous bacteria can successfully build a colony in the reservoir. When only nutrients are injected, the number of nutrients should be adequate to support the long-term metabolism of bacteria. In reality, the injected slugs were often very small, usually less than 0.05 PV. According to field experiences in China, the slug size should be at least 0.05 PV with a concentration of 2% <sup>[35]</sup>. Thirdly, the wells and facilities should be carefully prepared prior to MEOR operations. The facilities involved should be treated with steam to remove debris and undesirable microbes, so that the injected bacteria can safely reach the reservoir. For the projects in China, usually a slug of polymer or nutrient was injected in front of the bacteria in order to provide protection for the injected bacteria. Above all, MEOR has been implemented commercially in North America and China, which indicates the maturity of this technique.

## 5. Conclusion

(1) For the MEOR projects conducted in North American and Asia, we observed an increase in injection pressure, a decrease in IFT, and a decrease in oil viscosity. These phenomena verified the proposed MEOR mechanisms, including permeability modification (or selective plugging), IFT reduction, and oil degradation. (2) Most of the MEOR projects in this survey achieved good success rates. More than 70% of the wells treated by microbes showed positive responses. (3) All MEOR projects were profitable. (4) The field cases proved MEOR effective for challenging reservoir conditions, i.e., high temperature, high salinity, and heavy oil.

#### References

- [1] Alvarado V, Manrique E. Enhanced Oil Recovery. Gulf Professional Publishing. Boston 2010, 7-16.
- [2] Gao C, Shi J, Zhao F. Successful polymer flooding and surfactant-polymer flooding projects at Shengli Oilfield from 1992 to 2012. Petrol Exploration and Production Technology, 2014; 4 (1).
- [3] Perfumo A, Rancich I, Banat I. Possibilities and Challenges for Biosurfactants Use in Petroleum Industry. In: Sen R. (eds) Biosurfactants. Advances in Experimental Medicine and Biology, 2010; vol 672. Springer, New York, NY.
- [4] Geetha SJ, Banat IM, Joshi SJ. Biosurfactants: Production and potential applications in microbial enhanced oil recovery (MEOR). Biocatalysis and Agricultural Biotechnology, 2018; 14: 23-32.
- [5] Safdel M, Anbaz M, Daryasafar A, Jamialahmadi M. Microbial enhanced oil recovery, a critical review on worldwide implemented field trials in different countries. Renewable and Sustainable Energy Reviews, 2017;74 (3) 159-172,
- [6] Sen R. Biotechnology in petroleum recovery: the microbial EOR. Progress in Energy and Combustion Science, 2008; 34: 714-724.
- [7] Gao C, Zekri A, Tarabily K. Microbes enhance oil recovery through various mechanisms. Oil and Gas Journal, 2009; 107(31), 39-43
- [8] Patel J, Borgohain S, Kumar M, Rangarajan V, Somasundaran P, Sen R. Recent developments in microbial enhanced oil recovery, Renewable and Sustainable Energy Reviews, 2015; 52(6): 1539-1558,
- [9] Makkar RS, Cameotra SS. Structural characterization of a biosurfactant produced by Bacillus subtilis at 45 degrees C. J. Surf. Deter., 1999; 2: 367-372.
- [10] Hung HC, and Shreve GS. Effect of the hydrocarbon phase on interfacial and thermodynamic properties of two anionic glycolipid biosurfactants in hydrocarbon/water systems. J. Physical Chemistry B, 2001; 105: 12596-12600.
- [11] Liu R, Tao W. Screening of bacteria that degrades oil at Daqing field. Journal of Oil and Gas Technology, 2009; 31 (4), 143-145.
- [11] Yi S, Deng Y. Experimental study of emulsification by biosurfactants. Chemical Engineering of Oil and Gas, 2008; 37 (1), 59-61.
- [13] Ju Y, Li X, Wang W. Study of bacteria B36 for oil recovery. Oilfield Chemistry, 2002; 19 (3): 272-274.
- [14] Liu Y, Guo L, Wang S. Experiment of microbial gas production for Luo-801 block. Journal of Daqing Petroleum Institute, 2011; 35 (4): 58-61.
- [15] Lei G, Ma J, Wang W. 2009 Micro-mechanism of microbial enhanced oil recovery. Journal of China University of Petroleum, 2009; 33 (3): 108-113.
- [16] Wang C, Li D, Liu S. Effects of bacteria on heavy oil properties, Acta Petrolei Sinica, 2007; 28 (5). 89-92
- [17] Zahner R, Tapper S, Marcotte B, Govreau B. Lessons learnt from applications of a new organic oil recovery method that activates resident microbes, SPE Reservoir Evaluation & Engineering, 2012; 15(6): 688-694.
- [18] Ariadji T, Astuti D, Aditiawati P. Microbial huff and puff project at Mangunjaya field, SPE 196361 presented at Asia Pacific Oil Gas Conference, Jakarta, Indonesia, 17-19 October 2017.
- [19] Wu X, Le J, Wang R, Bai L. Progress of microbial enhanced oil recovery in Daqing. Microbiology China, 2013; 40(8): 1478-1486.
- [20] Li W, Liu R, Shi M. Microbial enhanced oil recovery in low permeability reservoir, Petroleum Exploration and Development, 2003; 30(5): 110-112.
- [21] Wang F, Wang Z, Wang X. MEOR pilot effect on block 50 of Chaoyanggou oil field. Petroleum Geology and Oil Field Development in Daqing, 2008; 27(3): 102-105.
- [22] Guo W, Hou Z, Shi M. Recovery mechanism and application of two strains in extra-low permeability reservoir of Daqing. Petroleum Exploration and Development, 2007; 34(1): 73-78.
- [23] Wang X. Application of MEOR in producing ultra-heavy oil from thin pay zones. Petroleum and Petrochemical Today, 2016; 24 (5): 20-25.
- [24] Song Y, Wei B, Zhao F. Anaerobe chain formation in reservoir and enhancement of oil recovery in L801. Oilfield Chemistry, 2004; 21(2): 182-186.
- [25] Cao G, Xu D, Zhang S. Stimulation of internal bacteria at Zhan3 block. Journal of Oil and Gas Technology. 2002; 34(7) 136-140.
- [26] Yi S, and Liao Y. Effect of bacteria on heavy oil viscosity and field applications. Journal of Oil and Gas Technology, 2009; 31(1) 134-137.
- [27] Li M, Wang H, Qian Y. Biochemical tracking and evaluation of microbial flooding at 7-Zhong block. Oilfield Chemistry, 2017; 34(2) 323-328.
- [28] Yuan S, Dong X, Zhao M, Ding H. Trial of MEOR at 7-Zhong block. China Petroleum and Chemical Standards and Quality, 2017; 36(1) 66-70.
- [29] Xu E. Multi-cyclic microbes huff-puff for heavy oil recovery in Liaohe fields. Oilfield Chemistry, 2006; 23(3) 263-267.
- [30] Huang Y, Liang F, Zhang X, Liu R. Microbial enhanced oil recovery in extra-heavy crude reservoir. Oilfield Chemistry, 2002; 19(2) 178-181.
- [31] Wang X, Xiang L, Zhang Y. Application of microbial high pour-point oil recovery in Liaohe field. Lithologic Reservoirs, 2017; 29(5) 162-168.
- [32] Ke C, Lu G, Li Y, Sun W, Zhang Q, Zhang X. A pilot study on large-scale microbial enhanced oil recovery (MEOR) in Baolige Oilfield. International Biodeterioration & Biodegradation, 2018; 127(2) 247-253.
- [33] Ren F, Yu J, Chen J, Huo R. Surface multiplication of produced water after MEOR. Oilfield Chemistry, 2015; 32(2) 251-254.
- [34] Gao C, Zekri A. Applications of microbial enhanced oil recovery technology in past decade. Energy Sources Part A, 2011; 33(10) 972-989.
- [35] Le J, Wu X, Wang R, Zhang J, Bai L, Hou Z. Progress in pilot testing of microbial enhanced oil recovery in the Daqing field of North China. International Biodeterioration & Biodegradation, 2015; 97(1) 188-194.

To whom correspondence should be addressed: Assoc. prof. Dr. Chang Hong Gao, American University of Ras Al Khaimah, Department of Chemical and PetroleumEngineering, UAE, <u>Changhong.gao@aurak.ac.ae</u>

# Article

# **Open Access**

### IMPACT OF MINING DEPTH ON UNIT CAPACITY

V. V. Fitsak, E. S. Lomakina, A. A. Strakhova\*

Saint-Petersburg Mining University, 21st line, 2199000, Saint-Petersburg, Russia

Received November 13, 2018; Accepted January 11, 2019

#### Abstract

Based on the selected options of room-and-pillar systems, there are distinguished the main criteria and technical-and-economic indices having an impact on the rationality of mining systems' use when decreasing the depth of room work conductance.

Keywords: room-and-pillar system; economic-mathematic modeling (EMM); technical and economic indices (TE).

#### 1. Introduction

Issues of parameters' optimization in the mining industry of Russia were extensively researched by Galaev, Agoshkov, Bokiy, Imenitov, Shevyakov, Gorodetskiy, Shestakov, Pushkarev, Drobot, and Bich <sup>[4-13]</sup>.

Herewith, it is universally acknowledged that efficiency of ore production to a large extent depends on establishing of rational technological parameters and intensity of mining.

Research technique used for solution of these tasks is, as a rule, complex, and includes different methods of logic analysis, physical modeling, analogies, technical and economic analysis, analytical comparison of options, directed search for optimal decisions and use of the mathematical tool of graph theory, linear and dynamic programming, reliability, etc.

As the experience of many works shows, nowadays, the use is widely made of economicmathematic modeling methods allowing to represent complex relations of a rather large amount of technical, organizational and cost factors having an effect on the selection of rational parameters of a mining system.

A mining system of any mine includes the performance of preliminary break-off of ore, its breaking, drawing, and delivery, and must ensure the safety of works, maximum extraction of a commercial mineral, minimum expenses on mining and processing.

Development of a system mathematic model must be preceded by a study of qualitative and quantitative phenomena peculiar to the system. Therefore, during the system analysis and mathematic description, it is very important to divide the whole totality of the phenomena into subsystems characterizing separate technological processes.

During this work, economic-mathematic modeling is used as the main technique for determining optimal process parameters of mining units. With the purpose to ensure the reliability of obtained results and wide possibilities of the technique's practical application, the developed models of mine works scheduling were made up: on the basis of used at Northern Urals bauxite mines (NUBM) technical-and-economic indices and scheduling algorithms, predicted conditions of development and their effect on process parameters of mining operations <sup>[1]</sup>.

One of the important requirements to the technique presupposed that the economic-mathematic model (EMM) structure should be very flexible in terms of a simple adaptation to possible technical, organizational and cost variations, as well as in terms of different scheduling tasks solution and issues of parameters' optimization.

Main items of the approach to the elaboration of mining processes' EMM result from the character of the set research task – substantiation of development of a room work front.



Fig 1. Flow diagram of effective development limits

It is expedient to avoid the use of large bodies of data, reliable determination of which for future periods of development is either very laborious or even impossible. For this reason, we included into the composition of initial parameters only the data which in the fullest measure represents the specifics of the main conditions of particular mine sections development. Some data was determined on the basis of a comparison with the actual indices obtained under similar conditions and including different development trends.

The use was also made of the widely applied at the enterprise system of specific and average weighted technical and economic indices which made it possible to take into account the impact of the main mining-and-geological and mine technical factors when planning expansion for a long period.

With the purpose to fully describe all technological processes at the production unit, the use was made of a combination of different techniques for determination of parameters that to the fullest extent made allowance for peculiarities of the determined values and included empirical data and results of analytical research <sup>[2]</sup>.

By an optimization criterion for optimum design tasks, it is necessary to understand an assigned estimated figure, in the role of which there can be taken any resources at the society's disposal: labor, energy, mineral, material, financial and others. However, the roundup index, which most fully corresponds to the main aim of the social economy development and represents the main equivalent of the maximum society satisfaction, shall be the social labor costs. Consequently, in this case, the general criterion of optimization is the flat cost of commercial mineral production.

In compliance with the main principles of operations study, the considered mathematic model is a system consisting of the main target function (flat cost of production of 1 ton of ore), partial criteria (unit efficiency and level of ore extraction), variable parameters with limits and interval of their change, technological limitations and intermediate values.

In general, the task can be put down in the following way:

$$C_{prod} = C_{backfill} + C_{dev.op.} + C_{item} + C_{disec}$$
, RUB/t

where:  $C_{backfill}$  is the flat cost of the backfill, RUB/t;  $C_{dev.op.}$  is the flat cost of mining and development, RUB/t;  $C_{item}$  is the flat cost of production by items, RUB/t;  $C_{disec.}$  is the diseconomy from ore losses in pillars, RUB/t.

(1)

A systematic approach to optimization requires a certain identity of the target function and general criteria of optimality. This ensures indestructibility of centralization, purposefulness and general criterion interests.

Along with the production flat cost, determining factors for selection of an optimal mining system during the transition to deep levels are technical-and-economic parameters.

Unit capacity, accepted as a criterion, as well as the determined amount of output product, depends on the ore body thickness and the room width. In accordance with general principles of the economic-mathematic modeling, the latter must also necessarily contain a criterion determining the quality of the output product. In this work – it's extraction ratio  $K_{extr}$ .

In order to solve the task of defining the optimal limits of use of room-and-pillar systems different options, the following flow diagrams were selected: room-and-pillar system with leaving of ore- and chain pillars arranged along the strike of an ore body (Fig. 2); room-and-pillar system with development of a working excavation (Fig. 3); room-and-pillar system with leaving of a combined support of a concrete-ore-concrete type (Fig. 4); room-and-pillar system with leaving of a combined support of an ore-concrete-ore type (Fig. 5).



Fig. 2 Room-and-pillar system with arrangement of chain pillars along the strike. 1 – haulage gate, 2 – transport ramp, 3 – haulage crosscut, 4 – ore chute, 5 – room, 6 – pillar.



 1 – haulage gate, 2 – transport ramp, 3 – haulage crosscut, 4 – ore chute, 5 – room, 6 – pillar.



Based on these options of mining systems, values of ore reserves distribution by work stages were introduced into the economic-mathematic model, and a unit capacity was calculated (see Figure 6).

Reliability of these values can be compared with available for other similar mines data on labor productivity of a face worker as one of the main production indices, but only for small depths (up to 800 m). The comparative assessment shows no significant difference.



Along with this data, a comparison was made with the use of available economic information of the mine proper for the second quarter of 2010 <sup>[3]</sup>. The flat cost of the commercial mineral production constitutes:

- during room-and-pillar development 164.5 RUB/t,
- during production with the development of a working excavation 186.3 RUB/t.

It is necessary to point out that mining works at (NUBM) mines are already performed at the depths of 1000 m. This data is also totally confirmed by the calculated values of the mining cost when using these mining methods.

#### References

- [1] Shestakov VA. Rational use of subsurface, Moscow, «Nedra», 1990.
- [2] Pushkarev LI, Drobot BP, Bich JA. Use of room-and-pillar system in conditions of NUBM Mining Journal, 1986; (5): 35 – 38.
- [3] Fitsak VV. Effective boundaries of the application of options chamber-pillar development system. S-Pb. Journal of Mining Institute, 2002; 150(2): 54-56.
- [4] Agoshkov MI, Malakhov GM. Underground mining of ore deposits, Moscow, "Nedra", 1966.
  [5] Bich YaA, Piskunov YuD, Muratov NA. Mining operations in disjunctive disturbances in strategies
- [5] Bich YaA, Piskunov YuD, Muratov NA. Mining operations in disjunctive disturbances in strata prone to dynamic phenomena. Control of rock pressure and control of rock bumps. Collection of scientific papers. L, VNIMI, 1986, p. 75 79.
- [6] Boky BI. Mining, Moscow: State Scientific and Technical Publishing House of Mining Literature, 1959.
- [7] Galaev NZ. Management of the state of rocks in underground mining of ore deposits, Leningrad, 1979.
- [8] Gorodetsky PI. Development of ore deposits, M: State scientific and technical publishing literature on mining. 1962.
- [9] Drobot BP. Preservation of the chamber-and-pillar development system at great depths. Mining Journal, 1986; (4): 34 - 36.
- [10] Imenitov VR. The processes of underground mining in the development of ore deposits, Moscow, "Nedra", 1978.
- [11] Pushkarev LI, Drobot BP, Beach YaA. Application of chamber-and-pillar development system in the conditions of SUBR. Mining Journal, 1986; (5): 35 38.
- [12] Shevyakov LD. Development of mineral deposits, 3<sup>rd</sup> ed. M., 1956.
- [13] Shestakov VA. Rational use of mineral resources, Moscow, "Nedra", 1990.

To whom correspondence should be addressed: Dr. A. A. Strakhova, Saint-Petersburg Mining University, 21<sup>st</sup> line, 2199000, Saint-Petersburg, Russia, <u>anastasia.strx@gmail.com</u>

# Article

# **Open Access**

### KINETICS STUDY OF MODIFIED COAL TAR PITCH FOAMING

Iryna Krutko\*, Iryna Danylo, Viacheslav Kaulin

Donetsk National Technical University, 85300, Pokrovsk, 2 Shybankova Sq., Ukraine

Received November 9, 2018; Accepted January 11, 2019

#### Abstract

The foaming kinetics of a modified coal tar pitch (MCTP) with a complex blowing agent (CBA) under free foaming conditions was investigated. The kinetics study showed that a rate and a foaming criterion depend on both the CBA amount and polyvinylchloride amount expended on coal tar pitch modification. Using CBA for foaming the coal tar pitch modified with polyvinylchloride, it is possible to obtain solid foams (at 150°C) with a porosity of 24 to 76% and an apparent density of 0.31 to 1.0 g/cm<sup>3</sup> depending on the MCTP composition. The higher the polyvinylchloride content in MCTP, the lower the density and the higher the porosity of the resulting solid foam. The research results showed the possibility of obtaining the gas-filled material based on MCTP using CBA. To obtain solid foams with a stable fine-meshed and homogeneous structure, it is necessary to optimize the conditions of MCTP foaming process. To this end, research will continue to study the effect of the pressure and the foaming temperature of MCTP on the morphological characteristics of solid foams based on it.

Keywords: modified coal tar pitch; complex blowing agent; foaming; kinetics; solid foams...

#### 1. Introduction

Coal tar pitch is widely used as a polymer matrix to produce carbon foams <sup>[1-7]</sup>. Carbon foams (solid foams) are gas filled materials in which the dispersed phase is gas, and the dispersion medium is solid. Unique properties make the solid foams effective, constructive materials and potential for use in various industries as lightweight aggregates of constructions, heat and sound insulators, materials for liquid and gas filtration and others.

Coal tar pitch (CTP) is a residue obtained during coal tar rectification, which mainly consists of high-boiling multiring aromatic and heterocyclic compounds. CTP is cheap raw material, but it cannot be used for the production of carbon foam plastics without pre-treatment since its plastic properties usually do not meet the foaming requirements <sup>[8]</sup>. Pre-treatment consists of a modification of the CTP, as a result of which its rheological properties and structure change. There are various methods of CTP modification, including the polymerization or condensation of the pitch, by heat treatment at 380-450°C <sup>[6,9]</sup> or by treatment with different chemical reagents <sup>[6,10-14]</sup> to change its viscosity and anisotropy degree.

The authors <sup>[15]</sup> proposed a low-temperature (up to 170°C) modification of a CTP with polyvinylchloride. CTP modified by polyvinylchloride (MCTP) refers to thermoplastics and has a set of properties that correspond to amorphous polymers <sup>[16]</sup>. MCTP shows viscosity anomaly, which is characteristic of high-molecular compounds and has rheological properties that can allow to use it as a precursor for solid foams obtaining <sup>[17]</sup>.

MCTP is much cheaper than classical polymers, so it is economically feasible to use it as a pitch-polymeric matrix to obtain solid foams.

To form a porous structure in the gas-filled composites production, the blowing agents are used. MCTP rheological properties <sup>[18]</sup> indicate that it is advisable to use the chemical blowing agents for its foaming. MCTP has a viscosity of 55-190 Pa·s in the temperature range 125-155°C <sup>[18]</sup>.

The chemical blowing agent azodicarbonamide (ADCA) was chosen as a foaming agent. At temperatures of 200-210°C, the ADCA decomposition is accompanied by chemical reactions with the mainly molecular nitrogen formation (gas number 210-220 cm<sup>3</sup>/g) <sup>[19-21]</sup>. Such a decomposition temperature is too high for MCTP foaming due to its rheological properties changing <sup>[18]</sup>.

The foaming process depends on MCTP viscosity. At temperatures 130-150°Cthe MCTP is in a highly elastic and viscous-flow state, that is, it has a viscosity which can provide the foam formation. At temperatures 200-210°C the MCTP shows the Newtonian flow, that is, it has destroyed structure <sup>[18]</sup>, its viscosity is too low to obtain the stable foam.

To reduce the ADCA decomposition temperature, an initiator – Zn stearate  $(ZnSt_2)$  has been used. Previous studies have shown <sup>[22]</sup>, that the addition of  $ZnSt_2$  in the amount of 0.25-0.5 weight part (further wt. part) to 1 wt. part ADCA allows reducing the ADCA decomposition temperature to 140-150°C (ADCA gas number 195-220 cm<sup>3</sup>/g).

Currently, there is no information in literature sources about foaming of CTP modified by polyvinylchloride with the chemical blowing agents using. Therefore, the topic of the presented work is the investigation of complex blowing agent ADCA-ZnSt<sub>2</sub> influence on the kinetics of CTP foaming modified by polyvinylchloride. To this end, the relevant experiments were carried out, where the amount of used complex blowing agent ADCA-ZnSt<sub>2</sub> was varied from 1 to 5 weight part per 100 weight part of MCTP (weight part per 100 weight part further wt. p./100 wt. p.).

#### 2. Experimental

### 2.1. Materials

For the study, CTP granules (6-8 mm) grade B (DSTU 8389:2015) were used: the METTLER softening point – 108°C; density 1.314 g/cm<sup>3</sup>; content of substances insoluble in toluene - 31%, in quinoline - 9%, coke residue 56%; viscosity at 140°C – 9.3 Pa·s, at 160°C – 1.34 Pa·s; water content - 0.1%.

Polyvinylchloride C-6370-G (PVC) in accordance with the requirements of GOST 14332 - powder with a particle size of 100-200 microns; density 1.35 g/cm<sup>3</sup>; bulk density 0.55 g/cm<sup>3</sup>;  $K_F=63$ ; melting point 150-220°C (with destruction).

Azodicarbonamide NH<sub>2</sub>CON=NCONH<sub>2</sub> (CAS: 123-77-3). ADCA is yellow-orange crystalline substance odorless; decomposition temperature 210°C; gas number 218 cm<sup>3</sup>/g; the content of the basic substance 95%. Optimal decomposition temperature –210°C and higher, decomposition reaction is exothermic and autocatalytic.

Zn stearate  $(C_{17}H_{35}COO)_2Zn)$  (CAS:1592-23-0)-white powder; melting point 130°C; Zn content 10.1%; powder bulk density 0.5 g/cm<sup>3</sup>. Complex blowing agent (CBA) was prepared by mixing of ADCA and ZnSt<sub>2</sub> in the ratio of ADCA:ZnSt<sub>2</sub>=1:0.25 (wt. part).

# 2.2. Foaming method

First, a mixture of CTP with different amount of PVC (3-20 wt. p./ 100 wt. p. of CTP) was subjected to low temperature modification for 2 hours at T = 170 °C. After modification, the mixture was cooled and crushed to a powdered state.

The MCTP powder was mixed with a given amount of CBA (1 to 5 wt. p./ 100 wt. p. of MCTP) to a homogeneous state. The resulting mixture was filled into form by 2/3 of the volume, was compacted and closed a lid. The form was a cylindrical container (diameter - 3.5 cm, height - 2 cm, volume - 19.2 cm<sup>3</sup>) with a lid.

The foaming process was carried out at atmospheric pressure in the closed form in a thermostat at T = 150 °C for 60 minutes. At the end of the foaming, the form was quickly cooled to room temperature under a stream of cold water for  $\tau = 2$  min. Solid foam tablet was removed from the form, and its volume was measured.

Under the experimental conditions, a method based on the separation (condensation) of the gas phase in the volume of the MCTP (under free foaming conditions) was implemented. At atmospheric pressure, the powdered mixture melted upon heating foamed because of CBA

decomposition, and the form was filled with foam under the pressure of the resulting gases. Fixation of the formed macrostructure of the foamed pitch occurred as a result of cooling. At cooling the viscosity of liquid matrix increased up to a loss of fluidity, i.e., the liquid matrix was transformed into a rigid material.

To estimate the efficiency of MCTP foaming by the CBA, the value of the foaming criterion  $(C_f)$  was used:

$$C_f = \frac{V_f}{V_0},$$

where:  $V_0$  MCTP volume after foaming without of CBA;  $V_F$ -MCTP volume after foaming with CBA addition.

# 2.3. Research methods

To estimate the thermochemical transformations occurring in the system CTP-PVC under the action of ADCA and CBA, the thermogravimetric analysis and FTIR-spectroscopy have been used. The thermogravimetric analysis was carried out with Netzsch TG 409 PC Luxx in a dynamic heating mode up to 600°C in a nitrogen flow (80 mL/min) with a rate of oven temperature rises 10°C/min. Infrared investigations of the samples were performed on a Fourier IRspectrometer Nicolet iZ10 Spectrometer in the range of 500-4500 cm<sup>-1</sup>.

#### 3. Result and discussion

First, the thermogravimetric analysis of dry mixtures of CTP, PVC, and ADCA was performed to determine the temperature of intense gas evolution.

Thermogravimetric analysis of dry mixtures of CTP, PVC and ADCA showed that ADCA (5. wt. p./100 wt. p. of CTP) decreases the weight loss temperature (5 and 10%) and increases the rate of decomposition comparing to CTP without a blowing agent (Table 1). In addition, in the presence of PVC, a further increase in the rate of the components mixtures decomposition is observed. From this, we can conclude that PVC initiates thermal decomposition reactions, accompanied by the release of volatile substances.

	Mixtu	re compo wt. part	osition, t	5% we	ight loss	10% we	eight loss
Nº	СТР	PVC	ADCA	T, ℃	Weight loss rate v, %/min	T, ℃	Weight loss rate v, %/min
1	100	0	0	266	1.1	301	1.7
2	100	0	5	248	1.6	278	2.5
3	100	5	5	255	2.8	268	5.5
4	100	10	5	255	2.1	280	2.8
5	100	20	5	255	2.8	275	3.5

Table 1 The results of thermogravimetric analysis of CTP mixtures with PVC and ADCA



Fig. 1. Thermogravimetric curves of ADCA

From the analysis of the thermogravimetric curves of the samples (Fig. 1, 2) it can be seen that the change in the character of the DTG curves is mainly due to the presence of ADCA in mixtures. For ADCA (Fig. 1), the maximum weight loss rate of 52%/min is observed at 238°C; weight loss is 34%. The maximum weight loss rate for mixtures with a PVC content of 5 - 20 wt. part is in the range of 2.8 - 5.5%/min, while the weight loss is about 10% (Table 1)



The shift of the temperature of the maximum weight loss rate of the mixtures compared to ADCA to the region of higher temperatures of 268-280°C (Fig. 2) is explained by the decrease in the chemical reactions rate of the blowing agent decomposition in the viscous medium of CTP and PVC. Thus, thermogravimetric analysis of dry mixtures of CTP, PVC, and ADCA showed that the use of ADCA without an initiator would require a temperature above the ADCA decomposition temperature to foam the mixture of CTP and PVC. However, the undesirable processes of CTP and PVC destruction are accelerated at such temperatures. In addition, the low viscosity of CTP and the products of its interaction with PVC will not allow obtaining the stable foam.

Fig. 2 Thermogravimetric curves of CTP (1) and mixtures of CTP with PVC and ADCA. Ratio CTP: PVC: ADCA (wt. part): 2)-100:0:5; 3)- 100:5:5; 4)- 00:10:5; 5)- 100:20:5

To investigate the foaming kinetics of CTP modified with PVC, the experiments were conducted in which a complex blowing agent (ADCA-ZnSt<sub>2</sub>) was used in an amount from 1 to 5 wt. p./100 wt. p. of MCTP.

The foaming kinetics of CTP modified with different amounts of PVC (3 - 20 wt. p./100 wt. p. of CTP), depending on the amount of CBA at 150°C is shown in Fig. 3-5.

3.5





Fig. 3 Kinetics of the MCTP foaming at the ratio MCTP:CBA = 100:1 (wt. part) at T =  $150^{\circ}$ C depending on the modifier PVC amount (wt. p./100 wt. p. of CTP): 1) - 3; 2) - 7; 3) - 10; 4) - 20

Fig. 4 Kinetics of MCTP foaming at the ratio MCTP:CBA = 100:5 (wt. part) at T =  $150^{\circ}$ C depending on the modifier PVC amount (wt. p./100 wt. p. of CTP): 1) - 3; 2) - 7; 3) - 10; 4) - 20

During the experiments, it was found that the necessary condition for the foaming process is the transfer of the powder composition into the melt, which takes about 15 minutes. Chemical reactions, leading to the release of gaseous substances, begin to activate only in the melt.

Kinetic curves (Fig. 3, 4) of the MCTP foaming at CBA amount of 1 and 5 wt. p./100 wt. p. of MCTP show the presence of the induction period from the 15th to the 30th minute, at which foaming is practically not observed. After the induction period, the chemical reactions of the CBA decomposition are activated, which is confirmed by the increase in the rate and in the



foaming criterion. The rate and the foaming criterion depend on PVC amount expended on the modification of the CTP.

Fig. 5 Kinetics of the MCTP foaming at the ratio MCTP:CBA = 100:3 (wt. part) at T = 150°C depending on the modifier PVC amount (wt. p./100 wt. p. of CTP): 1) - 3; 2) - 7; 3) - 10; 4) - 20. High rate T = 12 MCTP with T = 12 models at T



Fig.6 Dependence of the maximum foaming criterion value ( $C_{max}$ ) for the MCTP on the CBA amount at T=150°C and the holding time of 60 minutes. MCTP with PVC content (wt. p./100 wt. p. of CTP): 1) - 3; 2) - 7; 3) - 10; 4) - 15; 5) - 20.

The kinetic curves of the MCTP foaming at CBA amount of 3 wt. p./100 wt. p. of MCTP have a slightly different character (Fig.5). When foaming CTP, modified by 3 - 10 wt. part of PVC, the rate and foaming criterion is not high and practically do not depend on the amount of PVC. However, the high content of PVC (20 wt. p./100 wt. p. of CTP) in the MCTP leads to the fact that already at the stage of melting an intensive gas evolution begins, which is confirmed by a high foaming rate, which ends in the 30th minute.

Calculations of MCTP averaged foaming rate ( $u_f$ ) up to reaching the maximum value of C<sub>f</sub> at a temperature of 150°C showed that  $u_f$  depends on the amount of PVC in the MCTP, and on the amount of CBA (Table 2).

$$\vartheta_f = \frac{\Delta C_{max}}{t_{max} - t_{ind}}$$

where:  $U_f$  – averaged foaming rate, min<sup>-1</sup>;  $\Delta C_{max}$  – the change of foaming criterion  $C_f$  up to reach its maximum value;  $t_{ind}$  – induction period time, min;  $t_{max}$  – a time of maximum  $C_f$  reaching, min.

	MCTP con	nposition	CBA amount,		$10^{2}$
N⁰	CTP,	PVC,	wt. p./100 wt. p.	Cmax	$0^{-1}$
	wt. part	wt. part	of MCTP		min +
1	100	3	1	1.3	1.1
2	100	3	3	1.7	0.8
3	100	3	5	1.7	1.4
4	100	7	1	1.3	0.5
5	100	7	3	1.7	1.4
6	100	7	5	1.7	1.4
7	100	10	1	2.5	4.5
8	100	10	2	2.1	2.5
9	100	10	3	1.3	1.3
10	100	10	5	1.4	1.1
11	100	20	1	2.9	5.7
12	100	20	3	3.6	7.8
13	100	20	5	3.1	6.2

Table 2 Averaged foaming rates of MCTP up to reach the maximum C  $_{\rm f}$  value at a temperature of 150°C, depending on the content of PVC and CBA

An increase in the foaming rate is observed with an increase in the PVC content in the composition of the MCTP to 10-20 wt. p./100 wt. p. of CTP. At 20 wt. p./100 wt. p. of PVC in the MCTP the foaming rate is maximum and is  $5,7\cdot10^{-2} - 7,8\cdot10^{-2}$  min<sup>-1</sup>, depending on CBA amount (Table 2, exp.11-13).

It should be noted that the maximum foaming rate value is 4.5 10<sup>-2</sup> min<sup>-1</sup> for MCTP with a PVC content of 10 wt. p./100 wt. p. of CTP was observed only at CBA amount of 1 wt. p./100 wt. p. of MCTP. For such an MCTP composition, the foaming rate decreases with an increase in the CBA amount to 5 wt. p./100 wt. p. of MCTP (Table 2, exp.7-10).

For MCTP with low PVC content (3–7 wt. parts on 100 wt. parts CTP), the foaming rate is low and ranges from  $0.5 \cdot 10^{-2}$  to  $1.4 \cdot 10^{-2}$  min<sup>-1</sup> (Table 2, exp.1-6).

The dependence of the foaming criterion  $C_{max}$  on the PVC content and the CBA amount at T=150°C and the holding time of 60 min is presented in Fig.6. Analysis of the curves in Fig. 6 showed that for different compositions of the MCTP, the effect of CBA manifests itself in different ways. The maximum foaming criterion 2.9-3.6 is observed for MCTP modified by 20 wt. part of PVC at CBA amount 1-5 wt. p./100 wt. p. of MCTP. When foaming MCTP containing PVC 15 wt. part with an increase of CBA amount from 1 to 5 wt. part the foaming criterion increases from 1.4 to 2.85. For MCTP modified with 3-7 wt. part of PVC, with an increase in the CBA amount (1-5 wt. p./100 wt. p. of MCTP), there is a slight increase in  $C_{max}$  from 1.3 to 1.7. Only for MCTP modified with 10 wt. part of PVC, with an increase in CBA amount from 1 to 5 wt. part a decrease in the foaming criterion from 2.5 to 1.4 is observed.

From Table 3 it can be seen the properties of solid foam depend on both the CBA amount and the PVC content in the MCTP. When foaming MCTP with a high PVC content, (10 - 20 wt. p./100 wt. p. of CTP) solid foams with the highest porosity (up to 76%) and low apparent density (up to 0.31 g/cm3) are obtained. The solid foam properties depend on the PVC and CBA amount (Table 3, exp.7-13).

	MCTP con	nposition	CBA amount,	Apparent	Porosity
Nº	CTP,	PVC,	wt. p./100 wt.	density	06
	wt. part	wt. part	p. of MCTP	ρ, g/cm <sup>3</sup>	70
1	100	3	1	0.99	25
2	100	3	3	0.81	38
3	100	3	5	0.80	39
4	100	7	1	1.00	24
5	100	7	3	0.81	38
6	100	7	5	0.81	38
7	100	10	1	0.53	60
8	100	10	2	0.65	51
9	100	10	3	0.62	53
10	100	10	5	0.69	48
11	100	20	1	0.40	70
12	100	20	3	0.31	76
13	100	20	5	0.36	73

Table 3 Characterization of solid foams obtained by foaming the MCTP with a CBA at T=150 °C and Patm

With a low PVC content (3-7 wt. part) in the MCTP, the solid foam properties are mainly influenced by the CBA amount, the higher its consumption, the lower the apparent density and the higher the porosity (Table 3, exp.1-6). With an increase in CBA amount from 1 to 5 wt. part the apparent density decreases from 0.99 to 0.81 g/cm3, and the porosity increases from 24 to 39%.

In the process of research, it was found that for samples of solid foams containing 3, 7, 15, 20 wt. parts PVC, the optimal CBA amount is 3 wt. p/100 wt. p. of MCTP, and for solid foam containing 10 wt. parts PVC, the optimal CBA amount is 1 wt. p./100 wt. p. of MCTP.

As can be seen (Fig. 7), all foam samples have a porous structure. The pore size ranges from 200-500  $\mu$ m to 1 mm. The study of the obtained samples structure of solid foams showed that the gas-filled material is characterized by large pore size and heterogeneity. This is most

likely due to the mismatch of the gas evolution kinetics and cell growth with a change in the MCTP viscosity. MCTP foaming at atmospheric pressure and T=150°C leads to asynchrony of these processes, which makes it difficult to obtain a foam with a stable and homogeneous cellular structure. When CBA decomposes, gas bubbles are formed, which coalesce due to their merging, forming large cells or cavities inside the sample. It can be assumed that with the rapid CBA decomposition and low viscosity of the MCP at 150°C, the destruction of the cell walls is observed, and a material with a heterogeneous large-cell structure is obtained.

Infrared spectroscopy allowed determining the basic changes in chemical bonds and functional groups observed during MCTP foaming.





It is known that the absorption band at  $3040 \text{ cm}^{-1}$  corresponds to the stretching vibrations of the aromatic CH bond, and the band at  $1600 \text{ cm}^{-1}$  corresponds to the stretching vibrations of the C=C double bond <sup>[23]</sup>. The peaks of  $2700 - 2980 \text{ cm}^{-1}$  and  $1480 \text{ to } 1370 \text{ cm}^{-1}$  are related to the aliphatic hydrogen stretching absorption in CH<sub>2</sub> and CH<sub>3</sub> structures <sup>[24]</sup>. The peaks of  $2920 \text{ cm}^{-1}$  and about  $2860 \text{ cm}^{-1}$  are characteristic of CH<sub>2</sub>, and a peak of about  $2960 \text{ cm}^{-1}$  is characteristic of the methyl CH<sub>3</sub>-group. The absorption band  $1690 - 1730 \text{ cm}^{-1}$  characterizes the vibrations of the carbonyl group C=O in the CTP <sup>[25-26]</sup>.



Fig.8. FTIR-spectra of the initial CTP (1), foamed CTP (2) and MCTP solid foams (CBA amount 5 wt. p./100 wt. p. of MCTP). The composition of solid foams based on the MCTP (PVC amount, wt. p./100 wt. p. of CTP): 3) - 5; 4) - 10; 5) - 20

From the presented spectra (Fig. 8) it can be seen that all solid foams are characterized by an increase in aromaticity compared to the initial pitch, which is confirmed by an increase in the intensity of the absorption bands at  $3040 \text{ cm}^{-1}$ -stretching vibrations of CH aromatic bond, and also in the region of 1600 cm<sup>-1</sup> -stretching vibrations of the double bond C=C.

In solid foams, absorption bands of 2920, 2860 and 1450 cm<sup>-1</sup> are observed that characterize the methylene groups of CH<sub>2</sub>, which are most likely to be in the form of methylene bridges between the aromatic rings system. The absence of an absorption band of 2860 cm<sup>-1</sup>, which is typical of the methyl group CH<sub>3</sub>, indicates on its removal when the foam is obtained. The oxygen containing components of CTP are manifested in the form of absorption bands of C-O-C aromatic esters stretching vibrations at 1240 cm<sup>-1</sup>-asymmetric vibrations, and carbonyl groups C=O at a wavenumber of 1720 cm<sup>-1</sup>. In the process of MCTP foaming, destruction of the oxygen bonds with the removal of oxygen is observed, resulting in the disappearance of the absorption band C=O 1720 cm<sup>-1</sup> and decreasing the intensity of the absorption band of C-O-C aromatic esters at 1240 cm<sup>-1</sup>.

#### 4. Conclusion

Thermogravimetric analysis of dry mixtures of CTP, PVC, and ADCA showed that the use of ADKA without an initiator would require a temperature above the decomposition temperature of ADCA to foam a mixture of CTP and PVC. However, at such temperatures, undesirable processes of CTP and PVC destruction are accelerated. In addition, the low viscosity of CTP and the products of its interaction with PVC will not allow obtaining the stable foam.

The use of the ADCA-ZnSt<sub>2</sub> complex blowing agent (in the amount of 1 to 5 wt. p./100 wt. p. of MCTP) allowed foaming the MCTP at a temperature of 150°C, which is significantly lower than the ADCA decomposition temperature. The research of the MCTP foaming kinetics showed that the rate and the foaming criterion depend on both the CBA amount and the amount of PVC expended on the CTP modification. With increasing PVC content in MCTP from 3-7 to 10-20 wt. p./100 wt. p. of CTP, depending on the CBA amount, the rate increases by 3 to 9 times, and the foaming criterion increases by 2 to 3 times. The maximum foaming criterion of 3.6 and the maximum foaming rate of  $7.8 \cdot 10^{-2}$  min<sup>-1</sup> were observed for gas-filled compositions obtained by foaming MCTP with PVC content of 20 wt. p./100 wt. p. of CTP.

Using Fourier method of IR-spectroscopy, it was found that during the MCTP foaming, physicochemical transformations occur, in particular, destruction of oxygen-containing functional groups and elimination of methyl groups, which leads to an increase in the aromaticity of solid pitch foams.

Studies have shown that using CBA for foaming a CTP modified with PVC, it is possible to obtain solid foams (at 150°C) with a porosity of 24 to 76% and an apparent density of 0.31 to 1.0 g/cm<sup>3</sup> depending on the composition of the MCTP. The higher the PVC content in MCTP, the lower the density and the higher the porosity of the resulting solid foam.

The study of obtained solid foams structures showed that the gas-filled material is characterized by large pore size and heterogeneity. This is most likely due to the mismatch of the gas releasing kinetics and cell growth with a change in MCTP viscosity. MCTP foaming at atmospheric pressure and T = 150°C leads to asynchrony of these processes, which makes it difficult to obtain a foam with a stable and homogeneous cellular structure.

The investigation's results showed the possibility of obtaining the gas-filled material based on MCTP using CBA. To obtain solid foams with a stable fine-meshed and homogeneous structure, it is necessary to optimize the conditions of MCTP foaming process. To this end, research will continue to study the effect of the pressure and the foaming temperature of MCTP on the morphological characteristics of solid foams based on it.

#### References

- [1] Ping Z, Chen QL. Preparation and characterization of carbon foam derived from coal pitch. Journal of Analytical and Applied Pyrolysis, 2016; 122: 370-376.
- [2] Wang Y, He Z, Zhan L, Liu X. Coal tar pitch-based carbon foam for thermal insulating material. Materials Letters, 2016; 169: 95-98.
- [3] Tsyntsarski B, Petrova B, Budinova T, Petrov N, Velasco LF, Parra JB, Ania CO. Porosity development during steam activation of carbon foams from chemically modified pitch. Microporous and Mesoporous Materials, 2012; 154: 56–61.
- [4] Tzvetkov G, Tsyntsarski B, Balashev K, Spassov T. Microstructural investigations of carbon foams derived from modified coal-tar pitch. Micron, 2016; 89: 34–42.

- [5] He X, Li X, Wang X., Zhao N., Yu M., Wu M. Efficient preparation of porous carbons from coal tar pitch for high performance supercapacitors. New Carbon Materials, 2014; 29 (6): 493-502.
- [6] Liu H, Li T, Wang X, Zhang W, Zhao T. Preparation and characterization of carbon foams with high mechanical strength using modified coal tar pitches. Journal of Analytical and Applied Pyrolysis, 2014; 110: 442–447.
- [7] Liu X, Wang Y, Zhan L. Carbon foams prepared from coal tar pitch for building thermal insulation material with low cost. Chinese Journal of Chemical Engineering, 2018; 26 (2): 415-420.
- [8] Chen C, Kenne EB, Stiller AH, Stansberry PG, Zondlo JW. Carbon foam derived from various precursors. Carbon, 2006; 44 (8): 1535-1543.
- [9] Liu H, Li T, Shi Y, Wang X, Lv J, Zhang W. Effect of different secondary quinoline insoluble content on the cellular structure of carbon foam derived from coal tar pitch. Journal of Analytical and Applied Pyrolysis, 2014; 108: 310–315.
- [10] Yoo, MJ, Park, CW, Lim, YS, Kim, MS. Properties of Coal Tar Pitch Modified with Acid and Oxidation Treatment // Advanced Materials Research, 2013; 785-786: 735-738.
- [11] Tsyntsarski B, Petrova B, Budinova T, Petrov N, Krzesinska M, Pusz S, Majewska J, Tzvetkov P. Carbon foam derived from pitches modified with mineral acids by a low pressure foaming process. Carbon, 2010; 48 (12): 3523–3530.
- [12] Zeng C, Lin Q, Fang C, Xu D, Ma Z. Preparation and characterization of high surface area activated carbons from co-pyrolysis product of coal-tar pitch and rosin. Journal of Analytical and Applied Pyrolysis, 2013; 104: 372–377.
- [13] Fernandez JJ, Figueiras A, Granda M, Bermejo J, Menendez R. Modification of coal tar pitch by air-blowing. Variation of pitch composition and properties. Carbon, 1995; 33 (3): 295-307.
- [14] Tsyntsarski B, Petrova B, Budinova T, Petrov N, Popova A, Krzesinska M, Pusz S, Majewska J. Synthesis and characterization of carbon foam by low pressure foaming process using H<sub>2</sub>SO<sub>4</sub> modified pitch as precursor. Bulgarian Chemical Communi-cations, 2009; 41 (4): 397 – 403.
- [15] Krutko I, Kaulin V. Vplyv Khlorvmisnykh polimeriv na sklad ta strukturu kamianovuhilnoho peku. [Influence of polymers which contain chlorine on composition and structure of coal tar pitch]. Vestnik natsionalnogo tekhnicheskogo universiteta KHPI. 2015; (10): 148-151. (*in Ukrainian*).
- [16] Krutko I, Kaulin V. Teoretychni peredumovy vykorystannia kamianovuhilnoho peku yak polimernoho materialu [Theoretical preconditions of coal tar pitch using as the polymeric material]. Naukovi pratsi DonNTU, Seriia: Khimiia i khimichna tekhnologiia, 2010; 163 (15): 103-107. (*in Ukrainian*).
- [17] Krutko I, Kolbasa V. O vozmozhnosti polucheniya tverdykh pen na osnove modifitsirovannogo kamennougolnogo peka [About the possibility of the preparation of solid foams based on modified coal tar pitch]. Naukovi pratsi DonNTU, Seriia: Khimiia i khimichna tekhnologiia, 2013; 21 (2): 156-161. (*in Russian*)
- [18] Krutko I, Kaulin V, Satsiuk K. Reolohichni doslidzhennia modyfikovanykh kamianovuhilnykh pekiv [Rheological investigations of modified coal tar pitches]. Naukovi pratsi DonNTU, Seriia: Khimiia i khimichna tekhnologiia, 2011; 184 (16): 150-158. (*in Ukrainian*).
- [19] Żweifel H, Maier RD, Schiller M. Plastics Additives Handbook, 6th ed.; Hanser, 2009; p.1142.
- [20] Reyes-Labarta JA, Marcilla A. Kinetic study of the decompositions involved in the thermal degradation of commercial azodicarbonamide. J. Appl. Polym. Sci., 2008; 107(1): 339–346.
- [21] Petchwattanaa N, Bledzki SC. Influences of particle sizes and contents of chemical blowing agents on foaming wood plastic composites prepared from poly(vinyl chloride) and rice hull. Advanced Materials Research, 2011; 306-307: 869-873.

- [22] Danylo I, Krutko I. Use of chemical blowing agent for foaming modified coal tar pitch. IX international scientific-technical conference «Advance in petroleum and gas industry and petrochemistry» proceedings, Lviv, Ukraine, May 14–18, 2018, p. 61–64.
- [23] Papole G, Focke WW, Manyala N. Characterization of medium-temperature Sasol-Lurgi gasifier coal-tar pitch. Fuel, 2012; 98: 243-248.
- [24] Alcaniz-Monge J, Cazorla-Amoros D, Linares-Solano A. Characterization of coal-tar pitches by thermal analysis, infrared spectroscopy and solvent fractionation. Fuel, 2001; 80 (1): 41-48.
- [25] Lin QL, Li TH. Synthesis and properties of condensed polynuclear aromatics resin using coal tar pitch as monomer and terephthalic aldehyde as cross-linking agent. Polymer Materials Science and Engineering, 2007; (2): 62-64.
- [26] Krutko I, Yavir K, Kaulin V. The influence of the nature of stabilizer on the degradation of coal tar pitch. Voprosy khimii i khimicheskoi tekhnologii, 2018; (4): 97-102.

To whom correspondence should be addressed: Dr. I. Krutko, Donetsk National Technical University, 85300, Pokrovsk, Ukraine,<u>poshukdoc@gmail.com</u>

# Article

# **Open Access**

#### PROPERTIES OF DONETSK BASIN HARD COALS AND THE PRODUCTS OF THEIR HEAT TREATMENT REVEALED VIA MOSSBAUER SPECTROSCOPY

Andrii Koveria<sup>1</sup>, Lina Kieush<sup>2\*</sup>, Andrii Hrubyak<sup>3,</sup> and Volodymyr Kotsyubynsky<sup>4,</sup>

<sup>1</sup>National Technical University "Dnipro Polytechnic", Faculty of Geological Prospecting, Dnipro, Ukraine

<sup>2</sup>National Metallurgical Academy of Ukraine, Faculty of Metallurgy, Dnipro, Ukraine

<sup>3</sup>Institute of Metal Physics, National Academy of Science, Kyiv, Ukraine

<sup>4</sup>Vasyl Stefanyk Precarpathian National University, Faculty of Physics and Technology, Ivano-Frankivsk, Ukraine

Received November 25, 2018; Accepted January 18, 2019

#### Abstract

In this article, the authors present the results of the researches carried out on the properties of the Donetsk basin coals when they were in the original state, after pyrolysis and after combustion of the pyrolysed residue. The studies have been conducted via the Mossbauer spectroscopy. The changes in the structural and the magnetic properties of the iron-containing components of the hard coals after their heat treatment have been revealed and described. We assume that the obtained results can serve the theoretical needs and be of practical value for deeper understanding the processes occurring when hard coal processing under industrial conditions and their prediction, which can open the new approaches to the application both the coal products and the wastes of coal processing.

Keywords: Mossbauer spectroscopy; Pyrolysis; Combustion; Hard coals; Iron-containing components; Ash.

#### 1. Introduction

Coal is the main raw material for the production of heat, electricity, chemicals, fuels and reducing agents for metallurgy, etc. Despite the increasing usage of renewable sources, the world demand for coals is predicted to remain at a steadily high level, at least until 2035, due to the growing demand for energy <sup>[1]</sup>.

In Ukraine, as well as in many other countries of the world, coal is the main source of energy carrier for thermal power engineering and metallurgy while coal mining is of great economic importance thereof. Within the territory of Ukraine, the main coal reservoirs are found in the Donetsk and the Lviv-Volhynia coal basins, plus the Dnipro brown coal basin. Additionally, there are revealed low sulphur salt coals in the Western and the Northern Donbass and high-sulphur brown coal in Novo-Dmytrivske deposits. The main reservoirs of oil shale are located in the Baltic Depression (the boundary between the Kirovohrad Region and Cherkasy Region).

Coal as a product of different degrees of carbonisation, which the green plant remains underwent in the course of time, has a complicated and variable organic nature, it is chemically bounded to an inorganic substance dispersed randomly in the form of mineral inclusions, dissolved salts and inorganic substances.

The industrial coalfield of the Donetsk basin represents sandy-carbonate coaly rocks of carbon while the Lviv-Volhynia coalfield basin is sandy-clay rocks of lower and middle carbon. The coal deposits of the Donetsk basin belong to the Carbonic period (carbon) and are represented by all three stages, namely, lower, middle and upper. The share of the lower carbon is 11 % of all basin reservoirs, the middle one is 88 %, and the upper one is up to 1 % <sup>[2]</sup>.

The coals of the Donetsk basin are characterized by the presence of all types of coals plus anthracite; they are considered to be petrographically homogeneous. Its coal layers have a complex structure, the mines are predominantly of low coal capacity, and most of the mines are dangerous with their emissions of gas and coal. The average mining depth of the coal layers is approximately 650-700 m. The dirt bands are predominantly in argillaceous states. Due to the different amounts of the dirt bands and low thickness of the coal beds, the run-of-mine coals are characterized by high ash content (up to 40 %) and therefore require beneficiation operations for further usage in energy generation or metallurgical coke production.

The mineral substances within coal represent a mixture of various components. Predominantly, they are several silicates (silicates of aluminium, iron, calcium, sodium, potassium and magnesium in the form of clay minerals), iron disulphides (in the forms of pyrite and marcasite), several carbonates (carbonates of calcium, iron (in the form of siderite) and magnesium), several sulphates (sulphates of calcium, aluminium and iron), iron oxides and calcium oxides, several chlorides and finally compounds of rare elements. Moreover, there are organomineral compounds of coal, for instance, salts of humic acids and humates within coal content.

In general, the mineral substances within coal can be divided into the groups of internal (mineral impurities inherent from the initial material since they have been accumulated in the process of coal formation) and external (penetrated into the coal mixture in the process of extraction). The composition of the coal ash is quite diverse and differs not only with the coal type and its field features, but the differences are also found within one coal field, however, the content of internal mineral substances is more or less constant within the coal belonging to one and the same deposit and, as a rule, is up to 7 wt %. Determining the content of the coal mineral part is a complex task and, therefore, as a rule, the concerned enterprises are actually satisfied with determining the total number of mineral components using the ash content index.

Further, the prominent feature of the Donetsk basin coals is that the iron oxides can reach up to 88.5% in the mineral part of the coal content <sup>[3]</sup>. The principle iron compounds within coal are iron disulphides (in the form of pyrite, marcasite), sulphates, carbonates, oxides and hydroxides, mica-like clay minerals that contain iron (ileth) and complex humates. The iron organically bounded with the coal structure can occur in the form of iron acetate- $Fe(C_2H_3O_2)_2^{[4]}$ , along with a carboxyl group <sup>[5]</sup>, as well as in the protein-like structures and porphyrins <sup>[6]</sup>. The type of iron compounds and their amounts are surely in dependence with the coal basin, the coal seam and the coal type.

The most common iron compound found in coal is pyrite, which is in the form of concretions of various structures and sizes. In most cases, they are finely dispersed pyrite (<100 or <40 microns), closely linked with the organic matter. Since the iron content in aluminosilicate minerals is usually less than 3 % (based on  $Fe_2O_3$ ), the alumosilicate form is to prevail over other forms of iron compounds only when  $Fe_2O_3$  content in the ash is less than 2 %.

Furthermore, though coal is applied in various secondary processes, namely pyrolysis, combustion, gasification, and hydrogenation, only the primary processes, namely mining and beneficiation, play the crucial role in the amount and the composition of the mineral components present in coal.

The ash composition within coal is the really important issue for combustion since the ash melting temperature depends on this process as well as its ability to form fusible slags. In metallurgy, the composition of fuel ash determines the technological parameters of the processes. Thus, in the blast furnace practice, the ash composition within coke obtained from coals determines both the quality and the number of fluxes required for the cinder scorifying. In the basic oxygen furnace process, the slag viscosities and the slag heat capacities are important for calculating the thermal effect of fuel oxidation. The ash composition also determines the ways of recycling coal wastes after such processes as coal mining, beneficiation, and combustion. The search for the additional recycling opportunities for coal waste remained after coal treatment is an urgent task, both environmentally and economically, especially when taking into account the multi-tonnage of these wastes. In this aspect, the coal compositions

and properties are the determining factors for making the engineering solution on the suitability of the wastes for recycling. The most attractive ways to use them are in the secondary raw materials forms as those applied instead of the primary constituents and also in the further extraction of the useful components.

Eventually, there are the most valuable components of the coal mineral part, and it remains in its processing wastes – it is iron. In order to evaluate the possibility of using iron-containing wastes as raw materials and having the purpose of iron extraction, it is necessary to evaluate the peculiarities of the mineral composition and the structure of the iron-bearing components. The most effective method for determining and studying iron-containing components within substances is known to be Mossbauer spectroscopy.

Based on the developed background, the current publication aims at determining the ironcontaining components of the mineral part of the coals belonging to the Donetsk coal basin and at studying their changes resulting from the pyrolysis and the subsequent combustion of the remained residue.

As the research method, the Mossbauer spectroscopy has been used since it is reported as a unique analytical tool for identifying iron ore minerals <sup>[7]</sup>. The application of this method for the Fe<sup>57</sup> isotope is possible due to the iron content of up to 2.7 % or more within the research material. In this application, the Mossbauer spectroscopy has been widely used for almost 60 years, including the cases when the characterization of iron-containing components of the coal mineral part was required. Since the atomic weight of carbon in coal is low, the Mossbauer spectroscopy allows identifying iron-containing components within coal even in cases where the iron content does not exceed 1 %.

Moreover, the most widely spread studies conducted via the Mossbauer spectroscopy application are the studies of the magnetic microstructures, the changes in electron-nuclear interactions and the atomic media in solids, also the studies wherein it is necessary to identify the phase compositions and the structural properties of materials <sup>[8 9]</sup>. In particular, the method is actively used to investigate the catalyst reactivities in the production of synthetic fuels by the Fischer-Tropsch process <sup>[10-11]</sup>, plus the Mossbauer spectroscopy actively serves for the coal gasification process <sup>[12]</sup>. Understanding the regularities in the phase state changes within the iron-containing components of coal both during coal gasification and during coals combustion allows ensuring the efficiency of these processes regarding their completeness. Further, the presence of certain iron-containing substances in the products of coal mining, beneficiation, and processing is significant for solving the issues of the environmental impact of the wastes generated from coal and the rational ways of their recycling <sup>[13]</sup>.

Eventually, the Mossbauer spectroscopy can be applied for solving seismic geochemistry issues, practical and search geology. Another important problem to be solved with the Mossbauer spectroscopy is in monitoring the useful ore components during their extraction, in particular, when the presence of  $Fe^{2+}$  and  $Fe^{3+}$  and their dedicated ratios. This method is also used for defining the content of minerals for mining and the effective use of the mining equipment, as well as for increasing the equipment wear resistance when the further processing of the ores <sup>[1]</sup>. The study of the coal Mossbauer spectra allowed Alekseev *et al.* <sup>[14]</sup> to assume that the presence of explosive zones with high levels of methane is associated with the presence of double-valence iron in the coal, which acts as a catalyst. The optimal ratio of  $Fe^{2+}$  and  $Fe^{3+}$  if achieved can act as an efficiency indicator of the recovery process carried out by electric furnaces and to provide the best conditions for their operation <sup>[15]</sup>.

Since the influence of heat treatment on coal mineral part is an interesting problem for the studies, it is suggested to make the research on the processes of pyrolysis and combustion processes with the special focuses on their features.

# 1.1. Coal pyrolysis

Coal pyrolysis is a complex process that occurs when coal is being heated to a certain temperature without oxygen access. Taking into account the absence of any oxidants during

the process, there mainly occurs the transformation of the organic matter during coal pyrolysis. Thus, the changes in the elemental composition are observed in this process along with the increase in the carbon content while the decrease in the oxygen, hydrogen, nitrogen and sulphur contents. The mineral part of the coal during pyrolysis loses its hydrated water, also there occur the decomposition reactions (commonly, with pyrite and carbonates) in coal. In general, the mineral part of coal is almost unchanged, and practically all the mineral components are converted into solids. At the same time, due to the release of the volatile organic compounds of coal, the ash content of the residue is to be higher than that in the initial coal since there is the increase of the concentrations of the mineral components.

#### **1.2. Coal combustion**

In the combustion process, all organic components of coal are removed (in the form of  $CO_2$  and  $H_2O$ ) while the mineral components are subjected to a number of transformations resulting in the formation of the ash residue only. It is known that when burning coal in a muffle furnace, the mineral components undergo the following transformations:

- 1) Loss of moisture (dehydration) of aluminosilicates (clays), oxides and iron hydroxides and also gypsum is added to this list at the temperature above 500°C. Moreover, the formation of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub> and water occur.
- 2) Oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  (converted into the dedicated oxide):

 $4FeO + O_2 = 2Fe_2O_3.$ 

 Decomposition of carbonates with carbon dioxide emissions at the temperatures of 500-900°C:

CaCO₃ =	CaO +	CO <sub>2</sub> .	

 $MgCO_3 = MgO + CO_2.$ 

 $FeCO_3 = FeO + CO_2$ .

4) Formation of iron oxide, as described by Eq. 4. FeCO<sub>3</sub> is subsequently converted into oxide, and therefore the reaction takes place as shown by Eq. 5:

$$4FeCO_3 + O_2 = 2Fe_2O_3 + 4CO_2$$

5) Oxidation of iron disulphides (pyrite, marcasite) at temperatures of 450-600 °C (refer to Eq. 6):

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

6) Sulphuric anhydride, which is formed by the oxidation of pyrite and the combustion of organic sulphur, reacts with calcium carbonate and oxygen (refer to Eq. 7):

 $2CaCO_3 + 2SO_2 + O_2 = 2CaSO_4 + 2CO_2$ .

7) The formation of calcium sulphate occurs in the temperature range of 700-1100°C (refer to Eq. 8):

$$2CaO + 2SO_2 + O_2 = 2CaSO_4.$$

The reaction takes place as  $SO_2$  being released when organic sulphur burns while the oxidation of iron disulphide and the decomposition of carbonates occur.

8) Decomposition of iron sulphate at 850-950 °C (refer to Eq. 9):

 $2FeSO_4 = 2FeO + 2SO_2 + O_2$ .

Calcium sulphate at 1100°C starts its reaction with silica and aluminosilicates with the release of  $SO_2$  while CaSO<sub>4</sub> decomposes at 1300°C.

9) The conversion of chlorides and the compounds of alkali metals at the temperatures above 500°C.

Due to the changes in the chemical composition of the coal mineral component during the process of combustion, the ash composition and the ash mass are not equal to the mass and the composition of the mineral substances within the coal. As a result, the ash value after coal combustion has to be slightly less than that in the content of the initial mineral part.

(8)

(9)

(7)

(1)

(2) (3)

(4)

(5)

(6)

# 2. Experimental

# 2.1. Materials

With the purpose to study the iron-containing components of the coal mineral part, the coal from the Donetsk basin of Almazna Mine (Dobropillia city of Donetsk Region, Ukraine) was used for the research. The research samples were prepared from one coal rank, according to the current classification of Ukrainian coals it refers to GZhO rank <sup>[16]</sup>.

The Almazna Mine is characterized by a high content of methane, the  $l_1$  and  $m_5$ ', which are being worked out and has the capacity of 1.1-2.2 m and the slope of  $9-11^\circ$ . Table 1 shows the parameters of the coal proximate analysis and Table 2 represents its petrographic characteristics.

Table 1. Proximate analysis of the hard coal

Sample		Paramete	Fixed carbon, %				
Campic	Wa	Ad	V <sup>d</sup>	$V^{daf}$	St <sup>d</sup>	$P^{d}$	FC <sup>d</sup>
Rank of GZhO, Almazna Mine (Dobropillia city, Ukraine)	1.5	6.55	33.9	36.3	2.55	0.006	59.5

Table 2. Petrographical analysis of the hard coal

	Petrographical co	mponents, %		Sum fusainised components	Average reflec- tion of vitrinite
Vitrinite (Vt)	Semivitrinite (Sv)	Inertinite (I)	Liptinite (L)	ΣОК, %	Ro, %
84	0	11	5	11	0.86

The chemical compositions of the principle mineral components of coal, presented in Table 3, show a high content of silica (SiO<sub>2</sub>) - 37.97 %, hematite (Fe<sub>2</sub>O<sub>3</sub>) - 32.42 %, and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) - 22.2 %. Thus, with the ash content of coal  $A^d = 6.55$  %, the above mentioned components are 2.49 %, 2.12 % and 1.45 % by weight of coal, respectively.

Table 3. Chemical composition of the coal ash

Content, % Dry state							Index of ash basicity	
SiO2	Al2O3	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na2O	K2O	<b>SO</b> 3	Io
37.97	22.2	32.42	1.26	1.75	0.92	1.17	0.74	0.624

The index of ash basicity, calculated via Eq. 10 is 0.624.

 $I_{o} = (Fe_{2}O_{3} + CaO + MgO + Na_{2}O + K_{2}O)/(SiO_{2} + Al_{2}O_{3})$ (10)

If the index of coal basicity is calculated by means of Eq. 11,  $I_0$  has a rather high rate of 6.46 due to the high content of Fe<sub>2</sub>O<sub>3</sub>.

 $I_{o} = A^{d} \cdot 100 \cdot (Fe_{2}O_{3} + CaO + MgO + Na_{2}O + K_{2}O)/(100 - V^{daf}) \cdot (SiO_{2} + Al_{2}O_{3}).$ (11)

# 2.2. Methodology

The Mossbauer spectra allow identifying the chemical composition and the structure of the tested substance, as this method of analysis is based on the phenomenon of resonant radiation and absorption of  $\gamma$ -quanta while different chemical compounds used as radiation sources (radionuclides) or as sinks (nuclides) have their own characteristic spectrum of radiation or absorption.

The currently reported analysis has been performed on powdered samples via using MS-1104EM spectrometer, which was operated in a constant acceleration mode for the experiment and its operational parameters were as follows:  ${}^{57}$ Co (Rh) source activity - about 50 mCi, the metallic a-Fe line width - 0.29 mm/s, the calibration of isomeric shifts with respect to a-Fe. Additionally, the spectrum analysis has been carried out with the Univem software package.

The samples with the particle size less than 0.1 mm for the experiment were prepared in accordance with the standard procedures. The pyrolysis of the coal and the combustion of its

residue have been carried out under laboratory conditions in a muffle furnace, and the final temperature parameter has been 800°C.

#### 3. Results and discussion

The research has been conducted on the materials as follows: the coal, the residue after coal pyrolysis at the temperature up to 800°C and the ash remaining after the residue combustion at up to 800°C.

Schematically, the research procedure can be presented as shown in Fig. 1. The spectra characteristics revealed are given in Table 4 and their images - in Fig. 2-4.



Figure 1. Scheme of the conducted research

The obtained Mossbauer spectra results have been further analysed, and the summarized data are presented in Table 4.

Table 4. Parameters of the components in Mossbauer spectra (Results obtained with different heat treatments)

Sample	Component	IS, mms <sup>-1</sup>	QS, mms⁻¹	H Tesla	Relative inten- sity (%)	Interpretation
Hard coal	D1 (Fe <sup>2+</sup> )	0.28	0.55	0	25.12	Marcasite (FeS2)
Haru Coar	D2 (Fe <sup>2+</sup> )	0.32	0.64	0	74.88	Pyrite (FeS2)
	S1 (Fe <sup>3+</sup> )	0.37	-0.17	515	89.49	Hematite (a-Fe2O3)
at 800°C	D1 (Fe <sup>3+</sup> )	0.33	0.42	0	6.36	Fe <sup>3+</sup>
	D2 (Fe <sup>2+</sup> )	0.82	1.69	0	4.15	Fe <sup>2+</sup>
After combus-	S1 (Fe <sup>3+</sup> )	0.37	-0.19	51.5	87.47	Hematite (a-Fe <sub>2</sub> O <sub>3</sub> )
tion at 800°C	D1 (Fe <sup>3+</sup> )	0.22	0.85	0	12.53	Fe <sup>3+</sup> glass

# 3.1. Hard coal



The Mossbauer spectrum of the original coal was approximated by the superposition of two doublet components with the close values of the isomer shifts and excellent quadrupole splitting. According to the obtained parameters, the coal under analysis was represented by iron disulphides – pyrite and marcasite <sup>[17]</sup>, they differed in the types of crystal lattices. The share of pyrite was almost 75 %. The iron was in the bivalent state, and the bivalent iron is commonly known as the substance to concentrate in the clusters of evenly distributed volumes.

Figure 2. Mossbauer spectra of the hard coal

### 3.2. The residue after pyrolysis at the temperatures of up to 800°C

After pyrolysis at the temperatures of up to 800°C, the sample was analysed for the spectrum. The obtained results have shown that its composition consisted of a superposition of one sextet and two duplets. The iron valence varied with trivalent, but bivalency was also found with the sample. Thus, a doublet with a higher integral intensity had the velocity of 1.69 mm/s, indicating rather strongly distorted areas of iron and/or a relatively weak crystallinity of this component. The sextet with the isomer shift and quadrupole splitting and the magnetic field on the Fe<sup>57</sup> nuclei corresponds to the antiferromagnetic hematite. In this case, Fe<sub>2</sub>O<sub>3</sub> contained relatively large crystallites, as it was evidenced by the presence of a well-exposed sextet. The hematite share in the sample has been revealed as almost 90 %.

Pyrolysis is known as a process able to decompose iron disulphide. The beginning of the decomposition starts at about 450°C and almost completely finishes at 600°C, reaching the maximum intensity within the range of 550-600°C. Thus, at the temperature of 800°C, the pyrite and the marcasite are to be completely decomposed.



Figure 3. Mossbauer spectra of the residue after pyrolysis

Figure 4. Mossbauer spectra of the ash after combustion

The analysis of the spectrum showed that another major component within it is the trivalent  $Fe^{3+}$ . The comparison of the results allows us to assume that the finely divided iron oxides are formed when decomposing pyrite <sup>[18]</sup>.

#### 3.3. Ash after combustion

The ash spectrum has shown that the dedicated sample consisted of a combination of one sextet and one duplet (refer to Fig. 4.). The sextet possessed the hematite parameters. Therefore it draws the conclusion that the final type of iron after combustion is hematite. Additionally to hematite, there occured the finely divided iron oxides, and silicates along with the ferritic glass had been formed due to  $Fe^{3+}$ . In the middle of these glass spherulites, the magnetite is assumed to occur.

### 4. Conclusions

The Mossbauer spectroscopy is a convenient tool for the differentiation of various types of coals and the products of coal heat treatment by the properties of their iron-containing components. With regard to the heterogeneity of coals and the products of their processing, this method has considerable potential for studying the structural and magnetic properties of iron-containing components. In Ukraine, which is rich in coal of varying metamorphism degrees, the Mossbauer spectroscopy has not yet been widely used due to the lack of spectrometers in sufficient quantities.

The results of the Mossbauer spectroscopy with the typical coal of the Donetsk basin has provided the information on the properties of iron-containing components of the dedicated coals and the mineral changes within them after pyrolysis and combustion of the pyrolysed residue. The difference in the properties and forms of iron has been detected. Thus, the original hard coal is represented by pyrite and marcasite, but the hard coal residue after pyrolysis contains weak magnetic iron-containing phases (hematite, finely divided ferric oxide). After combustion of the pyrolysed residue, the final type of iron is hematite and the ironcontaining glass is also formed.

The obtained results have theoretical and practical value for better understanding and predicting processes occurring under industrial conditions, and they approach the coal products and the coal processing wastes to the recycling route. The presence of magnetic iron - containing phases grants the possibility of iron extraction by magnetic beneficiation. In this case, the presence of glass spherulites within the combustion products plays an adverse effect on the extraction effectiveness of that iron which is inside the coal products. In this case, it is necessary to apply to ground for the destruction of the spherulites.

#### Acknowledgments

The publication is produced within the framework of the project entitled "The Development of Techniques to Apply the Carbon Materials Produced from Renewable Raw Materials in the Metallurgy", 0117U003919.

#### Symbols

W <sup>a</sup>	Moisture (air dried basis);	L	Liptinite;
A <sup>d</sup>	Ash (dry basis);	ΣΟΚ	The sum of the fusainised components;
$V^d$	Volatile Matter (dry basis);	Ro	The average reflection of vitrinite;
V <sup>daf</sup>	Volatile Matter (dry, ash free basis);	Io	Index of ash basicity;
St <sup>d</sup>	Total Sulphur (dry basis);	D	Duplet;
$P^d$	Phosphor (dry basis);	S	Sextet;
$FC^d$	Fixed Carbon (dry basis);	IS	Isomer shift relative to a-Fe;
Vt	Vitrinite;	QS	Quadrupole splitting;
Sv	Semivitrinite;	Н	Hyperfine magnetic field.
Ι	Inertinite;		

#### References

- [1] Information on https://www.bankofcanada.ca/wp-content/uploads/2015/05/bp-energyoutlook-2035.pdf.
- [2] Handbook for Engineers in Cokemaking. The 6th volumes. Volume 1. Coals for coking. Coal mining. Preparation of coals for coking; Borisova LN, Shapoval YuG (Eds); INZHEK, Kharkov, 2010, p. 536 (in Russian).
- [3] Aronov SG, Nesterenko LL. Chemistry of Solid Fossil Fuels, Kharkov State University, Kharkov, 1960, p. 371. (in Russian).
- [4] Taneja SP, Jones CHW. Mossbauer studies of iron-bearing minerals in coal and coal ash. Fuel, 1984; 63:695-702.
- [5] Lefelhocz JF, Friedel RA, Kohman TP. Mossbauer spectroscopy of iron in coal. Geochim. Cosmochim. Acta, 1967; 31:2261-2273.

- [6] Herod AJ, Gibb TC, Herod AA, Xu B, Zhang S, Kandiyoti R. Iron complexes by Mossbauer spectroscopy in extracts from Point of Ayr coal. Fuel, 1996; 75:437-442.
- [7] Long GJ. Industrial Applications of the Mossbauer Effect, Plenum Press: New York, 1986, p. 806.
- [8] Kotsyubynsky VO, Grubiak AB, Moklyak VV, Pylypiv VM, Lisovsky RP. Structural, morphological, and magnetic properties of the mesoporous maghemite synthesized by a citrate method. Metallofiz. Noveishie Tekhnol., 2014; 36:1497-1512 (in Ukrainian).
- [9] Waanders FB, Mulaba-Bafubiandi AF, Lodya L. The South African industry use of Mossbauer spectroscopy to solve operational problems. Hyperfine Interact., 2014; 226:721-735.
- [10] Lazar K. Mossbauer spectroscopy in catalysis. Hyperfine Interact., 2013; 217:57-65.
- [11] Niemantsverdriet JW, van der Kraan AM, van Dijk WL, van der Baan HS. Behaviour of metallic iron catalysts during Fisher-Tropsch synthesis studied with Mossbauer spectroscopy, X-ray diffraction, carbon content determination and reaction kinetic measurements. J. Phys. Chem., 1980; 84:3364–3370.
- [12] Waanders FB. Iron mineral changes of two coal types occurring during gasification, 29th, Annual International Pittsburgh Coal Conference, October 15-18, Pittsburgh, PA, USA, 2012, p. 2679.
- [13] Waanders FB, Silva Luis FO, Saikia Binoy K. The use Mossbauer spectroscopy in environmental research. Hyperfine Interact., 2017; 238:52-64.
- [14] Alekseev AD, Ulyanova EV, Vasilkovsky VA, Razumov ON, Zimina SV, Skoblik AP. Features of the coal structure of outburst zones. Mining information and analytical bulletin (scientific and technical journal), 2010; 8:152-163 (in Russian).
- [15] Andrews L, Pistorius PC, Waanders FB. Electron beam and Mossbauer techniques combined to optimize base metal partitioning in the furnace. Michrochim. Acta, 2008; 161:445–450.
- [16] National Standard of Ukraine 3472:2015. Brown coals, hard coals and anthracite. Classification, 2015 (in Ukrainian).
- [17] Evans BJ, Johnson RG, Senftle FE, Blaine Cecil C, Dulong F. The <sup>57</sup>Fe Mossbauer parameters of pyrite and marcasite with different provenances. Geochim. Cosmochim. Acta., 1982; 46:761-775.
- [18] Kotsyubynsky V, Ostafiychuk B, Moklyak V, Hrubiak A. Synthesis, characterization and electrochemical properties of mesoporous maghemite γ-Fe<sub>2</sub>O<sub>3</sub>. Solid State Phenom., 2015; 230:120–126.

To whom correspondence should be addressed Dr. Lina Kieush, National Metallurgical Academy of Ukraine, 49600, Gagarina av., 4, Dnipro, Ukraine, <u>linakeush@gmail.com</u>

# Article

# OPTIMAL SIZING OF MUD GAS SEPARATORS IN WELL PLANNING FOR EFFECTIVE WELL CONTROL IN DRILLING OPERATIONS

Boniface A. Oriji<sup>1</sup>, Offodum G. Okechukwu<sup>2</sup>

- <sup>1</sup> Department of Petroleum Engineering, University of Port Harcourt, East West Road, Choba, Port Harcourt, Nigeria
- <sup>2</sup> Institute of Petroleum Studies, University of Port Harcourt, East West Road, Choba, Port Harcourt, Nigeria

Received November 28, 2018; Accepted January 18, 2019

#### Abstract

Gas kicks are circulated out of the well through mud gas separators by applying well control procedures. The large volumes of gas reaching the surface are directed to the mud gas separator where they are separated from the mud and safely vented out. This paper investigates the optimal capacity (size) of the mud gas separator to effectively separate and vent large gas cuts from mud safely and in a controlled manner. The paper presents a model for the mud gas separation from a functional point of view, and a procedural technique combined with well control data for proper sizing of a mud gas separator. The procedure and simulation illustrated how blow-through can be avoided in any mud gas separator and how to troubleshoot an ineffectively sized separator. A model was developed to effectively size mud gas separator internal diameters. In the case study presented and validated, the optimum mud gas separator internal diameter was found to be 27.3 inches with a mud leg pressure of 3.6 psi under well conditions of peak gas flow rate of 2.74 MMSCF/D using a 230 ft gas vent line with 3 right-sharp bends resulting to a vent line pressure of 1 psi. This model will enhance the sizing and operation of mud gas separators, and will also be a good guide for the upgrade of undersized mud gas separators.

Keywords: mud gas separator; Blow-through; vent line pressure; mud seal leg; well control.

#### 1. Introduction

As the complexity of exploration of oil and gas in terms of depth, high temperature/high pressure (HT/HP) continually increases, the drilling of these reservoirs and wells have been a challenge in the drilling industry. Pressures of 10,000 psi and above; pore pressures of at least 0.8 psi/ft with associated temperatures greater than 350°F are common in such complex terrain <sup>[1]</sup>.

Severe well control incidents have compelled investigation and re-examination of the equipment and procedures used in drilling these wells. Gas venting rates resulting from kicks in high-pressure wells can approach the equivalent production of a commercial gas well as would be demonstrated in this paper. Gas kicks pose the potentially worst problems encountered during drilling; they occur when formation pressure exceeds the mud hydrostatic pressure. In a situation where nothing is done, the gas kick may go out of hand and become a full blowout. Loss of lives; severe injuries; environmental pollution and a loss in revenue are all consequences of a blowout <sup>[2]</sup>. As such, the gas is removed by circulating mud and maintaining wellbore pressures to avoid more gas influx.

When a kick is being circulated out of a well, the gas and mud which returns to the surface are both channelled towards the choke line and then goes into the Mud Gas Separator (MGS). Pockets of free gas are separated from the mud in the MGS, which also acts as a venting unit

for the separated gas. In an event where the MGS gets loaded beyond its capacity, the separation may end up being inefficient and thereby resulting in a very dangerous situation where the mud and gas are being returned together into the mud pits and other mud processing facilities.

Separator malfunction can cause live crude, condensate, and drilling mud to be expelled by the gas through the gas vent line. Especially for platforms off shores where the derrick top is the likely point of the gas vent line discharge, it is extremely dangerous as the liquids will most likely fall back on the drilling floor (platform). The volatile condensate/oil mixture will collect close to the deck space and can be ignited by a spark.

Due to the hazards of mud gas separator blow-through, there is a need for gas processing equipment to handle increasing volumes of gas influx in the industry. Typical practice does not consider the MGS limitations, however rather focuses on well control, expecting that the MGS can deal with whatever gas volume is present. The challenge is clear-cut, that as oil and gas exploration continues into deeper and higher pressure reservoirs, the safe operations of the MGS are often exceeded. Although MGS modification and re-design has improved its capacity appreciably, space restrictions, particularly in mobile rigs, have imposed an inherent challenge.

Thus, the importance of proper sizing and design of the separator cannot be overstated. In pursuant to this, this paper considers the separation procedure from a functional point of view, and a procedural technique has been developed to curtail the danger of blow-through in an MGS as well as troubleshooting of a poorly sized MGS.

According to Low and Jansen in <sup>[1]</sup>, regular drilling operations tend to be more focused on well control issues and therefore neglects the shortcomings of the MGS with the assumption that the equipment will deal with whatever gas influx into the well. They added that changes had been made to make the MGS smaller and lighter to save footprint and weight resulting in a reduced gas-handling capacity. However, due to deeper and high pressure drilling, the trend has been reversed. Larger separators, larger-diameter gas vent lines, and longer mud seal legs are now the order of the day and are still affected by the severe space limitations of drilling platforms. They considered the blow-through capacity, calculated the maximum possible casing pressure and developed a kick decision model to determine if a given gas influx could be controlled by the MGS on the rig. The decision model considered the likely risks to be encountered in well control.

Williamson and Dawe in <sup>[2]</sup> came up with a combination of models which aimed at establishing algorithms that could easily estimate MGS parameters as functions of time while controlling the well. They estimated the liquid and gas entrapment parameters, MGS internal pressure and height of liquid level accordingly. They went on to state that the point when the pressure safety between mud leg seal hydrostatic and internal pressures is minimum is a very critical period for the MGS. They also stated that mud leg seal fluid weight affects the blowthrough capacity. They concluded that heating the MGS increases the liquid entrainment, an undesirable condition which can be reduced by using the largest possible MGS diameter.

Lee in <sup>[3]</sup> carried out a study on MGS design and gas handling system; he stated that the operating capacity of the gas handling system must not be exceeded for efficient separation. In line with this, Lee in <sup>[3]</sup> highlighted separating, venting, and liquid-entrainment capacities as the performance characteristics or efficiency limitations of a MGS. He modelled and calculated these parameters accordingly to suitably size a MGS.

Butchko *et al.* in <sup>[4]</sup> stated that the maximum anticipated flow rate of the gas is key when designing the MGS. They suggested an approach to calculate gas pressure and volume and considered vent line and separator sizing. They also added the effects of vessel internals, fabrication, and maintenance on MGS operation.

MacDougall in <sup>[5]</sup> discussed the evaluation and economical upgrade of MGS to meet design criteria instead of renting or building a new one. He stated that peak gas flow rate, mud leg, separator ID and vent line friction pressure are important factors that influence proper sizing of MGS. He also considered the possible effects of oil-based muds on the sizing and design requirements. By simulating a kick scenario, he accessed the sizing parameters and also proposed guidelines for possible mud gas separator upgrade to meet sizing criteria. He added that closed-bottom MGS is the preferred configuration to open-bottom and float-type MGS. He carried out further studies to investigate how the minimum separator ID kill rate and effective length affected the friction pressure in the vent line.

### 2. Methods

A typical kick is considered to properly estimate peak gas flow rate. Normally, some factors such as; the well location, the well size, well type and depth will affect the kick <sup>[5]</sup>. Calculations were made and simulated accordingly in the Splitter program.

The Driller's method <sup>[6]</sup> was used for calculations since other well control methods would give lower gas peak flow rate values. Driller's method parameters provide worst-case well control scenario values for the separator sizing <sup>[7-8]</sup>. Normally, the worst case kick (gas kick) is used for the kick data. In this case, we had a 16404-ft. straight hole, 9 5/8 x 8 1/2" casing at 14000 ft., 6 5/8 x 2 13/16" DC at 340-ft, 5"x 50.2 lbm/ft HWDP at 465 ft., 5" 16.6 lbm/ft DP, 5 1/2" x 13" triplex pump at 95% efficiency and 0.091 bbl/stroke output. Slow pump rate at 34 spm, 15 ppg old mud weight, and 20 bbls pit gain were investigated and the optimum MGS sizing parameters were obtained.

Slow pump rate at 810 psi at 34 spm, old Mud Weight was 15 ppg, pit gain was 20 bbls, degree of underbalance was 0.68, initial SIDPP was 580 psi, volume of kick opposite drill collar was 8.8 bbl, volume of kick opposite drill pipe was 11.2 bbl, annular capacity factor was 0.0459 bbl/ft and the Initial SICP was 825 psi

The internal diameter of the MGS has directly related its capacity (The bigger, the better). It is also influenced by the inlet pipe size (the bigger, the better) and on the height between the inlet and the outlet to the vent line. Therefore, blow-through conditions may exist because of insufficient separator cut caused by small vessel internal diameter (ID). The industry standard approach to the sizing of MGS is to use API 12J guidelines. They are simple and non-conservative and do not consider items such as the inlet pipe ID<sup>[1,8]</sup>. The minimum Separator ID was estimated to be 27.3 inches.

#### 3. Equations used for computations

The following equations stated below were used in this study to size the mud gas separator for this case study well. The Slow Circulation Rate, SCR was calculated using Eq. (1). The effective length of the gas vent line was calculated using Eq. (2). The initial SIDPP was calculated using Eq. (3). The initial SICP was calculated using Eq. (4). The annular capacity factor was calculated using Eq. (5). The volume of kick opposite drill collar was calculated using Eq. (6). The volume of kick opposite drill pipe was calculated using Eq. (7). The maximum casing pressure at the surface was calculated using Eq. (8). The volume of gas upstream of the choke was calculated using Eq. (13). The time to pump gas out of the well was calculated using Eq. (14). The volume of gas downstream of the choke was calculated using Eq. (15). The peak gas flow rate was calculated using Eq. (16). The vent line friction was calculated using Eq. (17). The minimum mud leg required was calculated using Eq. (18). The mud droplets falling velocity was calculated using Eq. (19). The minimum separator ID was calculated using Eq. (20). Volume  $SCR = \frac{Volume}{Displacement}$ . SPM (1)where SCR is the slow circulation rate in bbls/min; volume is in bbls; displacement in stk; and SPM is the displacement rate in stk/min  $L_e = L + Equivalent \ lenght$ (2) where Le is the effective length of gas vent line in ft., and L is the vent line length in ft. Initial SIDPP = Degree of underbalance. TVD. 0.052(3) where TVD is the True vertical depth in ft.  $I.S = Initial SIDPP + \frac{DCL+VDP}{ACE}$ (4)

where I.S is the initial SICP in psi; DCL is the Drill Collar length in ft; VDP is the volume of kick opposite drill pipe in bbls; ACF is the Annular Capacity Factor in bbl/ft.

$$ACF = \frac{ID^2 - DP^2}{1029 4}$$
(5)

where ACF is the Annular Capacity Factor in bbl/ft, and ID is the casing Internal Diameter in inches, and DP is the diameter of drill pipe in inches.

(6)

$$VDC = DCL \times \frac{ID^2 - DC^2}{1029.4}$$

where VDC is the volume of kick opposite drill collar in bbls, and DCL is the drill collar length in ft, ID is the casing Internal Diameter in inches, and DC is the diameter of the drill collar in inches.

$$VDP = PG - VDC \tag{7}$$

where VDP is the volume of kick opposite drill pipe in bbls, and PG is the pit gain in bbls, and VDC is the volume of kick opposite drill collar in bbls. (8)

$$P_{C}MAX = \frac{SIDPP}{2} + \sqrt{\left(\frac{SIDPP}{2}\right)^{2} + A \times B \times C \times D}$$

where  $P_cMAX$  is the maximum casing pressure at the surface in psi, and SIDPP is the shut in drill pipe pressure in psi, and A, B, C, and D are constants defined by Eqs. (9) to (12).

 $A = SIDPP + 0.052 \times OMW \times TVD$  (9) where SIDPP is the shut in drill pipe pressure in psi, OMW is the original mud weight in ppg, and TVD is the true vertical depth in ft.

$$B = \frac{PG}{ACF} \tag{10}$$

where PG is pit gain in bbls, and ACF is the annular capacity fa	ctor in bbl/ft.
$C = OMW \times 0.052 - 0.1$	(11)
Where OMW is the original mud weight in ppg.	
$D = 4.03 - 0.38 \times In(A)$	(12)
$VCC = DC \times A \times D/$	(13)

 $VGC = PG \times A \times D/PcMAX$ 

where VGC is the volume of gas upstream of choke in bbls, and PG is the pit gain in bbls, A and D are constants that have been defined by Eqs. (9) and (12), and PcMAX is the maximum casing pressure at the surface in psi.

$$TPG = \frac{VGC}{SCR} \tag{14}$$

where TPG is the time to pump gas out of well in minutes, and VGC is the same as in Eq. (13), and SCR is the same as in Eq. (1).

 $VGD = \frac{PcMAX \times VGC}{14.7} \tag{15}$ 

where VGD is the volume of gas downstream of choke in bbls, and PcMAX is same as in Eq. (8), and VGC is the same as in Eq. (13).

$$PGF = \frac{VGD}{TPG}$$
(16)

where PGF is the peak gas flow rate in SCF/D, and VGD is same as in Eq. (15), and TPG is the same as in Eq. (14).

$$VLF = 5 \times 10^{-12} \times VEL \times \frac{PGF^2}{ID^5}$$
(17)

where VLF is the vent line friction in psi, and PGF is the same as in Eq. (16), and the ID is the gas vent line internal diameter in inches.

$$MMR = \frac{VLF}{0.052 \times OMW}$$

where MMR is the minimum mud leg required in ft., and VLF is the same as in Eq. (17), and OMW is the original mud weight in ppg.

$$MDFV = 0.15 \times \sqrt{\frac{OMW - 0.008}{0.008}}$$

(19)

(18)

where MDFV is the mud droplets falling velocity in ft/s, and OMW is the same as in Eq. (18).  $MSID = 15.56 \times \sqrt{SCR}$  (20)

where MSID is the minimum separator ID in inches, and SCR is the same as in Eq. (1).

### 4. Results and discussion

The performance of the MGS has been depicted in Fig. 1 below; a (purple) vertical line represents the MGS performance, based on API Bulletin 12J and assumed industry empirical numbers for "K" factors. For efficiency in separation, the flow rate of the gas should be less than this vertical line and the horizontal line intersection (left side of the vertical line). If the gas rate is higher than this value, there will be inefficient separation; liquid droplets will be able to flow up the gas vent line and gas will be entrained in the liquid passing through the seal leg. This hampers the overall performance of the separation system. The vent line performance is dependent on gas friction loss calculation.



Fig. 1. Mud gas separator operation performance. Purple – MGS performance; Brown, Teal, Blue – Liquid load lines; Green – seal leg capacity line; Red – Gas load line.

For the scenario where there is effective separation (gas rate less than the intersection of the vertical separation capacity line), the (red) Gas Load line can be used.

For the scenario where there is inefficient separation, i.e. the gas rate exceeds the vertical separation capacity line, one of the three Liquid Load Lines is used (Brown, Teal, and Blue). There is no certainty as to how bad the liquid loading is – caution is probably the approach so the worst case condition, which is the blue line, should be considered as the norm.

The intersection of the (Green) Seal Leg Capacity line (equals the hydrostatic pressure of the U-tube full of the selected seal leg fluid density) with the chosen vent line performance line gives the blow-through capacity.

Table 1 below presents the mud gas separator performance data used for this study.

Table 1. Mud gas separator performance data

MGS data			
Temp flowing gas (deg F)	50	Seal Leg Height (ft)	12
Gas Specific Gravity	0.69	Density of Seal Leg Fluid	6
Vent Line ID (in)	7	Mud Density (ppg)	15
Vent Line Length (ft)	230	MGS Height (ft)	22
Other Vent Line Losses (ft -equiv)	210	Separator Diameter (ft)	2.27

From Fig. 1, the separation capacity (see the purple vertical line) is 2.75 MMSCF/D, approximately the value of peak gas flow rate obtained by the Splitter program (2742826 SCF/D). The line intersects gas load line (red line) indicating a vent line friction pressure of 1 psi, the same value obtained by Splitter program (1 psi). If the gas rate is above 2.75 MMSCF/D, signifying inefficient separation, the blue line (vent performance line) must then be used. In this case, this intersects the Seal Leg capacity (green) line at 3.1 MMSCF/D. The blow-through capacity is therefore 3.1 MMSCF/D.

Occasionally, when a MGS is picked for the rig contract, the drilling engineer and supervisor must investigate the suitability of the separator with respect to well location. This analysis is usually done during the process of rig bidding <sup>[5]</sup>. In a situation where the separator is found to be insufficient, upgrading the separator might make more economic sense instead of building a newly suitable separator. When the hydrostatic pressure of the mud seal leg is less than the friction pressure in the vent line, separation becomes inefficient.

#### 4.1. Reduce the circulating kill rate

Considering excess friction pressures in the vent line and the vessel ID, the MGS operation may be improved by a reduction in the kill rate circulation. Reducing the kill rate makes more economic sense in the face of this sizing challenge. For instance, if we reduce the kill rate from say 3.5 bbl/min to 1.5 bbl/min, there will also be a proportional decrease in the peak gas flow rate. Using Eqs. (14) and (16), the time required to vent gas and the peak gas flow rate were respectively computed as shown below

$$TPG = \frac{69.64}{1.5} = 47 Minutes \quad PGF = \frac{7635 \times 8085.6}{47} = 1329464 SCF / D$$

We can notice the glaring difference in the peak gas flow rate from the previous value of 2742826 SCF/D. This significant drop in the peak gas flow rate, in turn, decreases the friction pressure in the vent line by approximately 77 percent (77%) and therefore improves the operation as can be seen below: using Eq. (17), the vent line friction was calculated as seen below.

$$VLF = 5 \times 10^{-12} \times 440 \times \left(\frac{1323010^2}{7^2}\right) = 0.23 \, Psi$$

# 4.2. Increase the mud leg

Increasing the mud seal leg height may be another solution. Let's say if, from our case study, we happen to increase the mud leg from the 12 ft to 15 ft, it invariably means that the hydrostatic pressure in the mud leg will then become 4.5 psi (15 \* 0.3), which is a significant increase from the 3.6 psi previously gotten with the 12 ft mud leg, thereby resulting in a more efficient MGS operation.

### 4.3. Gas vent line bends/corners adjustment

The effective length of the vent line and the friction pressure in the vent line are greatly affected by the type and number of bends in the vent line. If the sharp-right bend on separator sized in the case study is replaced with a more rounded-right bend, there will be a significant difference on the effective vent line length and vent line friction pressure values. Using Eqs. (2) and (17) respectively we got the following results  $L_c = 230 \times (3 \times 1) = 233 \text{ ft}.$ 

$$VLF = 5 \times 10^{-12} \times 233 \times \left(\frac{2742826^2}{7^5}\right) = 0.52 \ Psi$$

Hence, changing the type of bend reduced the vent line effective length, and significantly reduced the friction pressure by 50%.

#### 4.4. Vent line ID increase

The most expensive alternative may be to increase the vent line ID, but this may just be the only possibility of increasing the separator efficiency <sup>[5]</sup>. Larger vent line IDs will reduce the vent line friction pressure calculation. Therefore, if an 8-inch vent line ID were used instead of 7, the calculation for vent line friction pressure would change to

$$VLF = 5 \times 10^{-12} \times 440 \times \left(\frac{2742826^2}{8^5}\right) = 0.51 \ Psi$$

The vent line friction pressure decreases from 0.52 to 0.51 psi indicating better separator efficiency.

#### 5. Conclusions

The optimal mud gas separator ID and separation capacity obtained in this study were 27.3 inches and 2.74 MMSCF/D respectively. Various solutions were proffered in an attempt to upgrade an existing insufficiently sized MGS in order to meet standard guidelines rather than build or rent an entirely new MGS.

The procedural technique presented will prevent separator blow-through during well control operations, and the following inferences are drawn:

- It is feasible and desirable to control the maximum gas flow rate downstream the choke entering an MGS.
- The kill pump rate is an assessment of the ability of the MGS to handle a kick safely and a basis for optimal well control.
- The severity of bends and corners significantly impact on the friction pressure.
- Increasing the mud seal leg aids effective MGS operation.
- The risk of blow-through in an MGS is reduced greatly if gas is limited to separation capacity.

#### Nomenclatures

ACF	Annular capacity factor, bbl/ft	PGF	Peak gas flow rate, SCF/D
DCL	Drill collar length, ft	SCR	Slow circulation rate, bbl/min
I.S	Initial SICP, Psi	SICP	Shut-in circulating pressure, psi
L	Gas vent line length, ft	SIDPP	Shut-in drill pipe pressure, psi
Le	Gas vent line effective length, ft.	TPG	Time to pump gas out of well, min.
MDFV	Mud droplet filling velocity, ft	TVD	True vertical depth, ft
MMR	Minimum mud leg required, ft	VDC	Volume of kick opposite drill collar, bbl
MSID	Minimum separator ID, inch	VDP	Volume of kick opposite drill pipe, bbl
OMW	Original mud weight, ppg	VGC	Volume of gas upstream of the choke, bbl
PcMAX	Maximum casing pressure at the	VGD	Volume of gas downstream of choke, bbl
	surface, psi		
PG	Pit gain, bbl	VLF	Vent line friction, psi

#### Abbreviations

BBL	Barrels	OMW	Original Mud Weight
DC	Drill Collar	PPG	Pounds per gallon
DP	Drill Pipe	SICP	Shut-in Circulating Pressure
HWDP	Heavy Weight Drill Pipe	SIDPP	Shut-in Drill Pipe Pressure
ID	Internal Diameter	SPM	Stroke Per Minute
MGS	Mud Gas Separator		

#### References

- [1] Low E, and Jansen C. A method for handling gas kicks safely in high pressure wells. *Journal* of Petroleum Technology, 1993; 45(6), 1-6, SPE 21964.
- [2] Williamson M, and Dawe R. mud gas separator response to well control procedure. *Proceed-ings of the SPE/IADC Drilling Conference*, Dallas, Texas, USA, February 15-18, 1994, 1-10.
- [3] Lee P. Surface gas handling and mud gas separator design principles. *Department of Natural Resources and Mines, Queensland 2016*, 1-124
- [4] Butchko D, Davies GE, and Reid RR. Design of atmospheric, open-bottom mud/gas separators. *Proceedings of the SPE/IADC Drilling Conference*, New Orleans, Louisiana, USA, 5-8 March 1985, SPE/IADC 13485.
- [5] MacDougall G. Mud/gas separator sizing and evaluation. *SPE Drilling Engineering* 1991, 6(4), SPE 20430, 1-6.
- [6] Roy RS, Nini CJ, Sonnemann P, and Gillis B. Driller's Method vs Wait and Weight Method: One offers distinct well control advantages, retrieved from http://www.drillingcontractor.org/driller's-method-vs-wait-and-weight-method-one-offers-distinct-well-control-advantages-1444.
- [7] Leach C. BP Amoco/Chevron training alliance advanced well control. Well control and systems design Inc., 1999
- [8] Blow out engineers. Well control reference guide. Sierra Hamilton Holdings 2017, LLC. https://sierra-hamilton.com/pdfs/BE-WC-Reference-Guide-REV-0-Web.pdf

To whom correspondence should be addressed Dr. Boniface A. Oriji, Department of Petroleum Engineering, University of Port Harcourt, East West Road, Choba, Port Harcourt, Nigeria

# Article

# SYNTHETIC DENSITY LOG AND EFFECTIVE DENSITY POROSITY ESTIMATION OF KATI FORMATION, SERI ISKANDAR, PERAK

Sufizikri Sahari<sup>1\*</sup>, Khairul Arifin Mohd Noh<sup>2</sup>, Ahmed Mohamed Ahmed Salim<sup>3</sup>

Department of Petroleum Geosciences, Universiti Teknologi PETRONAS, Malaysia

Received November 22, 2018; Accepted January 15, 2019

#### Abstract

This paper focuses on rock physics study on the Kati formation in Seri Iskandar, Perak in Malaysia, particularly in modelling the P wave velocity and bulk density log by using petrophysical relationship through well log data, and estimate the total and effective porosity from the synthetic log. The absence of density log data and incomplete depth coverage of slowness log from this well have challenged the computation of the formation porosity. Thus, Faust's formula and Gardner's equations were used to obtain the synthetic P wave velocity log (SYN\_VP) and synthetic density log (SYN\_DEN) respectively. The SYN\_VP estimated by using Faust's equation shows a good result with normalize root mean square (NRMSE) of 6.24%. In the same depth, SYN\_DEN estimated by Gardner's equation with NRMSE of 5% and have an exceptional tie with measured bulk density from 111 core samples. A total of 28 core samples have been measured for its effective porosity with helium porosimeter and ranged less than 5% in average. Effective porosity log generated from SYN\_DEN resulted in good match with effective porosity from core with NRMSE 1.44%. The study use core data to validate the model, and NRMSE is used to show the error percentage calculated between the modelled log and core data. The lower the NRMSE value indicates less error model and concluded as reliable synthetic log.

Keywords: Kati Formation; Synthetic Log; Well Log; Effective Porosity; Petrophysics.

#### 1. Introduction

Many old oil fields have incomplete log parameters compared to modern fields. The old days may record the data manually thus present the limited information. To re – evaluate the oil field, a complete set of log data is needed to justify whether the field have a potential for a revisit and potential recovery. Somehow, to acquire a complete data set means increasing the cost as well as the risk. However, the absent log can be projected from another log by using petrophysical relationship. Therefore, this study demonstrates similar methodology used by the industry in accomplishing the prediction of the density log from available log by using proven petrophysical relationship i.e. Faust and Gardner equations, for Kati Formation in Seri Iskandar, Perak. Then, the total porosity and effective porosity of the formation can be estimated and more data can be generated to analyze Kati formation in Seri Iskandar with less ambiguity.

#### 2. Study area

The Kati Formation previously named as Kati Beds, lies in between the granites of the Bintang and Kledang ranges. It was introduced by Foo<sup>[1]</sup>, to define a formation that occurs in Kuala Kangsar area and extends southward along the western bank of Sungai Perak into Kinta Valley. Alkhali & Chow<sup>[2]</sup> mentioned that Kati Formation has many similarities with Kubang Pasu Formation and according to Muhammad Hanif *et al.*<sup>[3]</sup>, Singa Formation depict the identical characteristic with Kubang Pasu Formation, which make Kati, Kubang Pasu and Singa Formation correlated with each other. However, Singa Formation distribution focused in Langkawi's islands and extended to Gunung Raya and Pulau Langgun area <sup>[4]</sup>. Meanwhile in Kubang Pasu and Singa Formation, there are fossil found imprint in red mudstone layers called as Posidonomya in several locations i.e. Langkawi Island, Perlis and Kedah, which suggest the age of the fossil ranged from Middle Devonian to Carboniferous <sup>[5]</sup>.



Figure 1 Geological map of Kati Formation and location of CTW-01 well in Seri Iskandar, Perak, Malaysia (modified after Alkhali & Chow 2014 <sup>[3]</sup>)

In contrast, no fossil has been found within Kati Formation. However, it has been estimated to range from Late Palaeozoic Carboniferous to Permian aged <sup>[2]</sup>. As in Figure 2, the formation aged as major Upper Paleozoic rocks group in western zone of Peninsular Malaysia by previous researcher <sup>[2]</sup>. The Kati Formation generally consisted of a mainly monotonous sequence of interbedded metamorphosed reddish brown carbonaceous shale, mud- stones, and sand-stones, with minor siltstone "argillaceous and arenaceous rocks" <sup>[1,6]</sup>. The most recent study of Kati formation has been focused in Seri Iskandar with the idea of Paleozoic hydrocarbon plays <sup>[2]</sup>. Their qualitative approached research has given a new insight on this Upper Paleozoic rocks. Their studies have contributed to a new assessment on the elements of hydrocarbon systems. The Paleozoic sandstone exposed in Seri Iskandar were evaluated to be potential hydrocarbon reservoir.

As new quantitative approach, this study utilized well log data. In petrophysical analysis, porosity is an important parameter to be determined to analyze the rock. The absence of log data needed to compute the porosity for Kati formation i.e. density log and complete depth coverage of slowness log; has challenged the porosity estimation for the formation. Therefore, the objectives of this paper are to model the synthetic slowness log and density log so the porosity can be estimated. In this study, the synthetic slowness log is needed to cover the depth range from 300 - 415.3m. So that, the synthetic density log can be generated and estimation of the formation bulk density can be made. From that, the effective porosity can be calculated by using synthetic density log as an input. The result then compared with effective porosity of the outcome.

# 3. Petrophysical relationship

In rock physics, the geophysical observation and the rock physical properties such as porosity pore fluid content and composition, are closely related <sup>[7]</sup>. In petrophysics, the technical analysis from laboratory data as well as borehole measurement become the key to get the reservoir properties i.e. shale volume fraction, porosity, permeability and water saturation. Nevertheless, some of the property is not possible to measure it directly due to the philosophy of indirectness. Thus, some other property that is related to the required property is needed. For that fact, interpretive algorithms that relate measurable parameters to reservoir parameters framework are built within the petrophysics <sup>[8]</sup>. Rock physics parameters that related to the storage capacity, fluid flow capacity are porosity and permeability. The absence of the porosity data makes the analysis more challenging. However, with resistivity data, those unavailable data i.e. density log, can be estimated using the petrophysical relationship i.e. Faust and Gardner empirical relationship <sup>[9]</sup>





# 3.1. P wave velocity from resistivity by Faust

Expression for the velocity in a tightly packed spherical particle model which put under pressure has been derived by Gassmann <sup>[10]</sup>. He observed the elastic constant of such a model vary with pressure. It makes the P wave velocities vary as 1/6<sup>th</sup> power of the pressure. Then, Faust <sup>[11]</sup>, come out with empirical formula for velocity which, in term of the depth of burial, Z, and the formation resistivity, R. Noted that 'a' constant in Faust's equation is different from Gardner's equation.

Faust's empirical equation:

$$V_p = a(RZ)^{\frac{1}{6}}$$
 (1)  
where:  $V_p = P$  wave velocity, m/s; a = constant; R = resistivity, ohm-m; Z = depth.

# 3.2. Density from P wave velocity by Gardner

Bulk density is a vital indicator to delineate shale, in cases of oil sands, accurate density estimation is needed so that the location of the shales can be identified thus interference during the recovery process can be avoided <sup>[12]</sup>. From a series of controlled field and laboratory measurements of brine-saturated rocks, excluding evaporates, Gardner et al. <sup>[13]</sup> has found an empirical relationship between density and velocity.

Gardner's empirical equation with suggested a and m:  $\rho = aV^m$ where:  $\rho$  = density; V = P wave velocity; a = 0.31; m = 0.25.

### 3.3. Porosity from density

Density log can be utilized to estimate rock porosities by using the following equation;  $\rho_{ma} - \rho_{log}$ Ø

$$\rho = \frac{\rho_{ma}}{\rho_{ma} - \rho_f}$$

(3)

(2)

where:  $\phi$  = total porosity;  $\rho$ ma = matrix density;  $\rho$ log = log density;  $\rho$ f = fluid density.

Common grain density value which are widely utilize are tabulated in the Table 1. As recommended by Gardner et al. <sup>[13]</sup>, the values for density filtrates are 0.9, 1.0, and 1.1 g/cc for oil based mud, freshwater and saturated salt water respectively.

Table 1. Common density value for some minerals and fluid

Mineral	Density, g/cc	Fluid	Density, g/cc
Quartz	2.65	Fresh water	1.00
Calcite	2.71	Saline water	1.15
Dolomite	2.87	Oil	0.85
Anhydrite	2.96		

# 4. Materials and methods



# 4.1. Synthetic slowness log

The well data from CTW-01 with total logging depth of 415.3m has been used in this study i.e. Gamma ray (GAMMA), Resistivity (RES), and Slowness log (BHC\_DELT), as in Figure 2. Apart from that, measured density from core sample are also included in this study as a comparison to the synthetic density (SYN\_DEN). The synthetic density log estimation starts by modelling the slowness log first because the available slowness log does not cover the remaining depth after 300m. During data quality check at early stage, the log has been filtered, despiked and smoothed to remove the bad data such as data with negative value.
The Faust's equation has been utilized to determine the synthetic slowness log (SYN\_DELT) by applying the equation (1) to the resistivity log and then inverses the obtained P wave velocity (SYN\_VP) as in Figure 3. Next, the SYN\_DELT log will be compared with reference slowness log measured from the well (BHC\_DELT) in the same track to identify the correlation. At this stage, the log has been divided into 3 intervals as; trained data, tested data, and estimated data as in Figure 5. Then, the linear regression model has been built to determine the relationship between estimated slowness log (SYN\_DELT) and reference slowness log (BHC\_DELT) as in Figure 6. The normalize root mean square error (NRMSE) has been calculated to validate the model as in Table 5. The NRMSE indicates how much error or noise associated with the model. Therefore, the lower the NRMSE the better the model. NRMSE equation:

 $NRMSE = \frac{\left(\sqrt{\frac{1}{n}\sum_{i=1}^{n}(INPUT - REFERENCE)^2}\right)^{1}}{\left(\frac{1}{n}\sum_{i=1}^{n}REFERENCE\right)^{2}}$ (4)

## 4.2. Synthetic density log

To model the synthetic density log, the Gardner's empirical formula has been used. As in the equation (2), one of the parameter for the empirical relationship is P wave velocity, VP. Thus, the SYN\_DELT will be inverted to get the P wave velocity as slowness is 1/VP, therefore the P wave velocity used in the equation (2) will be SYN\_VP. As in Figure 9, the SYN\_DEN log is the outcome calculated using the equation (2). Then, to validate the SYN\_DEN log, a total of 111 data samples from core density has been loaded to the log track to train and test the SYN\_DEN. Depth interval from 100-250m, has been assigned as a trained data interval and the rest of the depth is the tested data interval as in Figure 10. The linear regression model between core density data (CORE\_DEN) and SYN\_DEN has been plotted to determine the relationship and the NRMSE will be calculated to show the error of the synthetic density log in comparison with core density data.

#### 4.3. Effective porosity from density

After generating the SYN\_DEN, porosity can be calculated by using petrophysical empirical relationship equation (3). Porosity data acquired from core sample will be compared to the porosity estimated from the log. Total of 25 core sample has been run through the helium porosimetry apparatus to estimate the core effective porosity (CORE\_POR) of the samples. The result from the experiment is tabulated in Table 2.

Depth,	PHIE,								
m	%	m	%	m	%	m	%	m	%
108.8	5.99	135.2	3.66	187.0	3.51	259.6	1.24	342.3	1.24
112.8	4.58	136.4	2.33	189.0	1.25	268.3	1.37	349.0	1.57
120.1	4.28	137.5	3.51	191.7	2.49	277.1	0.19	350.5	1.05
122.9	3.99	139.8	4.00	193.5	2.31	280.4	1.13	396.4	1.02
125.0	2.23	140.0	2.74	195.6	2.41	283.0	0.37		
130.2	4.38	141.8	3.67	214.8	1.32	295.6	0.17		
132.6	2.81	186.5	4.52	230.0	1.49	335.4	1.31		

 Table 2 Effective porosity measured from core samples

To compare the porosity estimated from the core samples, the porosity estimated from the SYN\_DEN log must be corrected for the shale effect to get the modelled effective density porosity (PHIE\_D), so that the data from both core and log are in the same dimension. Shale volume analysis from GAMMA will be the input for shale correction. The GAMMA log has been divided into 10 intervals to estimate the shale volume. The effective density porosity is derived from total porosity as in equation (4), (5), (6) and computed as in Table 3.

Total porosity from density: $\phi_{n} = \frac{\rho_{matrix} - \rho_{bulk}}{\rho_{matrix} - \rho_{bulk}}$	(1)
$\varphi_{Total} = \rho_{matrix} - \rho_{fluid}$	(4)
Shale total porosity from density:	
$\phi_{T \ shale} = \frac{\rho_{matrix} - \rho_{shale}}{\rho_{matrix} - \rho_{fluid}},$	(5)
Effective porosity from density:	
$\phi_{Effective} = \phi_{Total} - (\phi_{T shale} * VSH),$	(6)

Table 3. Effective porosity computation summary

Input		Para	meters	Output		
Name	Description	Name	Description	Name	Description	
Bulk density	Density log reading in zone of in- terest	Bulk den- sity matrix	Density log at 100% ma- trix.	Total po- rosity	Total porosity - not corrected for shale effect	
Shale vol- ume Bulk density matrix	Calculated shale vol- ume Matrix bulk density	Bulk den- sity shale Bulk den- sity fluid	Density log at 100% shale. Fluid density i.e. fresh wa- ter.	Effective porosity	Effective porosity - corrected for shale effect	
Bulk density shale	Shale bulk density					
Bulk density fluid	Fluid bulk density					

#### 5. Result and discussion

## 5.1. Synthetic log

The RES log shows to be responsive towards the lithology changes as the values deviated accordingly with the lithology boundaries. It is found that within high GAMMA interval, the resistivity values lower compared to the lower GAMMA interval as in Figure 2. High GAMMA value indicates shale and shaly sediment where the presence of clay mineral reduces the resistivity due to its character which is tended to bind with water molecule. This responsive character of resistivity, shows the good data quality. As Crain <sup>[14]</sup>, Faust's empirical formula does not account for gas effect. This well is having no gas bearing interval; therefore, it is suitable to use this petrophysical relationship. RES (64N) and BHC\_DELT logs have been set as input for this study with total logging depth of 415.3m and 300m respectively.

Synthetic slowness (SYN\_DELT) obtained from Faust's empirical equation with RES (64N) and depth as input, and the constant, 'a' is 635. The data has been trained on the assigned 100-200m depth interval to find the best constant based on the NRMSE value as shown in Figure 5. The next approximately 200-300m depth is used to test the constant. Three intervals with bad data group has been excluded in computation because of the spiked data were too high. As in Figure 5, due to the unavailable BHC\_DELT data within 300-400m, the same trained and tested constant from depth 100-300m has been used to project and estimate the slowness on the 300-400m depth interval using the same empirical equation.



Figure 2. Track from left: depth reference, total gamma ray, formation resistivity log, followed by slowness log. Measured slowness log only up to 300m depth.



Figure 3. On track 3, SYN\_DELT is the slowness log calculated from Faust's equation. The equation product is in P wave velocity. The reason why SYN\_DELT is generated; by inverting the product from Faust's equation, the comparison between BHC\_DELT and calculated SYN\_DELT can be made. From that, the NRMSE can be identify and the error between BHC\_DELT and SYN\_DELT can be measured.



Figure 5. The log track shown the BHC\_DELT and SYN\_DELT overlain together. Three intervals have been created to train, test and estimate the slowness log. The trained and tested data interval has been highlighted to measure the NRMSE



Figure 4. The histogram shows the highlighted reference mean i.e. BHC\_DELT. The distinguished spike data intervals however, were excluded



Figure 6. Note the RMSE value obtained from cross plot between BHC\_DELT and SYN\_DELT in between application interval. Then the NRMSE is calculated and the value is 6.24%. The lower the NRMSE percentage indicates better relationship between modelled and reference log



Figure 7. On track 3 the SYN\_VP has been acquired from Faust's equation. SYN\_DEN has been identified by using Gardner's relationship as on track 4

For this analysis, the relationship between SYN\_DELT and BHC\_DELT is excellent with NRMSE value of 6.24%. Then, the SYN\_VP is used to estimate the formation density using the Gardner's formula. The SYN\_DEN has been produced as in Figure 9 by utilizing the Faust and Gardner empirical equation with specifically identified constant for CTW-01. Table 4 summarize the constant used together with associated empirical formula. As shown, the density of the rock increased as it gains in depth due to compaction and diagenesis.



Figure 9. The log track shown the CORE\_DEN and SYN\_DEN overlain together



Figure 8. The histogram shows the CORE\_DEN statistic values



Figure 10. The cross plot indicates the RMSE value between CORE\_DEN and SYN\_DEN. The calculated NRMSE is 5%



Figure 11. The histogram shown the statistic value for effective porosity from core





Figure 12. The cross plot indicates the RMSE value for PHIE\_D and CORE\_POR. Total of 28 sample have been selected for effective porosity measurement



Figure 13. From left, the first track is depth reference track, followed by modelled density (SYN\_DEN), modelled density total porosity (PHIT\_D), effective porosity from modelled density (PHIE\_D) overlain with effective core porosity (CORE\_POR), shale volume (VSH\_Final), and lastly is the zonation log. Shale volume is needed for effective porosity computation. Shale volume analysis using GAMMA has been done to estimate the shale fraction within certain interval. On track 4, modelled effective porosity from density shown excellent correlation with effective porosity measured from core with NRMSE 1.44%. To identify the accuracy of the estimated density, total of 111 samples of core density has been loaded into the track as in Figure 10. The SYN\_DEN has been divided into two intervals; trained data interval and tested data interval. From that, the 'a' and 'm' can be identified by adjusting its value until the density model fit with the core value. The NRMSE value has been calculated to ensure the relationship between the SYN\_DEN and CORE\_DEN in a good controlled value ranges. As a result, 'a' and 'm' values are 0.335 and 0.28 respectively with NRMSE value of 4.83%. This study gives an advantage not only in covering the unavailable density log data, yet from the SYN\_VP, it estimates the absence of slowness log data within the range of 296.4 – 415.3m depth. By utilizing the Faust and Gardner empirical equation with specifically identified constant for CTW-01. Table 4 summarize the constant used together with associated empirical formula. As shown, the density of the rock increased as it gains in depth due to compaction and diagenesis

## 5.2. Effective porosity from synthetic density log

Based on synthetic density estimated from Gardner's empirical equation, the porosity log can be predicted by transforming the synthetic density log. The result has been combined with helium porosity data obtain from core sample to justify the log. The transformation considers the fluid within the formation is freshwater and the lithology are sand, shaly metasedimentary rock according to the core sample, therefore,  $\rho_{fluid} = 1.0$  g/cc and  $\rho_{ma} = 2.63$  g/cc. Figure 13 shows the synthetic total and effective porosity log obtained by transforming the synthetic density log by using equation (4), (5) and (6).

By transforming the synthetic density log into the synthetic porosity log, helium porosity data from core sample can be compare directly in one track. Result shown in Figure 13, conclude that the synthetic log data estimated from Faust and Gardner empirical equation valid for depth of 100 – 415.3m depth based on the low NRMSE value and visual cross comparison from the core and log data. the NRMSE value for PHIE\_D and CORE\_POR correlation is 1.44% The effective porosity for this formation is below than 5% in average (Table 2). The porosity of the rock reduced as the depth increase. From 100 – 415.3m depth, the lithology is most likely metasedimentary rock, shale and interbedded shaly metasandstone with fractures and iron stained. Physically, from the core sample, metasedimentary rock is denser compare to the normal weathered sandstone. These factors effected the pore volume of the rock which is why we could see a very low and insignificant total porosity not to mention the effective porosity within 100-415.3m depth interval.

Petrophysical relationship	Constant	Value
Faust	а	635
	m	0.28
Gardner	a	0.34

Table 4. Constant value for Faust's and Gardner's formula for the synthetic log

\*Note that 'a' for Faust and Gardner is a different constant specific only for their equation

	-				
Input	Reference	RMSE <sup>1*</sup>	Reference	Reference	NRMSE
-			mean <sup>2*</sup> .	sample number	%
SYN_DELT	BHC_DELT	39.76	637.44, us/m	15024	6.24
SYN_DEN	CORE_DEN	0.13	2.60, g/cm <sup>3</sup>	111	5.00
PHIE_D	CORE_POR	3.43	2.39, %	28	1.44

Table 5 NRMSE computation summary

<sup>1\*,2\*</sup> Refer equation 4 for NRMSE computation. Note that for porosity the unit is already in percentage thus the final answer does not need a percentage conversion

## 6. Conclusion

The paper describes the process on predicting the density log data by using few available logs i.e. resistivity. Petrophysical relationship and framework has been fully utilized particularly from Faust's and Gardner's empirical relationship to create the synthetic density log data as well as porosity data for well CTW-01. As in Table 4, the constant value for each equation has been changes until the synthetic log and porosity log fit the reference data i.e. measured log and core data. The tabulated constant in the table is chosen based on the best fitting model with reference data that resulted low normalized root mean square, NRMSE. Table 5 summarize the computed NRMSE value for all the estimated logs. All the modelled logs shown good match and relationship with measured core and well reference data. Effective porosity for Kati formation in Seri Iskandar analyses from CTW-01 is below than 5%. A very low effective porosity range make the rock itself impossible to be a conventional reservoir rock for hydrocarbon. Nevertheless, in unconventional perspective, this formation has a potential to be a fractured reservoir like basement granite reservoir. This is because, from the core sample, lots of fractures found and most of the iron stained present within the open fractured intervals. It indicates the presence of the fresh water.

Therefore, further study is needed to analyze Kati formation with unconventional approach and advance logging tools must be used to acquire the data i.e. neutron log, spectral gamma ray, focus micro imaging log.

#### Acknowledgment

Special thanks to the research supervisor, Dr. Khairul Arifin Md. Noh and co-supervisor Dr. Ahmed Mohamed Ahmed Salim who have been provided me an assistance and guidance to complete this paper. Thank you to Universiti Teknologi Petronas for providing all the utilities and all department lab technicians and staff, that involved directly or indirectly in assisting the research activity.

#### References

- [1] Foo KY. Geology and Mineral Resources of the Taiping-Kuala Kangsar Area, Perak Darul Ridzuan. Geological Survey of Malaysia 1990, Map Report 1, 145.
- [2] Alkhali HA, Chow WS. 2014. The Kati Formation: A Review. Proceedings of the International Conference on Integrated Petroleum Engineering and geosciences, Icipeg 2014, 303–12. https://doi.org/10.1007/978-981-287-368-2.
- [4] Roslan MHK, Aziz ChAMohamed KR Facies and Sedimentary Environment of Singa Formation of Langkawi, Malaysia. Sains Malaysiana 2016; 45(2): 1897 1904.
- [5] Jasin B. Posidonomya (Bivalvia) from Northwest Peninsular Malaysia and Its Significance. Sains Malaysiana, 2015; 44(2): 217 – 223.
- [6] Wong TW. Geology and Mineral Resources of the Lumut-Teluk Intan Area, Perak Darul Ridzuan. Geological Survey of Malaysia 1991, Map Report 3, 96.
- [7] Mavko G, Mukerji T, Dvorkin J. The Rock Physics Handbook: Tools for Seismic Analysis of Porous Media. Cambridge University Press, 2<sup>nd</sup>ed. 2009, New York.
- [8] Worthington P. The Petrophysics of Problematic Reservoirs. Journal of Petroleum Technology, 2011; 63 (12): 88–97.
- [9] Guntoro T, Putri I, Bahri AS. Petrophysical Relationship to Predict Synthetic Porosity Log. AAPG Annual Convention, 2013; 41124 (41124): 1–12.
- [10] Gassmann F. Elastic Waves Through a Packing of Spheres. Geophysics, 1951; 16 (4): 673–85.
- [11] Faust LY. A Velocity Function Including Lithologic Variation. Geophysics, 1953; 18 (2): 271–88.
- [12] Gray FD, Anderson PF, Gunderson JA. Prediction of Shale Plugs between Wells in Heavy Oil Sands Using Seismic Attributes. Natural Resources Research, 2006; 15 (2): 103–9.
- [13] Gardner GHF, Gardner LW, Gregory AR. Formation Velocity and Density The Diagnostic Basics for Stratigraphic Traps. Geophysics, 1974; 39 (6): 770–80.
- [14] Crain ER. Crain's Petrophysical Handbook. Online Shareware Petrophysics Training and Reference Manual 2012: E.R. (Ross) Crain. http://www.spec2000.net/01-index.htm.

To whom correspondence should be addressed: Dr. Sufizikri Sahari, Department of Petroleum Geosciences, Universiti Teknologi PETRONAS, Malaysia, <u>sufizikri g03612@utp.edu.my</u>

# Article

**Open Access** 

## TPO-GC AND TG-DTA INVESTIGATION OF DRY DECOKING PROCESS IN OLEFIN PLANTS

Farhad Ghadyanlou and Ahmad Azari\*

Faculty of Petroleum, Gas, and Petrochemical Engineering (FPGPE), Persian Gulf University (PGU), P.O. Box 75169-13817, Bushehr, Iran

Received November 27, 2018; Accepted January 18, 2019

#### Abstract

The aim of this work is to investigate the combustion mechanism of catalytic coke formed in the olefin plants furnaces as a chemical reaction fouling. The objectives are removing the steam injection and modeling a dry oxidation process based upon Thermogravimetry (TG) and Temperature-Programmed Oxidation-Gas Chromatography (TOP-GC) experiments. Comprehensive data were obtained for 5.0-15.0 % vol. oxygen content in the combustion atmosphere while the temperature was tuned from 600 to more than 1000°C. The concentrations of carbon monoxide and carbon dioxide were determined as TPO criteria for reaction rate and kinetic parameters along with the mass loss in TG tests. The results revealed the optimum decoking temperature in order to decrease the decoking run-time, improve energy conservation and enhance the cleaning efficiency. DTG thermogram revealed the temperatures that the combustion rate of catalytic coke increased gradually. TPO-GC experiments approved the optimal decoking temperature in accordance with the plant's operation manual. The propounded dry decoking mechanism depicted the combustion reaction of carbon and CO<sub>2</sub> follows by O<sub>2</sub> chemisorption at carbon surface, obtaining the activation energy, converting to the activated complex and production of CO<sub>2</sub>.

Keywords: Combustion; Coke; Oxidation; Pyrolysis; Furnace; Modeling, Parametric Study.

#### **1. Introduction**

Steam cracking of hydrocarbons is one important process of the petrochemical industry for olefin production. Carbon deposition phenomena or coke formation deposit on the inner wall of coils is carbonaceous material that results of undesirable side reactions in steam cracking process and a major concern that limits run the length of the furnace in ethylene plants <sup>[1-2]</sup>. There is a numerous investigation on the mechanisms of carbon deposition under various conditions <sup>[1-12]</sup>. Generally, there are three categories of coke formation are as the following:

- a. Catalytic coke with the filamentous structure of carbonaceous deposition as shown in Figure 1. is results of heterogeneous reaction where occur on the metal surface's active sites (Cr, Ni, Co) and generally doing main role in radiant coil coking in furnaces [1-2, 10, 13].
- b. Pyrolytic or gas phase coke deposition occurs by a radical mechanism where procurators joint with existing carbon layer and due to the growth of coke.
- c. Coke formation by condensation mechanism is amorphous structure and happens in the low temperature sections <sup>[1, 3, 14]</sup>.

Coke is poor heat conductor, and due to reducing heat transfer rate from flue gas to process gas in coils, increase pressure drop by growing coke layer and reducing cross section of coil, lower ethylene yield and heat input increased if the feed conversion maintained constant then coil skin temperature, gradually increased until reaches design temperature of reactor tube and finally cause to shut-down the furnace for coke removing during burning - off carbonaceous deposition via controlled combustion where carried out by means of a steam/air mixture [1, 3, 12-13]. The amount of coke accumulation depends on feed characteristics, operating severity, the material of coil, run length and the addition of inhibitors <sup>[10, 12]</sup>.



Figure 1. Catalytic coke formation mechanism [15]

There are two alternative industrial decoking technologies exist currently for coke removal that difference of them is end points of decoke effluent. Effluent can be sent to decoke drum or injecting to from bottom or either to the lower end walls of firebox by symmetrical piping configuration for keep particle emissions below 50 mg/Nm<sup>3</sup> during decoke which the second one applied in modern furnaces <sup>[16]</sup>. Optimization of decoke operation is one of the main interests from the point of view of energy consumption and time of production loss reduction in olefin plants; therefore, it is necessary to determine the mechanisms of coke combustion reactions by real-time analyzing of the deposited coke produced in industrial plants <sup>[6]</sup>.



Coke combustion is assigned as a de-volatilization process followed by the combustion of residual coke <sup>[17-19]</sup> along with the side reaction of gasification <sup>[20-22]</sup>. The combustion behavior of fine <sup>[23]</sup> and coarse <sup>[24-27]</sup> coal particles in the N<sub>2</sub>/O<sub>2</sub> atmosphere was studied, and a model was propounded based on devolatilized products and heat-mass transfer phenomena was propounded. In the process of combustion, the carbon atoms in the coke structure react with surrounded oxygen from the point of weak bonds as depicted in Figure 2.

Figure 2. Graphical implementation of coke decomposition in combustion phenomena

The process of various cokes oxidation or combustion has been largely investigated in the field of heterogeneous catalysts <sup>[28-30]</sup>, pulverized coal <sup>[31]</sup>, mineralogical coal <sup>[32]</sup>, coal chars <sup>[33]</sup>, boiler coal <sup>[34]</sup> and mineral coal <sup>[35]</sup>.

There are many investigations reported by different researchers on various carbonaceous materials gasification and combustion like coal, coal char, coke, petcoke, sewage sludge char <sup>[36-61]</sup>, biomass <sup>[62-73]</sup>, coal-biomass blends <sup>[74-75]</sup> and municipal solid wastes <sup>[76-78]</sup>. Some of

the alternative reaction kinetics used by different workers illustrated in Table 1 and there are excellent reviews available which can consider on gasification and combustion of coal and chars <sup>[22, 79-85]</sup>, carbon based deposits <sup>[86]</sup>, municipal solid waste <sup>[87]</sup> and carbonaceous adsorbents <sup>[88-89]</sup> and Biomass <sup>[90-95]</sup>.

Table 1. Various reaction mechanisms for carbonaceous material gasification and combustion kinetics by various researchers

Authors	Type of carbona- ceous material	Weight (g)	Reaction model	Exp. in- strument	T, ℃	Ref.
Jelemensky <i>et al.</i>	Coal char	0.002-0.003	$C + O_2 \rightarrow CO_2$ $C + CO_2 \rightarrow 2CO$ $C + 0.5O_2 \rightarrow CO$ $CO + 0.5O_2 \rightarrow CO_2$	TG	amb800	[96]
Keskitalo <i>et</i> <i>al.</i>	Coke of a Ferri- erite Catalyst	0.01	$\begin{array}{c} \mathcal{C} + 0.5\mathcal{O}_2 \rightarrow \mathcal{C}\mathcal{O}_g \\ \mathcal{C} + \mathcal{O}_2 \rightarrow \mathcal{C}\mathcal{O}_{2g} \end{array}$	TPO-GC	amb850	[97]
Gil <i>et al.</i>	Coal and pine sawdust	0.05	A (solid) $\rightarrow$ B (char) + C1 (gas) B (char) $\rightarrow$ C2 (gas) + D (ash)	TG-DTG	amb615	[98]
Micco <i>et al.</i>	Coal	0.10,0.16,0.30	$\mathcal{C}_{(s)} + \mathcal{CO}_{2(g)} \leftrightarrow \mathcal{2CO}_{(g)}$	drop tube furnace (DTF)	825-920	[99]
Nakasaka <i>et</i> <i>al.</i>	Coked MFI-type zeolite	0.1	$\begin{array}{l} \mathcal{C}_{(s)} + 0.5 \mathcal{O}_{2(g)} \to \mathcal{CO}_{(g)} \\ \mathcal{C}_{(s)} + \mathcal{O}_{2(g)} \to \mathcal{CO}_{2(g)} \\ H + 0.25 \mathcal{O}_{2(g)} \to 0.5 H_2 \mathcal{O} \end{array}$	fixed-bed flow reac- tor, TG	550-650	[100]
Li <i>et al.</i>	Coal	0.005	$C + CO2 \leftrightarrow 2CO$	TPO-TG	amb1450	[101]
Mandapati <i>et</i> <i>al.</i>	Coal char	0.01	$C + CO_2 \rightarrow C(0) + CO$ $C(0) + CO \rightarrow C + CO_2$ $C(0) \rightarrow C + CO$ $Coal + O_2 \rightarrow Coal - X - O_2$	ΤG	amb1000	[102]
Zhang and et al.	Coal	0.1	→ X transformation) X denotes the five ele- ments in coal	TGA	<200	[103]
Jing <i>et. al.</i>	Coal	0.005	$C + CO_2 \leftrightarrow C(O) + CO$ $C(O) + C \rightarrow CO + C_f$	TG	amb1300	[104]
Veca <i>et al.</i>	Coal char	0.2-0.3	$C + CO2 \rightarrow 2CO$	TGA	800-1100	[105]
Urych	Coal	0.2-0.3	Coal $\rightarrow$ x (volatiles) + (1 - x) (char) x - the fraction of vola- tiles	TGA/DSC	298-1173	[106]
Veca & Adrover	Coal char	0.02-0.03	$C + CO_2 \leftrightarrow 2CO$	TG	800-1000	[105]
Nunes <i>et al.</i>	Coal	0.03	$\begin{array}{c} C + O_2 \rightarrow C(0) \\ C(0) \rightarrow C0 \end{array}$	TG	1173K	[107]
Ding <i>et al.</i>	Coal char and petroleum coke char	0.008	$C + H_2O \leftrightarrow CO + H_2$ $CO + H_2O \leftrightarrow CO_2 + H_2$ $C + CO_2 \leftrightarrow 2CO$	drop tube furnace (DTF)-TG	1100-1400	[108]
Chen <i>et al.</i>	Coal	0.3	$C + CO_2 \leftrightarrow CO + C(O)$ $C(O) \leftrightarrow CO + C$ and $C + H_2O \leftrightarrow H_2 + C(O)$ $C(O) \leftrightarrow CO + C$	TG	1173- 1273K	[109]
Tanner <i>et al.</i>	Coal	0.01-0.015	$\begin{array}{c} C + CO_2 \leftrightarrow 2CO \\ C + H_2O \leftrightarrow CO + H_2 \end{array}$	drop tube furnace (DTF)-TG	600-1100	[110]
Czerski <i>et.</i> <i>al.</i>	Coal	0.46	$C + CO2 \leftrightarrow 2CO$	TG	Amb-1100	[111]
Liu <i>et al.</i>	coal char	0.5	$\begin{array}{c} C + CO2 \bigoplus C(0) + CO \\ C(0) \rightarrow CO \end{array}$	HP TG	1050	[112]

The coke removal with decoking process reported in six heterogeneous and homogeneous reactions by Y. Zhang *et al.* <sup>[113]</sup> as *Eqs. 1-6*:

 $C_{(s)} + O_{2(g)} \leftrightarrow CO_{2(g)}$ 

(1)

$C_{(s)} + H_2 O_{(g)} \leftrightarrow C O_{(g)} + H_{2(g)}$	(2)
$C_{(s)} + 0.5O_{2(g)} \leftrightarrow CO_{(g)}$	(3)
$CO_{(g)} + 0.5O_{2(g)} \leftrightarrow CO_{2(g)}$	(4)
$C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)}$	(5)
$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$	(6)

Heynderickx *et al.* <sup>[14]</sup> assumed coke is burning off phenomena undergoing with two fundamental endothermic gasification and oxidation reactions mechanism (*Eq.1*) and (*Eq.2*). In this study investigation was undertaken involving dry oxidation, therefore, reactions (*Eq.2*) and (*Eq.6*) is discarded. Boudouard reaction (*Eq.5*) ignored in addition because the ratio of CO to CO<sub>2</sub> decrease with increasing temperature and carbon monoxide convert to carbon dioxide rapidly. Finally, the set of reactions reduced to *Eqs.* 1, 3, 4 that enthalpies of formation at 298K respectively are as the following <sup>[113-115]</sup>.

 $\Delta H_{R1} = -394 \ kJ/mol$   $\Delta H_{R3} = -110 \ kJ/mol$  $\Delta H_{R4} = -284 \ kJ/mol$ 



(7) (8) (9)

This work aimed to study the combustion characteristics of catalytic coke formed in the furnaces of an olefin plant which extract from a real piece of the coked coil that showed in Figure 3. For this purpose, the coke samples were combusted in a fixed bed tubular reactor under different  $O_2/N_2$  atmospheres from 600 to 1000°C, and coke characters were identified by TG/DTG (Thermogravimetry/ Differential Thermogravimetry) analysis and the TPO-GC experiments were conducted under non-isothermal conditions at controlled  $O_2/N_2$  rates.

Figure 3. The cross-section of a piece of the radiant coil with inner wall coke deposit

The main objective was the development of a combustion model for nonporous catalytic coke based upon the weight percent of oxygen.

## 2. Experimental method

## 2.1. Materials and chemicals

Coke samples used in experiments were obtained from a piece of radiation coil of an ethane cracker furnace as shown in Figure 3 where were milled in the size of 1-2 mm and Table 2 illustrated the components of this coke.

Test name	Test Method	Percent wt.
Ash	ASTM D3174-11	0.8
Volatile	ASTM D3175-11	0.5
Fixed C	ASTM D3172-89(02)	98.4
Sulfur	ASTM E1915-09	0.1

Table 2. Components of catalytic coke

#### 2.2. Experimental set-up

A horizontal cylindrical reactor with accessory equipment was heated in a digital furnace in the temperature range of 600-1000°C. The reactor was fed by air and nitrogen gasses while

the gas flows were determined and controlled by mass-flow meters (brooks, 5850S, USA) in the range of 10 to 100 mL/min. The reactor tube was manufactured by a thermal resistant metal alloy (SS-304) with a diameter of 15 mm and a length of 200 mm, and experiments were carried out with coke samples located in a reactor tube. The sides of the reactor tube were blinded two four-neck flanges after the coke loading. The temperatures of the furnace, representing the reactor temperature and the flow of inlet gas streams were recorded by a PC system. The effluent gas was analyzed by gas chromatography equipped along with the released gas stream. Figure 4 shows the schematic of the experimental setup.



Figure 4. Schematic of TPO-GC set up

Gas chromatography runs were performed by a gas chromatograph (CP3800, Varian, USA) and He carrier gas (BOC, CP grade). The runs were carried out on  $1.0 \text{ cm}^3$  fluent gas from the furnace in splitless mode, injector-temperature of 150°C and pressure of 15.0 psi. The packed column consisted of HAYESEPQ (80-100 mesh) with dimensions of 2 m × 1/8 inch OD × 2.0 mm internal diameters. The column temperature was set at 30°C for 4 min. The TCD filament temperature was set at 200°C.

The coke characteristics were determined by thermogravimety (TG) analyzer (209F1, Netszch, Germany) to obtain TG and DTG traces of the pyrolytic coke samples. The atmosphere was set on ambient air, and the flow rate was fixed on 25 mL/min. The sample weight was selected to be 50-100 mg heated in the range of 30-900°C by the ramp of 20°C/min in an alumina-pan. Data was compiled and processed by Proteus Analysis Software.

## 2.3. Characteristic tests

The samples of catalytic coke, which accurately were weighted to 100 mg, were dried at 100°C for 20 min, then it was heated at a constant rate (ramp) of 20°C/min from 100°C to 600°C under air atmosphere (100 mL/min), then held at 1000°C for 10 min to complete devolatilization step. After that, the air stream (100 mL/min) was injected and the temperature decreased to ambient.

## 2.4. Combustion procedure

The TPO experimental setup, which has been depicted schematically in Figure 4, was a tubular reactor located in the thermostatically-controlled furnace. The reactor was loaded by 190, 138 and 501 mg of catalytic coke samples for combustion studies. The reason why the small quantity of coke was used is to ensure the exothermicity combustion reactions and the endothermicity cracking reactions do not fluctuate the temperature of the reactor bed. The temperature was increased from the ambient conditions to  $600^{\circ}C$  ( $20^{\circ}C/min$ ), from  $600^{\circ}C$  to  $800^{\circ}C$  ( $10^{\circ}C/min$ ), from  $800^{\circ}C$  to  $1000^{\circ}C$  ( $5^{\circ}C/min$ ) and hold at  $1000^{\circ}C$  for 10 min. The temperatures were monitored by thermocouples placed around the reactor, and the pressure was fixed by pressure regulators at the outlet stream to the combustion-reactor. Along with the

reaction, the effluent gas stream passed through a sampling valve of gas chromatography resulted in the online determination of concentrations of carbon monoxide and carbon dioxide products. After the experiments, the residual coke in the reactor was flushed-out with nitrogen (100 mL/min) until 100°C. These residues were collected and weighted by analytical balance (Kern, Germany). The weight losses of residue samples of runs 1-3 were determined, and the results are depicted in Table 3.

Run	Primary weight (mg)	Secondary weight (mg)	Weight loss (%)
1	190	80	58
2	138	70	49
3	501	230	54

Table 3. The weight loss of residue samples of runs 1-3

# 3. Results and discussions

## 3.1. TG Experimental results

TG experiment at air atmosphere was conducted, and the results are presented in Figure 5.







The combustion started at 700°C, and its rate was maximized at 900°C leading to a 30% decrease in the mass of the coke. The nonporous structure of catalytic coke shows a smooth line in the temperatures less than 700°C since no trapped or adsorbed hydrocarbons and water were released, and no mass-loss was recorded. DTG curve highlighted that from 700°C to 900°C the combustion rate increases gradually.

Figure 6 drew regarding TG data and Arrhenius relationship and mass basis rate of combustion formula:

$$r_c = -\frac{1}{m} \frac{dm}{dt}$$

(10)

Slope changes at nick point in this figure indicate how the mechanisms controlled the rate of combustion. At the lower temperatures than 638°C the controlling mechanism is kinetic control, and at the higher temperatures than 638°C diffusion is controlling step which frequency coefficient and activation energies in these steps are 5.5847e+28,  $167571.4 \text{ s}^{-1}$  and 237330,  $59197 \text{ J.mol}^{-1}$ , respectively and finally, rates of combustion in these mechanisms defined as the following *Eqs.* while R=8.314 J/mol.K.

$r_c = 5.58 \times 10^{28} \exp\left(\frac{-237330}{RT}\right)$	(11)
$r_c = 167571.4 \ exp\left(\frac{-59197}{RT}\right)$	(12)

## 3.2. Combustion mechanism of decoking

As discussed before, the combustion phenomena of catalytic coke were assessed experimentally under an oxygen atmosphere (5.0, 10.0 and 15.0 % vol.) and at different temperatures (600-1000 $^{\circ}$ C) as their results presented in Table 4.

Table 4.	Characteristics	of experimental	runs
	0	o. o/.pooc	

Run	Oxygen (% Vol.)	Time (min)	T (°C)	Cco2 (% wt.)
		0	600	0.1953
		10	700	0.1683
		20	800	0.0782
1	5	30	850	0.7680
		40	900	0.1547
		50	950	0.3920
		60	1000	0.2419
		0	600	0.1359
		10	700	0.1121
		20	800	0.1170
		27	835	0.1731
2	10	30	850	0.1318
		40	900	0.1062
		50	950	1.0883
		60	1000	0.3389
		70	1010	0.1192
		0	600	0.0873
		10	/00	0.0704
		20	800	0.2393
2	1 5	27	835	0.0852
3	15	30	850	2.2566
		40	900	0.2957
		50	950	0.6548
		60	1010	0.2700
		/0	1010	0.151/

It is clearly obvious that the oxygen chemisorptions more in temperatures lower than 850°C in 1 and 3 runs and at the lower than 950°C in step 2 as seen in Table 4 and rapid CO<sub>2</sub> formed desorption in 850°C and 950°C at 1, 3 and 2 runs, respectively occur due to oxygen chemisorbbed before. The experimental results depicted that the maximum CO<sub>2</sub> concentration was determined at 850°C in with 5 and 15 vol.% of oxygen concentrations media and at 950°C in respect to 10 vol.% which are in accordance with the field data for gas-feed olefin furnaces.

According to the results of Table 4, by increasing the temperature along with time, the concentration of produced  $CO_2$  is changed because of the revolution of surface phenomena including adsorption of  $O_2$  at carbon surface, formation of activated complexes of C–C–O, breaking the C–C bonds and release of  $CO_2$ . The results of Table 4 were graphically implemented in Figure 7 to explain the decoking process based on the released concentration of  $CO_2$ .

The main concentrations of the released  $CO_2$  are attributed to two temperatures of 850 and 950°C. The areas behind the traces, which reveal the overall production of  $CO_2$  along with temperature rise, represent that  $CO_2$  production at  $O_2$  concentration of 15% vol. was twice than that of for both  $O_2$  concentrations of 5 or 15% vol. Moreover, it is obvious that combustion reactions are conducted at two temperature regions of 800-900°C and 900-1000°C, with a quench temperature of Q~900°C in which the decoking reactions are assigned to be quenched.

The orders of  $CO_2$  production at two decoking regions of 800-900°C and 900-1000°C are not identical because of different decoking mechanisms.

In the region of 800-900°C, the magnitude of  $CO_2$  production follows as  $O_2$  concentrations of 10% < 5% << 15%. On the other hand, in the region of 900-1000°C, that magnitude follows as 5% < 15% < 10% vol.  $O_2$ .



Figure 7. Comparative production of CO<sub>2</sub> at different O<sub>2</sub> concentrations and elevated temperatures

A combustion mechanism was propounded based upon the supposed reactions, which are assigned to occur in these conditions, and the results were matched with the experimental data gathered from TPO tests. Eqs. 1, 3 and 4 were proposed as the mechanism of these reactions as the following:

$$C(s) + O_2(g) \xrightarrow[k_1]{k_1} CO_2(g)$$
(13)

$$C(s) + 0.5O_2(g) \xrightarrow[k_2]{k_2} CO(g)$$
(14)

$$\operatorname{CO}(g) + 0.5O_2(g) \xrightarrow[k_3]{k_3} \operatorname{CO}_2(g)$$
 (15)

Respect to Eqs. 13, 14 and 15 and with the assumption of elementary reactions, the reaction rate of  $CO_2$  ( $r_{CO2}$ ) production is determined as Eq. 16.

$$\mathbf{r}_{\rm CO_2} = k_1 C_{O_2} - k_{-1} C_{CO_2} + k_3 C_{CO} C_{O_2}^{1/2} - k_{-3} C_{CO_2}$$
(16)

where:  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$ ,  $k_3$ , and  $k_{-3}$  represent the rate constants of reactions Eqs 13, 14 and 15, respectively.  $C_{02}$ ,  $C_{C0}$ , and  $C_{C02}$  show the concentration of oxygen, carbon monoxide and carbon dioxide gases as %wt.

Due to this fact that CO is intermediate; therefore, the concentration gradient with respect to time is assumed to be zero. Hence, according to the steady state hypothesis, the rate of CO reactions and its concentration is determined by *Eqs. 17* and *18*, respectively.

$$+ r_{\rm CO} = k_2 C_{\rm O_2}^{\frac{1}{2}} - k_{-2} C_{\rm CO} - k_3 C_{\rm CO} C_{O_2}^{\frac{1}{2}} + k_{-3} C_{\rm CO_2} = 0$$
(17)  
$$C_{\rm CO} = \frac{k_2 C_{O_2}^{\frac{1}{2}} + k_{-3} C_{\rm CO_2}}{k_{-2} + k_3 C_{O_2}^{\frac{1}{2}}}$$
(18)

In addition, GC reports revealed that the concentration of CO is determined to be negligible in the reaction atmosphere

By replacing Eq. 18 in Eq. 16 and simplification, Eq. 19 is obtained.

$$-\mathbf{r}_{CO_{2}} = \left[\frac{(k_{1}k_{-2} + k_{2}\mathbf{k}_{3})\mathbf{C}_{O_{2}} + k_{1}k_{3}\mathbf{C}_{O_{2}}^{3/2}}{k_{-2} + k_{3}\mathbf{C}_{O_{2}}^{1/2}}\right] - \left[\frac{k_{.1}k_{-2} + k_{-1}\mathbf{k}_{3}\mathbf{C}_{O_{2}}^{1/2} + k_{-2}k_{-3}}{k_{-2} + k_{3}\mathbf{C}_{O_{2}}^{1/2}}\right]\mathbf{C}_{CO_{2}}$$
(19)

According to the above-listed  $k_n$  values, Eqs. 20 and 21 are given.

$$k_{2}k_{3} \gg k_{1}k_{-2}$$
(20)  
$$k_{-2} << k_{3}C_{O_{2}}^{\frac{1}{2}}$$
(21)

Therefore, in the first assumption of this developed model, the  $k_1k_{-2}$  is negligible with respect to the  $k_2k_3$  of Eq. 19 and it can be neglected. Likewise, in the second assumption of the model, the  $k_1k_{-2}$  and  $k_{-2}k_{-3}$  are negligible with respect to the left term  $(k_{-1}k_3C_{0_2}^{1/2})$  of Eq. 19. Therefore, the rate of reaction (Eq. 19) is written as Eq. 22.



Figure 8. Reaction rate and CO<sub>2</sub> concentration of dry decoking in different O<sub>2</sub> concentrations of combustion atmosphere

(22)

The developed model reveals that the overall rate constant is a function of the concentrations of oxygen and carbon dioxide. Therefore, it is possible to determine the overall rate constant of combustion reaction using the concentrations of oxygen and carbon dioxide in the combustion atmosphere.

The experimental data obtained from the combustion of catalytic coke and they were fitted to Eq. 22 in order to assess the accuracy of the proposed mechanism (Table 4).

The graphical illustration of the experimental data is depicted in Figure 7 representing a positive reaction rate when the  $CO_2$  concentration increases and vice versa. Therefore, the bi-functional Eq. 22 is used to admit the variation of reaction signs.

The positive reaction rate at the increased  $CO_2$  concentration is attributed to high concentration of  $O_2$  in the combustion reaction leading to increasing the first term of Eq. 22, means moving to more positive values. On the other hand, when the  $CO_2$ concentration decreases, the reaction rate moves to the negative values since the reaction of carbon to  $CO_2$  follows by adsorption of  $O_2$  at carbon surface, obtaining the activation energy, converting to the activated complex and production of  $CO_2$ .

Therefore, at descending concentration of  $CO_2$ , the carbon surface is going to adsorb  $O_2$  and cannot react to it since the concentration of activated complex is low. At these conditions, the first term of Eq. 22 is reduced with respect to the second term, and the overall sign is negative.

The above discussions and the trend of Figure 8 were in accordance with three oxygen concentrations (5, 10 and 15% vol.) of combustion atmosphere, approving the proposed mechanism.

## 4. Conclusions

Dry oxidation of deposited catalytic coke on the coil surfaces of an ethane cracker furnace was studied by TG/DTA, and TPO-GC techniques and the main conclusions were drown are

- 1- Arrhenius diagram analysis showed a change in controlling steps of combustion rate occurs at around 640°C (break point).
- 2- DTG thermogram revealed that in the range of 700-900°C the combustion rate of catalytic coke increased gradually. The maximum combustion rate was determined by TPO-GC experiments to be at 850°C, which is in accordance with the plant's operation manual.
- 3- The positive reaction rate at the increased  $CO_2$  concentration is attributed to high concentration of  $O_2$  in the combustion reaction leading to moving the reaction rate to more positive values.
- 4- The proposed mechanism depicted that the combustion reaction of carbon and CO<sub>2</sub> follows by chemisorption of oxygen at carbon surface, obtaining the activation energy, converting to the activated complex and production of CO<sub>2</sub>.
- 5- At the concentration of 5% and 15 % vol. oxygen and lower temperatures than 850°C, the rate of O<sub>2</sub> chemisorption is higher, and the rate of carbon monoxide formation is more in 850°C, and it similarly occurs for the concentration of 10 % vol, at 950°C. It is demonstrated that burning off coke in decoking of steam cracker furnaces is optimized by TG/DTA and TPO TPO-GC techniques usage leading to more energy conservation.

#### Acknowledgements

The authors acknowledge the extended help from the R&D department of Morvarid petrochemical complex to accomplish the experiments.

#### References

- [1] Browne J, Broutin P, and Ropital F. Coke deposition under steam cracking conditions Study of the influence of the feedstock conversion by micropilots experiments. Materials and Corrosion. 1998; 49(5): 360–366.
- [2] Cai H, Krzywicki A, and Oballa MC. Coke formation in steam crackers for ethylene production. Chemical Engineering and Processing: Process Intensification. 2002; 41(3): 199-214.
- [3] Abghari SZ. Investigation of Coke Formation in Steam Cracking of Atmospheric Gasoil. Journal of Petroleum Science Research (JPSR). April 2013; 2(2): 82-91.
- [4] Kopinke FD, Zimmermann G, and Nowak S. On the mechanism of coke formation in steam cracking—conclusions from results obtained by tracer experiments. Carbon. 1998; 26(2): 117-124.
- [5] Reyniers GC, Froment GF, Kopinke F-D, and Zimmermann G. Coke Formation in the Thermal Cracking of Hydrocarbons. 4. Modeling of Coke Formation in Naphtha Cracking. Ind. Eng. Chem. Res. 1994; 33(11): 2584–2590.
- [6] Kopinke FD, Zimmermann G, Reyniers GC, and Froment GF. Relative rates of coke formation from hydrocarbons in steam cracking of naphtha. 2. Paraffins, naphthenes, mono-, di-, and cyclo-olefins, and acetylenes. Ind. Eng. Chem. Res. 1993; 32(1): 56–61.
- [7] Wang J, Reyniers M-F, and Marin GB. Influence of dimethyl disulfide on coke formation during steam cracking of hydrocarbons. Ind. Eng. Chem. Res. 2007; 46 (12): 4134–4148.
- [8] Alselaa RAM and Elfghi FM. Reduction of coke accumulation and energy resources by adding steam and carbon dioxide in naphtha based ethylene production. Chemical and Process Engineering Research. 2014; 28: 21 –31.
- [9] Chan KYG, Inal F, and Senkan S. Suppression of Coke Formation in the Steam Cracking of Alkanes: Ethane and Propane. Ind. Eng. Chem. Res. 1998; 37(3): 901–907.
- [10] Jambor B and Hajekova E. Formation of coke deposits and coke inhibition methods during steam cracking. Pet Coal, 2015; 57(2): 143-153.
- [11] Vandewalle LA, Van Cauwenberge DJ, Dedeyne JN, Van Geem KM, and Marin GB. Dynamic simulation of fouling in steam cracking reactors using CFD. Chemical Engineering Journal. 2017; 329:77-87.
- [12] Kucora I, Paunjoric P, Tolmac J, Vulovic M, Speight JG, and Radovanovic L. Coke formation in pyrolysis furnaces in the petrochemical industry. Petroleum Science and Technology. 2017; 35(3): 213-221.

- [13] Heynderickx GJ and Froment GF. Simulation and Comparison of the Run Length of an Ethane Cracking Furnace with Reactor Tubes of Circular and Elliptical Cross Sections. Industrial & Engineering Chemistry Research. 1998; 37(3): 914-922.
- [14] Heynderickx GJ, Schools EM, and Marin GB. Simulation of the decoking of an ethane cracker with a steam/air mixture. Chemical Engineering Science. 2006; 61(6): 1779-1789.
- [15] Muñoz Gandarillas AsE, Van Geem KM, Reyniers M-Fo, and Marin GB. Influence of the reactor material composition on coke formation during ethane steam cracking. Industrial & Engineering Chemistry Research. 2014; 53(15): 6358-6371.
- [16] Enqvist KJ, Oy BP, Torpe D, Noretyl A, and Middleton J. Dust Emissions during Cracking Furnace Decoking–Regulations Versus the Measured Performance. in 2008 Spring National Meeting. 2008.
- [17] Essenhigh RH, Misra MK, and Shaw DW. Ignition of coal particles: a review. Combustion and Flame. 1989; 77(1): 3-30.
- [18] Liu X, Xu M, Si J, Gu Y, Xiong C, and Yao H. Effect of sodium on the structure and reactivity of the chars formed under N2 and CO2 atmospheres. Energy & Fuels. 2011; 26(1): 185-192.
- [19] Su S, Song Y, Wang Y, Li T, Hu S, Xiang J, and Li C-Z. Effects of CO2 and heating rate on the characteristics of chars prepared in CO2 and N2 atmospheres. Fuel. 2015; 142: 243-249.
- [20] Xu J, Su S, Sun Z, Qing M, Xiong Z, Wang Y, Jiang L, Hu S, and Xiang J. Effects of steam and CO2 on the characteristics of chars during devolatilization in oxy-steam combustion process. Applied Energy. 2016; 182: 20-28.
- [21] Yi B-j, Zhang L-q, Yuan Q-x, Yan S-p, and Zheng C-g. The evolution of coal char structure under the oxy-fuel combustion containing high H<sub>2</sub>O. Fuel Processing Technology. 2016; 152: 294-302.
- [22] Bhunia S, Sadhukhan AK, and Gupta P. Modelling and experimental studies on oxy-fuel combustion of coarse size coal char. Fuel Processing Technology. 2017; 158: 73-84.
- [23] Maffei T, Khatami R, Pierucci S, Faravelli T, Ranzi E, and Levendis YA. Experimental and modeling study of single coal particle combustion in O2/N2 and oxy-fuel (O2/CO2) atmospheres. Combustion and Flame. 2013; 160(11): 2559-2572.
- [24] Sadhukhan AK, Gupta P, and Kumar Saha R. Modeling and experimental studies on combustion characteristics of porous coal char: Volume reaction model. International Journal of Chemical Kinetics. 2010; 42(5): 299-315.
- [25] Roy B and Bhattacharya S. Combustion of single char particles from Victorian brown coal under oxy-fuel fluidized bed conditions. Fuel. 2016; 165: 477-483.
- [26] Brix J, Navascués LG, Nielsen JB, Bonnek PL, Larsen HE, Clausen S, Glarborg P, and Jensen AD. Oxy-fuel combustion of millimeter-sized coal char: Particle temperatures and NO formation. Fuel. 2013; 106: 72-78.
- [27] Scala F and Chirone R. Fluidized bed combustion of single coal char particles at high CO<sub>2</sub> concentration. Chemical Engineering Journal. 2010; 165(3): 902-906.
- [28] Nalitham RV, Tarrer AR, Guin JA, and Curtis CW. Kinetics of coke oxidation from solvent refined coal hydrotreating catalysts. Industrial & Engineering Chemistry Process Design and Development. 1985; 24(1): 160-167.
- [29] Le Minh C, Jones RA, Craven IE, and Brown TC. Temperature-programmed oxidation of coke deposited on cracking catalysts: combustion mechanism dependence. Energy & fuels. 1997; 11(2): 463-469.
- [30] Sánchez B, Gross MS, Dalla Costa B, and Querini CA. Coke analysis by temperature-programmed oxidation: Morphology characterization. Applied Catalysis A: General. 2009; 364(1): 35-41.
- [31] Wang G-w, Zhang J-l, Shao J-g, Hui S, and Zuo H-b. Thermogravimetric analysis of coal char combustion kinetics. Journal of Iron and Steel Research, International. 2014; 21(10): 897-904.
- [32] Everson RC, Neomagus HW, van der Merwe GW, Koekemoer A, and Bunt JR. The properties of large coal particles and reaction kinetics of corresponding chars. Fuel. 2015; 140: 17-26.
- [33] Zhang L, Zou C, Wu D, Liu Y, and Zheng C. A study of coal chars combustion in O<sub>2</sub>/H<sub>2</sub>O mixtures by thermogravimetric analysis. Journal of Thermal Analysis and Calorimetry. 2016; 126(2): 995-1005.
- [34] McConnell J, Goshayeshi B, and Sutherland JC. An evaluation of the efficacy of various coal combustion models for predicting char burnout. Fuel. 2017; 201: 53-64.
- [35] Zeng X, Zheng S, Zhou H, Fang Q, and Lou C. Char burnout characteristics of five coals below and above ash flow temperature: TG, SEM, and EDS analysis. Applied Thermal Engineering. 2016; 103: 1156-1163.

- [36] Hull AS and Agarwal PK. Estimation of kinetic rate parameters for coal combustion from measurements of the ignition temperature. Fuel. 1998; 77(9-10): 1051-1058.
- [37] Cozzani V. Reactivity in oxygen and carbon dioxide of char formed in the pyrolysis of refusederived fuel. Industrial & engineering chemistry research. 2000; 39(4): 864-872.
- [38] Žajdlik R, Remiarová B, and Markoš J. Experimental and modelling investigations of single coal particle combustion. Chemical Engineering Science. 2001; 56(4): 1355-1361.
- [39] Struis R, von Scala C, Stucki S, and Prins R. Gasification reactivity of charcoal with CO<sub>2</sub>. Part I: Conversion and structural phenomena. Chemical Engineering Science. 2002; 57(17): 3581-3592.
- [40] Everson R, Neomagus H, and Kaitano R. The modeling of the combustion of high-ash coal-char particles suitable for pressurised fluidized bed combustion: shrinking reacted core model. Fuel. 2005; 84(9): 1136-1143.
- [41] Everson RC, Neomagus HW, and Njapha D. Kinetic analysis of non-isothermal thermogravimetric analyser results using a new method for the evaluation of the temperature integral and multi-heating rates. Fuel. 2006; 85(3): 418-422.
- [42] Yang H, Chen H, Ju F, Yan R, and Zhang S. Influence of pressure on coal pyrolysis and char gasification. Energy & Fuels. 2007; 21(6): 3165-3170.
- [43] Wu Y, Wu S, Gu J, and Gao J. Differences in physical properties and CO<sub>2</sub> gasification reactivity between coal char and petroleum coke. Process Safety and Environmental Protection. 2009; 87(5): 323-330.
- [44] Sommariva S, Maffei T, Migliavacca G, Faravelli T, and Ranzi E. A predictive multi-step kinetic model of coal devolatilization. Fuel. 2010; 89(2): 318-328.
- [45] Scala F and Chirone R. Combustion of single coal char particles under fluidized bed oxyfiring conditions. Industrial & Engineering Chemistry Research. 2010; 49(21): 11029-11036.
- [46] Karimi A, Semagina N, and Gray MR. Kinetics of catalytic steam gasification of bitumen coke. Fuel. 2011; 90(3): 1285-1291.
- [47] Hattingh BB, Everson RC, Neomagus HW, and Bunt JR. Assessing the catalytic effect of coal ash constituents on the CO2 gasification rate of high ash, South African coal. Fuel processing technology. 2011; 92(10): 2048-2054.
- [48] Mianowski A, Robak Z, Tomaszewicz M, and Stelmach S. The Boudouard–Bell reaction analysis under high pressure conditions. Journal of thermal analysis and calorimetry. 2012; 110(1): 93-102.
- [49] Senneca O and Cortese L. Kinetics of coal oxy-combustion by means of different experimental techniques. Fuel. 2012; 102: 751-759.
- [50] Nikrityuk PA, Gräbner M, Kestel M, and Meyer B. Numerical study of the influence of heterogeneous kinetics on the carbon consumption by oxidation of a single coal particle. Fuel. 2013; 114: 88-98.
- [51] Yuan L and Smith AC. Experimental study on CO and CO<sub>2</sub> emissions from spontaneous heating of coals at varying temperatures and O2 concentrations. Journal of loss prevention in the process industries. 2013; 26(6): 1321-1327.
- [52] Li P, Yu Q, Xie H, Qin Q, and Wang K. CO<sub>2</sub> gasification rate analysis of Datong coal using slag granules as heat carrier for heat recovery from blast furnace slag by using a chemical reaction. Energy & Fuels. 2013; 27(8): 4810-4817.
- [53] Kenarsari SD and Zheng Y. CO2 gasification of coal under concentrated thermal radiation: A numerical study. Fuel Processing Technology. 2014; 118: 218-227.
- [54] Huo W, Zhou Z, Wang F, and Yu G. Mechanism analysis and experimental verification of pore diffusion on coke and coal char gasification with CO<sub>2</sub>. Chemical Engineering Journal. 2014; 244: 227-233.
- [55] Gomez A and Mahinpey N. A new model to estimate CO<sub>2</sub> coal gasification kinetics based only on parent coal characterization properties. Applied Energy. 2015; 137: 126-133.
- [56] Gonzalo-Tirado C and Jiménez S. Detailed analysis of the CO oxidation chemistry around a coal char particle under conventional and oxy-fuel combustion conditions. Combustion and Flame. 2015; 162(2): 478-485.
- [57] Vorobiev N, Geier M, Schiemann M, and Scherer V. Experimentation for char combustion kinetics measurements: bias from char preparation. Fuel Processing Technology. 2016; 151: 155-165.
- [58] Engin B and Atakül H. Air and oxy-fuel combustion kinetics of low rank lignites. Journal of the Energy Institute. 2016.
- [59] Ju Y and Lee C-H. Evaluation of the energy efficiency of the shell coal gasification process by coal type. Energy Conversion and Management. 2017; 143: 123-136.

- [60] JIAO S-h, LIN X-q, GUO A-j, Kun C, WANG Z-x, TONG J-j, GENG Y-x, LI R-m, and LIU Q-h. Effect of characteristics of inferior residues on thermal coke induction periods. Journal of Fuel Chemistry and Technology. 2017; 45(2): 165-171.
- [61] Prabhakar A, Sadhukhan AK, Kamila B, and Gupta P. Modeling and Experimental Studies on CO<sub>2</sub> Gasification of Coarse Coal Char Particle. Energy & Fuels. 2017; 31(3): 2652-2662.
- [62] Fushimi C, Araki K, Yamaguchi Y, and Tsutsumi A. Effect of heating rate on steam gasification of biomass. 2. Thermogravimetric-mass spectrometric (TG-MS) analysis of gas evolution. Industrial & Engineering Chemistry Research. 2003; 42(17): 3929-3936.
- [63] Melgar A, Perez JF, Laget H, and Horillo A. Thermochemical equilibrium modelling of a gasifying process. Energy conversion and management. 2007; 48(1): 59-67.
- [64] Branca C and Di Blasi C. Combustion kinetics of secondary biomass chars in the kinetic regime. Energy & Fuels. 2010; 24(10): 5741-5750.
- [65] Yuan S, Chen X-I, Li J, and Wang F-c. CO2 gasification kinetics of biomass char derived from high-temperature rapid pyrolysis. Energy & Fuels. 2011; 25(5): 2314-2321.
- [66] Umeki K, Moilanen A, Gómez-Barea A, and Konttinen J. A model of biomass char gasification describing the change in catalytic activity of ash. Chemical engineering journal. 2012; 207: 616-624.
- [67] Kok MV and Özgür E. Thermal analysis and kinetics of biomass samples. Fuel processing technology. 2013; 106: 739-743.
- [68] Barisano D, Canneto G, Nanna F, Villone A, Alvino E, Carnevale M, and Pinto G. Production of gaseous carriers via biomass gasification for energy purposes. Energy Procedia. 2014; 45: 2-11.
- [69] Fatehi H and Bai X-S. Effect of pore size on the gasification of biomass char. Energy Procedia. 2015; 75: 779-785.
- [70] Salem AM and Paul MC. Advanced kinetic modelling of biomass gasification based on optimum height of the reduction zone. International Journal of Advances in Science, Engineering and Technology. 2016; 4(3 Sp2): 182-185.
- [71] Bates RB, Altantzis C, and Ghoniem AF. Modeling of biomass char gasification, combustion, and attrition kinetics in fluidized beds. Energy & Fuels. 2016; 30(1): 360-376.
- [72] Jeong HJ, Hwang IS, Park SS, and Hwang J. Investigation on co-gasification of coal and biomass in Shell gasifier by using a validated gasification model. Fuel. 2017; 196: 371-377.
- [73] Wielgosiński G, Łechtańska P, and Namiecińska O. Emission of some pollutants from biomass combustion in comparison to hard coal combustion. Journal of the Energy Institute. 2016.
- [74] Jayaraman K, Kok MV, and Gokalp I. Thermogravimetric and mass spectrometric (TG-MS) analysis and kinetics of coal-biomass blends. Renewable Energy. 2017; 101: 293-300.
- [75] Xu Q, Pang S, and Levi T. Reaction kinetics and producer gas compositions of steam gasification of coal and biomass blend chars, part 2: Mathematical modelling and model validation. Chemical Engineering Science. 2011; 66(10): 2232-2240.
- [76] Collina E, Lasagni M, Tettamanti M, and Pitea D. Kinetics of MSWI fly ash thermal degradation.
   2. Mechanism of native carbon gasification. Environmental science & technology. 2000; 34(1): 137-142.
- [77] Couto ND, Silva VB, and Rouboa A. Thermodynamic Evaluation of Portuguese municipal solid waste gasification. Journal of Cleaner Production. 2016; 139: 622-635.
- [78] Liu G, Liao Y, Guo S, Ma X, Zeng C, and Wu J. Thermal behavior and kinetics of municipal solid waste during pyrolysis and combustion process. Applied Thermal Engineering. 2016; 98: 400-408.
- [79] Smith I. The combustion rates of coal chars: a review. in Symposium (International) on combustion. 1982. Elsevier.
- [80] Sun Z-q, Wu J-h, and Zhang D. CO<sub>2</sub> and H<sub>2</sub>O Gasification Kinetics of a Coal Char in the Presence of Methane. Energy & Fuels. 2008; 22(4): 2160-2165.
- [81] Irfan MF, Usman MR, and Kusakabe K. Coal gasification in CO<sub>2</sub> atmosphere and its kinetics since 1948: a brief review. Energy. 2011; 36(1): 12-40.
- [82] Slavinskaya NA. Chemical kinetic modeling in coal gasification processes: An overview. GT2010-23362, ASME Turbo Expo 2010. 2010.
- [83] Lahijani P, Zainal ZA, Mohammadi M, and Mohamed AR. Conversion of the greenhouse gas CO2 to the fuel gas CO via the Boudouard reaction: A review. Renewable and Sustainable Energy Reviews. 2015; 41: 615-632.
- [84] Garcia-Nunez JA, Pelaez-Samaniego MR, Garcia-Perez ME, Fonts I, Abrego J, Westerhof RJ, and Garcia-Perez M. Historical Developments of Pyrolysis Reactors: A Review. Energy & Fuels. 2017; 31(6): 5751-5775.

- [85] Hower JC, Groppo JG, Graham UM, Ward CR, Kostova IJ, Maroto-Valer MM, and Dai S. Coalderived unburned carbons in fly ash: A review. International Journal of Coal Geology. 2017.
- [86] Mahamulkar S, Yin K, Agrawal PK, Davis RJ, Jones CW, Malek A, and Shibata H. Formation and oxidation/gasification of carbonaceous deposits: a review. Industrial & Engineering Chemistry Research. 2016; 55(37): 9760-9818.
- [87] Chhabra V, Shastri Y, and Bhattacharya S. Kinetics of Pyrolysis of Mixed Municipal Solid Waste-A Review. Procedia Environmental Sciences. 2016; 35: 513-527.
- [88] Creamer AE and Gao B. Carbon-based adsorbents for post combustion CO<sub>2</sub> capture: A critical review. Environmental science & technology. 2016; 50(14): 7276-7289.
- [89] Jaramillo J, Álvarez PM, and Gómez-Serrano V. Oxidation of activated carbon by dry and wet methods: Surface chemistry and textural modifications. Fuel Processing Technology. 2010; 91(11): 1768-1775.
- [90] Prakash N and Karunanithi T. Kinetic modeling in biomass pyrolysis–a review. Journal of Applied Sciences Research. 2008; 4(12): 1627-1636.
- [91] Ranzi E, Cuoci A, Faravelli T, Frassoldati A, Migliavacca G, Pierucci S, and Sommariva S. Chemical kinetics of biomass pyrolysis. Energy & Fuels. 2008; 22(6): 4292-4300.
- [92] Abuelnuor A, Wahid M, Hosseini SE, Saat A, Saqr KM, Sait HH, and Osman M. Characteristics of biomass in flameless combustion: A review. Renewable and Sustainable Energy Reviews. 2014; 33: 363-370.
- [93] Rosselló TM, Li J, and Lue L. Kinetic models for biomass pyrolysis. Archives of Industrial Biotechnology. 2016; 1(1).
- [94] Claude V, Courson C, Kohler M, and Lambert SpD. Overview and essentials of biomass gasification technologies and their catalytic cleaning methods. Energy & Fuels. 2016; 30(11): 8791-8814.
- [95] Murillo J, Biernacki J, Northrup S, and Mohammad A. Biomass pyrolysis kinetics: A review of molecular-scale modeling contributions. Brazilian Journal of Chemical Engineering. 2017; 34(1): 1-18.
- [96] Jelemenský Ľ, Markoš J, Žajdlík R, and Remiarová B. Modelling of Nonlinear Behaviour during Combustion of Single Coal Char Particle. Chemical Papers. 2000; 54(6b): 473-481.
- [97] Keskitalo TJ, Lipiäinen KJ, and Krause AOI. Kinetic modeling of coke oxidation of a ferrierite catalyst. Industrial & engineering chemistry research. 2006; 45(19): 6458-6467.
- [98] Gil MV, Casal D, Pevida C, Pis J, and Rubiera F. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. Bioresource Technology. 2010; 101(14): 5601-5608.
- [99] De Micco G, Nasjleti A, and Bohe A. Kinetics of the gasification of a Rio Turbio coal under different pyrolysis temperatures. Fuel. 2012; 95: 537-543.
- [100] Nakasaka Y, Tago T, Konno H, Okabe A, and Masuda T. Kinetic study for burning regeneration of coked MFI-type zeolite and numerical modeling for regeneration process in a fixed-bed reactor. Chemical engineering journal. 2012; 207: 368-376.
- [101] Li P, Yu Q, Qin Q, and Lei W. Kinetics of CO<sub>2</sub>/Coal gasification in molten blast furnace slag. Industrial & Engineering Chemistry Research. 2012; 51(49): 15872-15883.
- [102] Mandapati RN, Daggupati S, Mahajani SM, Aghalayam P, Sapru RK, Sharma RK, and Ganesh A. Experiments and kinetic modeling for CO<sub>2</sub> gasification of Indian coal chars in the context of underground coal gasification. Industrial & Engineering Chemistry Research. 2012; 51(46): 15041-15052.
- [103] Zhang Y, Wu J, Chang L, Wang J, Xue S, and Li Z. Kinetic and thermodynamic studies on the mechanism of low-temperature oxidation of coal: A case study of Shendong coal (China). International Journal of Coal Geology. 2013; 120: 41-49.
- [104] Jing X, Wang Z, Zhang Q, Yu Z, Li C, Huang J, and Fang Y. Evaluation of CO<sub>2</sub> gasification reactivity of different coal rank chars by physicochemical properties. Energy & fuels. 2013; 27(12): 7287-7293.
- [105] Veca E and Adrover A. Isothermal kinetics of char-coal gasification with pure CO 2. Fuel. 2014; 123: 151-157.
- [106] Urych B. Determination of kinetic parameters of coal pyrolysis to simulate the process of underground coal gasification (UCG). Journal of Sustainable Mining. 2014; 13(1): 3-9.
- [107] Nunes K and Marcílio N. Determination of kinetic parameters of oxy-fuel combustion of coal with a high ash content. Brazilian Journal of Chemical Engineering. 2015; 32(1): 211-223.
- [108] Ding L, Zhou Z, Huo W, and Yu G. Comparison of steam -gasification characteristics of coal char and petroleum coke char in drop tube furnace. Chinese Journal of Chemical Engineering. 2015; 23(7): 1214-1224.

- [109] Chen C, Zhang S, Xu K, Luo G, and Yao H. Experimental and modeling study of char gasification with mixtures of CO2 and H2O. Energy & Fuels. 2015; 30(3): 1628-1635.
- [110] Tanner J and Bhattacharya S. Kinetics of CO<sub>2</sub> and steam gasification of Victorian brown coal chars. Chemical Engineering Journal. 2016; 285: 331-340.
- [111] Czerski G, Zubek K, Grzywacz P, and Porada S. Effect of Char Preparation Conditions on Gasification in a Carbon Dioxide Atmosphere. Energy & Fuels. 2017; 31(1): 815-823.
- [112] Liu L, Cao Y, Liu Q, and Yang J. Experimental and kinetic studies of coal-CO<sub>2</sub> gasification in isothermal and pressurized conditions. RSC Advances. 2017; 7(4): 2193-2201.
- [113] Zhang Y, Cai W, and Xin F. Simulation and Optimization of Coil Decoking in Ethane Pyrolysis Furnace. Chemical Engineering Communications. 2009; 196(8): 950-968.
- [114] Žajdlík R, Markoš J, Jelemenský Ľ, and Remiarová B. Single coal char particle combustion in the carbon dioxide atmosphere. Chemical Papers. 2000; 54(6b): 467-472.
- [115] Lee S, Speight JG, and Loyalka SK, Handbook of alternative fuel technologies. 2014: crc Press.

To whom correspondence should be addressed Dr. Ahmad Azari, Faculty of Petroleum, Gas and Petrochemical Engineering (FPGPE), Persian Gulf University (PGU), P.O. Box 75169-13817, Bushehr, Iran, e-mail address: azari.ahmad@gmail.com; azari.ahmad@pqu.ac.ir

# Article

EVALUATION OF ASMARI RESERVOIR PROPERTIES VIA PETROPHYSICAL LOGS IN MANSOUR-ABAD OIL FIELD, SW OF IRAN

Hossein Tabatabaei\*, Reza Poursamad

Department of Petroleum Engineering, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran

Received December 10, 2018; Accepted January 15, 2019

#### Abstract

Determining petrophysical parameters and reservoir evaluation has special importance in the oil industry. The precise knowledge of these parameters allows the petroleum engineers to have the tools they need in a given field to study precisely the production stages and, with their knowledge, will be more capable of developing oilfields. In this study, two wells in Asmari reservoir in Mansour Abad oil field has been investigated, and reservoir properties such as porosity, shale volume, and water saturation have been calculated, and the volume of water and oil have been determined. All calculations, cross-plots, and logs diagrams are done via software Geolog version 6.7.1. Studies show that the Asmari Formation in this field has a low average shale volume. On the other hand, Asmari reservoir has good porosity, especially in the upper part (Zone 3), and porosity variations of the field are not high. Also, the use of the M-N plot indicates the prevalence of carbonate lithology. In addition, based on Thorium-Potassium cross-plots, the dominant clay minerals were identified as Illite and mixed layer.

Keywords: Porosity; shale volume; water saturation; Asmari formation; Mansour Abad oil field.

#### 1. Introduction

Today, the evaluation of reservoir rocks has special importance in the oil industry <sup>[1]</sup>. Because of the economic accumulation of oil along with factors such as source rock, oil migration, oil traps, and cap rocks, it is also needed for a suitable reservoir rock. Therefore, identification of potential reservoir rocks and the study and evaluation of their reservoir quality in exploratory basins is necessary <sup>[2]</sup>. Detailed geological and petrophysical information is needed to study the reservoir rocks accurately. Geological information is obtained from well logs, cores and drilling cuttings and general geological information of the region. The purpose of petro physical research is to study the quality of reservoir in different parts of the formation, zoning the reservoir to determine the most suitable zones for optimal use of the reservoir and more intelligent development of oilfields <sup>[3]</sup>. Determination of the type of lithology, the rate of total porosity, the rate of effective (useful) porosity, water saturation ( $S_w$ ) of the formation, hydrocarbons and the calculation of shale amount are the most important parameters that should be determined in petro physical evaluation to realize the quality of the reservoir <sup>[4]</sup>. The correct estimation of these parameters plays an effective role in reservoir modeling, and the success rate of many exploration, drilling, development and exploitation activities of oil and gas reservoirs depends on the estimation accuracy of these parameters <sup>[5]</sup>. In the oil industry, reservoir parameters are determined by two common and applied methods of core analysis as a direct method and well logging evaluation as indirect method [6-7]. In this study, via data of petrophysical logs, these objectives are considered in the Asmari Formation.

#### 2. Geological setting

Most Zagros oil fields are stretched anticlines generated as a result of Paleocene, Late Miocene, and Paleo-Pleistocene orogenesis, forming uplift zones of Lurestan in the north and



Fars Zone in the South <sup>[8]</sup>. The Dezful is embayment between these zones, with an area of 60,000 km<sup>2</sup>. The Mansour-Abad oil field is located at 10km SE of the Behbahan City and in the Mid of Dezful Embayment basin (Figure 1). The Mansour-Abad oil field is an elongated doubly-plunging anticlinal structure with dimension of 29 km length and 5 km width base in UGC map (Figure 2), and it is considered one of the important productive oil fields in the Oligocene-Lower Miocene carbonate horizons (Asmari Formation) and the Middle Cretaceous carbonate horizons (Sarvak Formation)<sup>[9]</sup>.

Figure 1. Location of Mansour Abad oil field in Dezful embayment, near the other oil fields, Southwest of Iran



Figure 2. Location of Wells No. 8 and 10 in UGC map of Mansour Abad oil field

## 3. Methodology

Recognition of lithology, calculation of shale volume (Vsh), total porosity (PHIT), effective porosity (PHIE) and water saturation ( $S_w$ ), are the most important parameters in the petrophysical evaluation, and these are necessary to determine the quality of the formation <sup>[7]</sup>. In this study, the raw data from two wells (Wells No.8 and 10) in Mansour Abad oil field Geolog ver. 6.7.1 software has been used to determine reservoir parameters affecting the reservation quality of Asmari formations.

## 4. Result and discussion

In this study, 2 wells (Wells No. 8 and 10) in Mansour Abad oilfield have been considered for petrophysical studies. These wells have almost complete information and logging data. The most important results of this research are as follows:

## 4.1. Shale volume calculation

There are various methods for calculating shale volume <sup>[10]</sup>. In some cases, only a log can be calculated, and in some cases, a combination of two or more logs can be used to calculate

shale volume (Table 1). Here, for more accuracy and removal of the effect of uranium, we use the available CGR data to calculate:

$$V_{sh} = \frac{CGR - CGR_{min}}{CGR_{max} - CGR_{min}}$$

Table 1. Shale volume in a different zone of Mansour Abad wells (well No. 8 and 10).

Vsh %- Well No.	Zone 1	Zone 2	Zone 3	Zone 4	Average of Shale volume
MA- 8	5.8	5.5	0.1	12.8	6.5
MA- 10	1	1.5	0	28.6	7.77

### 4.2. Type of clay minerals determination

Shale does not have fixed mineralogy. Among clay minerals, Illite is found more often than other minerals, and chlorite is abundant, while kaolinite is relatively rare <sup>[10]</sup>. We need a CGR logs to determine the type of clay minerals in different wells, and Thorium-Potassium crossplots (Th vs. K) is used [11]. As shown in Figures 3 and 4, clay minerals are dominant in both wells:



Well No. 10 25 neavy\_th 20 aolinit mont mixed illite 10

POTA - THOR Cross-Plot

(1)



Figure 3. Type of clay minerals determination in well No. 8, Mansour Abad oil field

Figure 4. Type of clay minerals determination in well No. 10, Mansour Abad oil field

#### 4.3. Porosity calculation

There are several methods for calculating porosity, depending on the type of logs available in each well. Porosity logs, i.e., neutron-density logs and sonic logs, are used to calculate porosity. Porosity can be obtained from a log or a combination of different logs [12]. In this study, the porosity calculation (Table 2) was performed using the Sonic logs (Equation 2) and the neutron-density logs (Equation 3). Base in Table 2, Zone 3 has a good porosity in this formation.

$$\phi_{sonic} = \frac{DT - DT_{ma}}{DT_{fl} - DT_{ma}}$$
(2)  
$$\phi_{ND} = \sqrt{\frac{\phi_N^2 + \phi_D^2}{2}}$$
(3)

ø% - Well No.	Zone 1	Zone 2	Zone 3	Zone 4	Average of porosity
MA- 8	8.7	10.2	14	10.3	10.80
MA- 10	8.4	10.9	14.5	9.3	10.77

Table 2. Calculation of porosity in a different zone of Mansour Abad wells (well No. 8 and 10).

#### 4.4. Lithology detection with M-N Plot

One of the main uses of well logging logs is lithological detection. There are several methods for determining the lithology that their application is dependent on the availability and type of lithological-sensitive logs. There are various cross-plots that combine two or three charts, suggest two or three different mineralogy, one of the most suitable are M-N cross-plots<sup>[13]</sup>.

Considering the complex lithology of Asmari reservoir in the studied field, a combination of different logs can be useful for lithology detection, the best way to use M-N cross-plot. This cross-plot is obtained by combining three neutron, density, and sonic porosity logs. In this graph, the parameter M is the integration of the sonic-density measurement, and the N is the cross-plot slope of the neutron-density. M and N are obtained according to the following equations and are drawn against each other <sup>[14]</sup>.

$$M = \left[\frac{\Delta t_f - \Delta t}{\rho_b - \rho_f}\right] \times 0.01$$
$$N = \frac{\phi_{Nf} - \phi_N}{\rho_b - \rho_f}$$

Based on cross-plots drawn from the two wells, and according to the color range of CGR chart, the dominant lithology of carbonate detected (In well 8 and 10, dolomite is more than calcite). Also, well no. 8 shows shales more than well no. 10 (Figure 5 and 6).



Figure 5. Type of lithology determination in well No. 8, Mansour Abad oil field



(4)

(5)

## 4.5. Water saturation calculation

There are different methods to calculate water saturation <sup>[15]</sup>. Among these methods, the Indonesian equation is more efficient in carbonate rocks. In this study, the Indonesian equation is used as follows [16]:

$$\frac{1}{R_t} = \left[\frac{\phi m}{a \times R_w}^{0.5} + \frac{V_{sh}^{(1-0.5 \times V_{sh})}}{R_{sh}^{0.5}}\right]^2 \times S_w^n$$

(6)

To enhance the accuracy of formation water saturation calculations, we calculate it by software using Indonesian and Simandoux methods <sup>[17]</sup>. The volume of water in each well can be obtained in this way as a result of these calculations as shown in Table 3.

Table 3. Average of Water saturation in Mansour Abad wells base on Simandoux and Indonesia method

Sw % - Well No.	SWSIM	SWINDO
MA- 8	0.453	0.450
MA- 10	0.425	0.442

## 4.6. Asmari reservoir zoning

Based on lithological and petrophysical characteristics, Asmari reservoir is zoned in studied wells (Figure 7):



Figure 7. Determination of 4 zone in wells No. 8 and 10, Mansour Abad oil field

## 4.6.1. Well No.8

In well No.8, the drilled section of Asmari Formation includes 255m layers of carbonate rock. The Asmari formation in this well zoned into 4 zone. Zone 1 (from 2528m-2537m), zone 2 (from 2537m- 2571m), zone 3 (from 2571m-2760m) and zone 4 (from 2760m-2783m). In each of zones, the porosity and water saturation are respectively, 14% and 0.33 (for zone 1), 10.2 and 0.47 (for zone 2), 8.7% and 0.57 (for zone 3) and 10.3 and 0.43 (for zone 4). According to petrophysical calculations, the useful thickness and the effective thickness ratio to total thickness for each zone are 3 and 0.19 (Zone 1), 8 and 0.23 (Zone 2), 37 and 0.33 (Zone 3), 6 and 0.26 (Zone 4). The best zone for reservoir condition in this well is, zone 3.

# 4.6.2. Well No.10

In well No.10, Asmari Formation is included from 426m layers of carbonate rock. The Asmari formation in this well zoned into 4 zones. Zone 1 (from 2465m-2477m), zone 2 (from 2477m- 2517m), zone 3 (from 2517m-2733m) and zone 4 (from 2733m-2891m). In each of zones, the porosity and water saturation are respectively, 14.5% and 0.35 (for zone 1), 10.9% and 0.44 (for zone 2), 8.4% and 0.51 (for zone 3) and 9.3 and 0.47 (for zone 4). According

to petrophysical calculations, the useful thickness and the effective thickness ratio to total thickness for each zone are 3.5 and 0.18 (Zone 1), 8 and 0.2 (Zone 2), 41 and 0.29 (Zone 3), 27 and 0.17 (Zone 4). The best zone for reservoir condition in this well is, zone 3.

## 5. Conclusion

Based on the analysis of well logs and calculation of petrophysical reservoir parameters, the results are as follows:

- Asmari Formation in this field has a low average shale volume and the upper part of this formation is important in production, the reservoir is made of clean lithology and the amount of shale in the lower parts of the formation is slightly higher. The low amount of shale is probably due to the sedimentation of the formation in an energetic environment.
- Well logs analysis shows that this reservoir has good porosity, especially in the upper part of the formation. Porosity variations are not high at the surface of the field, but due to the low amount of shale, we conclude that most of these porosity are effective. Proper porosity in this field can be affected by sedimentation.
- The lithology of Asmari Formation has been estimated using various methods such as M-N cross-plots. This methods indicate the predominance of carbonate lithology (calcite, dolomite).
- In this study, Indonesian and Simandoux equations have been used to calculate water saturation. Due to the low amount of shale, the values obtained from these equations are very close.
- Based on the thresholds defined for the separation of gross and net sections, the thickness of these segments has been calculated. Due to the amount of low shale and good porosity, almost all of the formation is good reservoir, but due to the amount of water saturation, the thickness of the produced zone varies in wells.
- According to the lithological and petrophysical characteristics of Asmari reservoir in the studied wells, this field is classified into 4 zones, and base in petrophysical parameter, Zone 3, is suitable for reservoir condition.
- Based on thorium-potassium cross-plot, in both wells the dominant clay minerals have been identified as Illite.

#### References

- [1] Darling T. Well Logging and formation evaluation. Gulf Professional Publishing 2005, Elsevier, 326 pages.
- [2] Pickett GR. Formation evaluation, unpublished lecture notes. Colorado School of Mines 1974, Golden, Co.
- [3] Rider MH. The Geological interpretation of well logs. Blackie, Technology & Engineering 1986, 175 pages.
- [4] Shazly TF, Ramadan MAM. 2011, Well logs application in determining the impact of mineral types and proportions on the reservoir performance of Bahariya formation of Bassel-1x well, western desert Egypt. Journal of American Science, 2011; 7(1): 498-505.
- [5] Tiab D, Donaldson CE. Petrophysics, theory and practice of measuring reservoir rock and fluid transport properties. Gulf Professional Publishing, Elsevier 2004, Second edition, 926 pages.
- [6] Serra O. Fundamentals of well-log interpretation. University of Paris 2009, 487 pages.
- [7] Poupon A, Leveaux J. Evaluation of water saturation in shaly formations. trans. SPWLA 12th Annual logging symposium 1971, O1-2.
- [8] Aghanabati SA. Geology of Iran. Geological survey and mineral exploration of Iran 2003, p 586.
- [9] Motiei H. Geology of Iran. The stratigraphy of Zagros. 5st ed. Tehran1993, Iran: Geological Survey of Iran.
- [10] Patchett G. An Investigation of Shale Conductivity, the Log Analyst, 1975; 16(6): 25.
- [11] Waxman MH. Smith LJ. Electrical conductivities in oil bearing shaly sands. SPE Journal of Petroleum Technology, 1968; Tans.95-120pp.
- [12] Hearst JR, Nelson PH, and Paillet FL. Well Logging for Physical Properties, John Willey and Sons 2000, Ltd., Chilchester.
- [13] Rezaee MR. Application of Well Log Analysis, A short Course for N.I.O.C, 1997.
- [14] Burke JA, Schmidt AW, and Campbell RL. The Litho/Porosity Cross Plot. Log Analyst, 1969; 10(6): 25.

- [15] Archie GE. The electrical resistivity log as an aid in determining some reservoir characteristics, Petroleum Transactions of AIME, 1942; 146: 54–62.
- [16] Timu, A. An Investigation of Permeability, Porosity, and Residual Water Saturation Rela-tionships. SPWLA 9th Ann. Log. Symp.1968, Paper J.
- [17] Simandoux P. Mesure électriques en milieu poreux, application a mesure des saturations en eau, Etude du Comportment des massifs Argileux. Supplementary Issue, Revue de I'Institut Francais du Petrol. 1963

To whom correspondence should be addressed: Dr. Hossein Tabatabaei, Department of Petroleum Engineering, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran

# Article

# **Open Access**

PIPE IN CLINATION EFFECTS ON HIGH VISCOSITY OIL-GAS TWO PHASE FLOW CHARACTERISTICS

Yahaya D. Baba<sup>1,4</sup> Archibong-Eso Archibong<sup>2,4</sup>, Aliyu M. Aliyu<sup>2,4</sup>, Okereke U. Ndubuisi<sup>1,4</sup>, Akinola S. Oluwole<sup>5</sup>, Wasiu A. Ayoola<sup>6</sup>

<sup>1</sup> Department of Chemical and Petroleum Engineering, Afe Babalola University, Ekiti State, Nigeria

<sup>2</sup> Department of Mechanical Engineering, Cross River University of Technology, Calabar, Nigeria

<sup>3</sup> Gas Turbine and Transmission Research Centre, Faculty of Engineering, University of Nottingham, UK

<sup>4</sup> Oil and Gas Engineering Centre, Cranfield University, United Kingdom

<sup>5</sup> Department of Electrical Electronics and Computer Engineering, Afe Babalola University, Ekiti State, Nigeria

<sup>6</sup> Department of Metallurgical & Materials Engineering, Afe Babalola University, Ekiti State, Nigeria

Received October 9, 2018; Accepted December 21, 2018

#### Abstract

There is a growing interest in the exploration of high viscous unconventional reserves attributable to its huge reserves amidst an increasing decline in low viscous conventional reserves. In this paper, the effects of upward pipe inclination and liquid viscosity on two phase flow characteristics have been carried out experimentally in a 0.0256m ID pipe inclined at an angle of 15°. Air and mineral oil were used as test fluid with oil viscosities ranging from 0.7-5.0 Pa.s. The superficial velocities of gas and liquid velocities were varied respectively from 0.3 to 10 m/s and 0.06 to 0.3 m/s. Electrical tomographic capacitance sensor readings and visual observations revealed four flow patterns. Two phase characteristics measured include pressure gradient, liquid holdup, and slug flow features, i.e. slug frequency and slug liquid holdup. Analysis of the pressure gradient exhibited a gradual increase with increasing superficial gas velocity at a constant superficial liquid velocity which steeped when the superficial liquid velocity was increased. A similar trend was observed for pressure gradient as the angle of inclination is increased.

Keywords: Pressure gradient; liquid holdup; Flow pattern; Liquid viscosity; and ECT.

#### 1. Introduction

In the petrochemical, geothermal and nuclear industries, gas-liquid two phase flow in pipes is the most occurring phenomenon. A lot of studies have been carried in the literature on low viscosity two phase flows. However, with the diminishing reserves of "conventional" light crude oil, increased production costs amidst increased world energy demand over the last decade, industrial interest has shifted to the production of the significantly and more abundant "unconventional" heavy crude oil attributable its increasing importance as a veritable energy source. In addition to the fact that it accounts for over two-thirds of the world total oil reserve.

The existing technologies for the extraction, processing, and transportation adopted for heavy oil is costly due to their natural composition (i.e., viscosity) thereby making their production expensive, difficult to transport and refine. This whole process is quite expensive when compared to conventional crude oil. However, with improvement in technology, this once costly energy source is quickly becoming a more viable alternative. Hence, there is the need to carry out a further investigation so as to enhance its further production at reduced cost. The exploration of this vast resource for easy production and transportation requires a good understanding of multiphase flow system for which the knowledge of the effect of fluid viscosity is of great importance. Two phase flow are expected to exhibit a significant behaviour in high viscosity oils when compared to low viscosity oil as many flow characteristics such as flow pattern, slug mixing zone, and bubble entrainment.

A lot of study addressing the effects of pipe inclination on two phase flow have been carried out for low viscosity liquid while a handful of such studies address the behaviour of two phase flow in medium viscosity oil. There is relatively little that has been done on liquid viscosity range above 0.5 Pa. s in addition to the effects of pipe inclination. This study will, therefore, focus on relatively higher liquid viscosity range (i.e., 0.7-5.0 Pa. s) thereby creating a new databank that could be used to improve the understanding of the hydrodynamics of high viscosity liquid. The existing studies on low and medium liquid viscosity effects on two phase flow characteristics in inclined pipes are presented below.

A comprehensive pioneer study on the effects of pipe inclination on two phase flow in 20 mm ID pipe was carried out by <sup>[1]</sup> using air and water as test fluids with the test fluids in 20 mm ID pipe at varying pipe inclinations. He reported that pressure gradients are significantly affected by angles of inclination. <sup>[2]</sup> later developed a prediction model for two phase flow in inclined pipeline noting that pressure drop is greatly affected by the liquid holdup in the slug unit. Correspondingly <sup>[3]</sup> conducted experiments using 0.0508 and 0.0629 m ID inclined pipe to study effects of inclination. The authors noted that liquid holdup was strongly affected by pipe angle of inclination. The study saw the development of one of the most used prediction tool for pressure gradient and liquid holdup in the petroleum industry.

Weisman and Kang <sup>[4]</sup> gave one of the most important works on flow patterns in inclined pipelines. Their experiments were conducted on test facilities with pipe internal diameters of 0.012, 0.025 and 0.051 m pipelines for which correlation for the transition of annular flow for all pipeline inclinations was proposed:

$$(Fr_{sg})(KV_{sg}) = 25 \left(\frac{V_{sg}}{V_{sl}}\right)^{0.625}$$
 (1)

Kutateladze number,  $KV_{sg}(=V_{sg}/[g(\rho_L - \rho_G)\sigma]^{0.25})$  and Froude number,  $Fr_{sg}(=V_{sg}^2/gD)$  are functions of the superficial gas velocity.

Transition to dispersed bubbly flow was given by:

$$\left[\frac{(-dP/dz)}{g(\rho_l - \rho_g)}\right]^{0.5} \left[\frac{\left[g(\rho_L - \rho_G)D^2\right]}{\sigma}\right]^{0.5} \ge 9.7$$

$$\tag{2}$$

-dP/dz is the frictional pressure gradient of the single phase liquid flow in the pipe and  $\sigma$  is the interfacial tension.

The transition to stratified-wavy flow was given by:

$$Fr_{g}^{0.5} = \left(V_{sg}/V_{sl}\right)^{1.1}$$
(3)

For the separated-intermittent transition, the correlation proposed was thus:

$$\frac{\sigma}{D^2(\rho_l - \rho_g)} \int_{0.20}^{0.20} \left[ \frac{[DG_G]}{\mu_G} \right]_{0.5}^{0.5} = 8 \left[ \frac{V_{sg}}{V_{sl}} \right]^{0.16}$$
(4)

Transition from bubbly to intermittent flow is given by:

$$\frac{V_{sg}^{2}}{gD} = 0.2 \left[\frac{V_{m}}{gD}\right]^{1.56} (1 - 0.65 \cos\theta)^{2}$$
(5)

 $\theta$  is the pipeline inclinaton from the horizontal.

g

Gomez<sup>[5]</sup> also proposed a correlation given below for liquid holdup in slug body by correlating numerous experimental data from a variety of pipe diameters and inclinations

$$E_{\rm s} = e^{-(0.45\theta + CRe)}$$
  $0 < \theta \le 90^{\circ}$  (6)

where  $\theta$  is the angle of inclination from the horizontal,  $C = 2.48 \times 10^{-6}$  and the Reynolds number, *Re* is defined as:

$$Re = \frac{\rho_L V_M D}{\mu_L} \tag{7}$$

Most recently, studies involving the use of medium viscosity oil have been investigated. Among these studies are those by <sup>[6]</sup> who investigated horizontal slug flow pressure drop models in viscous oils of range 0.48 Pa.s. They noted an enlarged intermittent flow region in the flow pattern map existed with increasing oil viscosity. Gokcal <sup>[7-8]</sup>, later investigated the effects of high viscosity liquids on two-phase oil-gas flow in horizontal and near horizontal pipes. They corroborated the findings of <sup>[6]</sup> which noted an enlarged intermittent flow region. Their investigation revealed huge discrepancies between experimental results and the model predictions. They concluded that an increase in oil viscosity enhances the intermittency of the flow. The experimental results were used to evaluate different flow pattern maps, models and twophase flow correlations.

Furthermore <sup>[9]</sup> experimentally studied inclination effects on flow characteristics of high viscosity oil/gas two-phase flow. The study in which 400 experimental tests were carried out using oil viscosity ranging from 0.181 to 0.585 in a 0.0508 m ID pipe for  $\pm 2^{\circ}$  angles of inclinations.

## 2. Experimental setup

#### 2.1. Test facility description and measurement procedure

The experimental setup used for this investigation as shown in the schematics presented in Figure 1 is comprised of the following core sections: the fluid (oil, air, and water) handling section, test measurement/observation section and the instrumentation and data acquisition section. The test facility consists of a 5.5 m long and 0.0254 m internal diameter pipe fabricated from Perspex material. The observation and measuring instruments were placed at a distance of at least 100 pipe diameters from the last injection point to ensure full development of flow. Injection points were installed upstream of the test section for oil, and water.

A progressive cavity pump (PCP) with a capacity of  $2.18 \text{m}^3/\text{hr.}$ , is used to pump water through the test facility. Water volumetric flow rate is metered using an electromagnetic meter manufactured by Endress+Hauser, Promag 50P50 D50, with a range of  $0 - 2.18 \text{ m}^3/\text{hr.}$  Water was injected vertically through a Tee-section upstream of the main test line about 70 pipe diameters from the viewing sections.

Oil was stored in a  $0.15 \text{ m}^3$  tank capacity manufactured from plastic material and insulated with fibres on the periphery. A variable speed PCP with maximum capacity,  $0.72 \text{ m}^3/\text{hr}$ , was used in pumping oil, Endress + Hausser's Promass 831 DN 50, a Coriolis flowmeter, with range,  $0 \sim 180 \text{ m}^3/\text{hr}$ , was used in oil metering. The flowmeter has three outputs; mass flowrate, density, and viscosity with a measurement accuracy of 0.1%, 0.5 kg/m-3 and 0.5%respectively. The HART output from the meter is 4-20mA is connected to a data acquisition system for data gathering. Two main unit operations equipment used in the flow loop include; separator and chillers.

The separator is a rectangular shaped tank with viewing windows to allow for liquid levels and separation process monitoring, and an internal partition having weir for overflow. The multiphase fluid enters the first partition of the separator where the viewing windows are located, initial separation by gravity takes place in this section, the denser phase settles at the bottom while the dense phase moves to the second section for further separation. A mixture of oil, water, sand, and air requires a residence time of at least 10-12 hours for complete separation into its component phases. On complete separation of the phases, oil is recovered and reused.

The temperature control system for oil is a refrigerated bath circulator manufactured by Thermal Fisher<sup>®</sup>. Copper coils submerged in the oil and water tank are connected to the circulator, by running cold or hot glycol in the coils at specific time intervals, the temperature of oil and water in the tank can be controlled based on heat transfer. The circulator temperature ranges from 0 to +50°C, with an accuracy of  $\pm$  0.01°C. To ensure the equitable temperature of the oil, a recirculation flow for about 30 minutes is carried out.

GE Druck static pressure transducers, PMP 1400, with pressure range 0-4 barg and accuracy 0.04% over the full scale is used to obtain the static pressure in the test section; they

are placed 2.17 m apart with the first of them 60D from the last injection point to ensure fully developed flows. A differential pressure transducer, Honeywell STD120, with minimum pressure drop measurement of 100 Pa and an accuracy of  $\pm 0.05\%$  is used to measure the differential pressure.

The temperature of the test fluids on the test section is measured by means of J-type thermal couples with an accuracy of  $\pm 0.1$  °C placed at different locations. Data acquired from the flowmeters, differential pressure transducers, pressure transducers, and temperature sensors are saved to a Desktop Computer using a Labview® version 8.6.1 based system.



Figure 1. Schematics of the 1 inch test facility

The system consists of a National Instruments (NI) USB-6210 connector board interfaces that output signals from the instrumentation using BNC coaxial cables and the desktop computer. Three Sony camcorders, DSCH9 with 16 megapixels, high definition, and 60GB HDD are used for video recordings during the test to aid visual observations. The test facility schematic is shown in Figure 1 above.

## 2.1.1. Electrical capacitance tomography (ECT)



Figure 2. ECT System; (1)-Computer System, (2)-ECT Sensors embedded in the pipe and (3)-Data Acquisition System

As part of this preliminary experimental investigation, a process tomography equipment; Electrical Capacitance Tomography (ECT) designed by Industrial Tomography Systems, ITS, Manchester, UK was used. This tomography equipment has the capability to instantaneously obtain, reconstruct and display factual information of phase distribution inside the pipe is comprised of 3 units: a capacitance sensor, a capacitance measuring unit and a control computer as depicted in Figure 2. The precept of this equipment is based on the permittivity difference of dielectric materials with

electrodes lined at the periphery of pipe, for detection of mixture permittivity.

## 2.1.2. ECT static calibration test

The calibration of the ECT sensors is done to establish a scale for its tomography display with different phases represented by a different code. In this experimental investigation, oil which has the highest density and permittivity is coded in red while air with lowest density and permittivity is coded in blue as shown in Figure 3 The test was carried out using the 3-inch sensor, air and mineral oil CYL680 at room temperature. Prior to calibration, the pipe housing with ECT sensors are carefully cleaned, and each electrode is connected to the acquisition box in a correct sequence. The low and high reference results are respectively obtained by taking a reading from the empty pipe and when the pipe section is completely filled with oil with an allowable time given to ensure that there are no small gas bubbles entrained in the liquid phase.



Figure 3. Tomographic images of liquid holdup

## 2.1.3. Viscosity measurements



Figure 4. Brookfield DV-I<sup>™</sup> prime viscometer





Figure 5. Comparison of oil viscosity measured and supplied by the manufacturer

Generally, the viscosity is termed as the measure of the resistance of a fluid to flow. It is the measure of the gradual fluid deformation by shear or tensile stress caused by internal friction of fluid molecules flowing at different velocities. Though the test liquid (CYL680) used for this investigation were specified by industrial manufacturers; it was necessary however to validate their claims before the commencement of experimental runs for the purpose of enabling viscosity variations with temperature for the test matrix. Measurement of the oil's viscosity using Brookfield DV-I<sup>™</sup> prime viscometer (see Figure 4) at different temperature was carried out in the laboratory and compared with the manufacturer's specifications data shown in Figure 5.

Mineral oil manufactured by Total with the following properties viscosity: 0.220 Pa·s@40°C, density: 918 kg/m<sup>3</sup> @15.6 °C, API Gravity: 27.67, interfacial tension@25°C 0.031 N/m was used as the liquid phase while air was used as the gas phase for this experiment. The liquid and gas superficial velocities were respectively varied from 0.06 m/s to 2.0 m/s, and 0.3 m/s to 12 m/s. The pipe angle inclination values were from 0-30°.
# 3. Results

This section describes the experimental runs conducted on the 1 inch 30 degrees inclined test facility for which results for the average liquid holdup, tomographic and stacked tomographic image from ECT, analysis of high speed video recordings used for flow patterns determination were presented. The liquid holdup from ECT was also used for Probability Mass Function (PMF) to aid flow regime identification. Liquid holdup, slug frequency, and pressure gradient results were also presented here.

# 3.1. Flow patterns classification and determination

Flow patterns play a very important role in two phase flows with each regime exhibiting certain hydrodynamic behaviour. To date, there is no uniform procedure for describing and classifying flow patterns as there are subjective to the researcher's observation. For the present study, the designation of flow pattern observed in the high viscous oil-gas test were an interpretation of visual observation via viewing the section on the flow line, and analysis of video recordings for this investigation, Slug, pseudo-slug, and the wavy annular flow were observed in the inclined section. However, it is worth noting that the wavy annular flow characterised by rolling waves as shown in Figure 6 was observed as the dominant flow pattern. It was also observed that for oil viscosity was lower than 3.0 Pa.s for all oil and gas superficial velocities considered for this study, wavy annular flow was the only flow pattern observed. The dominance of the wavy annular flow can be attributed to the effect of gravity and viscosity on the flow patterns, i.e. when a pipeline is inclined upwards, gravity forces acting on the oil causes a reduction in oil velocity.

At  $V_{so}$  of 0.2 m/s and  $V_{sg}$  value ranging from 0.3-3.0 m/s for oil viscosity above 3.5 Pa.s, slug flow pattern was observed. This flow pattern with the front end shape like a cap/bullet is characterized by the wavy interface between the gas and the liquid body (slug) which are relatively short and frequent. Increasing superficial gas velocity is responsible for the oil-gas interface's instability in the film region as a result of an increase in flow turbulence.

The wavy annular flow was observed when  $V_{sg}$  reached 5.0 m/s. The energy dissipated as a result of the increased energy along the flow results in large amplitude of waves at the oilgas interface with top wall of the pipe significantly wetted by oil such that bulk of the oil remained at the bottom of of the pipe and the gas continually swept the liquid at the interface to the top of the pipe with gas mainly flowing at the core.



Figure 6. Flow pattern map for oil-gas two phase flows 1-inch inclined test section

# 3.2. Liquid holdup

Figure 7 shows a plot of inclination effects on time averaged liquid holdup measurement obtained and plotted as a function of gas superficial velocity. As can be seen from the plot, there is a reduction in the measured liquid up with increasing gas superficial velocity credited to an increase in the input gas of content within the cross sectional area of the pipeline. Though the liquid holdup trend at a lower gas flow rate in the inclined pipe is higher when compared to that of horizontal pipe attributed to the effects of gravity and viscosity forces. The trend observed conforms to those reported by <sup>[9-10]</sup>.



Figure 7. Effects of inclination on liquid holdup plotted as a function of superficial gas velocity for different oil viscosities (a/b)

### 3.3. Pressure gradient

The pressure gradient is crucial two-phase flow parameter taken into consideration during pipeline design and for the determination of pumping power requirements. This experimental investigation has revealed its strong dependence on the observed flow patterns, input liquid and gas contents, fluid physical properties and pipeline geometry/orientation. Presented in Figure 8 is a plot of pressure gradient for different oil viscosities and input liquid content. Pressure gradient generally increases with an increase in viscosity, and this can be explained by the increased shear on the pipe walls owing to viscosity effects which enhance shear around the pipe walls. Correspondingly, the pressure was observed to increase with an increase in superficial gas velocity due to the fact that pressure gradient is directly proportional to the square of the flow velocity, an increase in the gas superficial velocity will increase the pressure gradient in the pipeline. A similar trend has been reported by <sup>[9]</sup> and <sup>[11].</sup> The initial slight decrease and in some cases slight increase at the lower superficial gas velocities is due to the competing effect of a reduction in pipe wall fouling by the input gas superficial velocity which acts to reduce the pressure drop by reducing the shear in flow and the increase in pressure gradient with an increase in flow mixture



Figure 8. Pressure gradients as a function of superficial gas velocity (a/b)

### 3.4. Slug frequency

Slug frequency according to <sup>[12]</sup> is defined as the number of slug units passing at a specific position along a flow line over a certain period of time and an important parameter that needs to be considered during engineering design of pipelines. Slug frequency in this study was estimated from time series plots of liquid holdup variations. Generally speaking, an ideal slug configuration is characterised by crests and troughs which are respectively an indication passage slug body and slug film region. Several investigators in this field have suggested a liquid holdup threshold of 0.75, others 0.7 in order to differentiate between passing liquid slug body and wavy liquid film. For this study, a liquid holdup average was observed as such a threshold based on the estimation of <sup>[12]</sup> was used as presented in equation 8.

$$H_{th} = \frac{1}{2} [Max(H_{th}) - Min(H_{th})]$$

(8)

where  $H_{th}$  liquid holdup obtained from ECT.

So as to examine the effect of inclination for a given range of gas superficial velocity at different superficial liquid velocity, slug frequency as a function of gas superficial velocity was plotted as shown in Figure 9. This plot shows a proportionate increase in slug frequency with increasing gas superficial velocity. The frequency reaches a maximum and then starts decreasing even though the superficial gas velocity continues increasing. An increase in slug formation however a point is reached when the gas phase becomes very dominant within the cross section of the pipe which translates into a reduction in the liquid holdup and hence slug frequency. This conforms to the findings of <sup>[10]</sup> and <sup>[13]</sup> for a low viscous fluid. Also, the variation of slug frequency relative superficial gas velocity increases with increasing superficial liquid velocity attributed to increased liquid content in the cross sectional area of the pipe as indicated plots below. On the contrary, slug frequency decreases with the inclination, and this can be attributed to intermittent flow region as the angle of inclination increases.



### 4. Conclusion

Two-phase experimental runs were conducted for high viscous liquid-gas flows in both horizontal and inclined pipe to study the effects of inclination and viscosity effects on two phase flow parameters such as flow pattern, pressure gradient, liquid hold up and slug frequency. For the flow configurations, three flow patterns were observed, i.e. slug, pseudo slug and wavy annular which were also observed to be the dominating flow pattern. Advance instrumentation (i.e. ECT) used for measurement provided good tomographic images for flow pattern characterization. Measured parameters revealed strong dependence fluid properties and angle of pipe inclination.

#### Nomenclature

Symbol	Denotes	Units	Greek letter		
A	Area	m²	$\mu$	Viscosity	Pa.s
С	Constant		Es	Liquid holdup	
ID	Internal pipe diameter	т	ho	Density	kg/m <sup>3</sup>
Fr	Froude number		$\Delta \rho /-dP/dz$	Density diffe- rence	
g	Acceleration due to gravity	m. s <sup>-2</sup>	au	Shear stress	Pa
L	length	т	Subscripts		
hG,L	Height	т	f	Film zone	
Νμ	Viscosity number		g	Gas phase	
HL	Holdup		1	Liquid phase	
Nf	Inverse viscosity number		т	Mixture phase	
Re	Reynolds number		S	Superficial	
Vм	Mixture Velocity	m/s	t	Translational	
Vsg	Superficial Gas Velocity	m/s			
Vsl	Superficial Liquid Velocity	m/s			
KVsG	Kutateladze number				
C	Mathe due suive steve interation				

*Si Wetted perimeter interface* 

#### References

- [1] Sevigny R. An Investigation of Isothermal, Coeurrent, Two-Fluid TwoPhase Flow in an Inclined Tube, PhD dissertation, University of Rochester, New York, USA, 1962.
- [2] Bonnecaze RH, Erskine W, and Greskovich EJ. Holdup and pressure drop for two phase slug flow in inclined pipes, AIChE J 1971; 17: 1109–1113.
- [3] Beggs DH, and Brill JP. A Study of Two-Phase Flow in Inclined Pipes, Journal of Petroleum Technology, 1973; 25: 607–617.
- [4] Weisman J, and Kang SY. Flow pattern transitions in vertical and upwardly inclined lines, Int. J. Multiph. Flow, 1981; 7: 271–291.
- [5] Gomez LE, Shoham O, and Taitel Y. Prediction of slug liquid holdup: Horizontal to upward vertical flow. Int. J. Multiph. Flow, 2000; 26: 517–521.
- [6] Colmenares J, Ortega P, Padrino J, and Trallero JL. Slug Flow Model for the Prediction of Pressure Drop for High Viscosity Oils in a Horizontal Pipeline, Proc. SPE Int. Therm. Oper. Heavy Oil Symp., 2001; Porlamar-Margarita Island, Venezuela.
- [7] Gokcal B, Wang Q, Zhang H.-Q. and Sarica C. Effects of High Oil Viscosity on Oil/Gas Flow Behavior in Horizontal Pipes, SPE Annu. Tech. Conf. Exhib. 2006; 24–27, San Antonnio-Texas, USA.
- [8] Gokcal B, Al-Sarkhi S, and Sarica C. Effects of high oil viscosity on drift velocity for upward inclined pipes, SPE Annu. Tech. Conf. Exhib. ATCE 2008, Sept. 21, 2008 - Sept. 24, 2008; 963– 975, Denver-Colorado, USA.
- [9] Jeyachandra BC, Sarica C, Zhang H, and Pereyra E. Effects of Inclination on Flow Characteristics of High Viscosity Oil/Gas Two- Phase Flow, in SPE Annual Technical Conference and Exhibition, 2012; San Antonio-Texas, USA.
- [10] Gokcal B. An Experimental and Theoretical Investigation of Slug Flow for High Oil Viscosity in Horizontal Pipes, University of Tulsa, PhD Thesis, 2008.
- [11] Gomez LE, Shoham O, and Taitel Y. Horizontal to Vertical Upward Flow, International Journal of Multiphase Flow, 2000; 26: 517-521.

- [12] Baba YD, Archibong AE, Aliyu AM, and Ameen AI. Slug frequency in high viscosity oil-gas twophase fl ow : Experiment and prediction, Flow Meas. Instrum., 2017; 54: 109–123.
- [13] Hernandez-Perez V, Abdulkadir M, and Azzopardi BJ. Slugging Frequency Correlation for Inclined Gas-liquid Flow, World Acad. Sci., Eng., 2010; 2: 44–51, 2010.

To whom correspondence should be addressed: Dr. Yahaya D. Baba, Department of Chemical and Petroleum Engineering, Afe Babalola University, Ekiti State, Nigeria