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Impact of Oak wood ageing on the heat release rate and the yield of carbon monoxide during fire

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ABSTRACT

The presented paper deals with the assessment of the impact of Oak wood ageing on the maximum and average heat release rate, average rate of mass loss and yield of carbon monoxide (CO), related to the sample mass loss and heat released. In research, there were analyzed the samples of Oak wood (*Quercus robur* L.) with dimensions of 100 x 100 x 20 mm. The samples consisted of Oak wood felled 5 years ago and 160 years ago. The absolute moisture content of the samples was 0 *wt*%. The heat release rate, the average rate of mass loss and the yield of CO have been measured on a cone calorimeter by the test procedures in accordance with ISO 5660-1:2002, with the density of heat flux of 20 and 30 kW m^{-2}. The results obtained show that with the Oak wood ageing the rate of heat release, the average rate of mass loss and yield of CO significantly decreases. The impact of Oak wood ageing on the decrease in heat release rate increases with increasing heat flux density. Conversely, the impact of ageing on the decrease in the yield of CO and average rate of mass loss decreases with increasing heat flux density.

Keywords: Cone calorimeter • Fire risk • Heat release rate • Oak wood • Yield of carbon monoxide • Wood ageing

1. Introduction

The most relevant part of the fire loading of the majority of buildings is made of wood and wood materials (wood in furniture, floors, windows, doors, roof trusses and other building components and structures). Wood, as each material is subject to ageing (chemical changes), which may, depending on the length of exposure and external factors, result in significant chemical changes, which can significantly contribute to a change in its fire parameters in certain circumstances. For objective assessment of fire risk of the structures, in which the wood several tens to hundreds years old represents a substantial part of the fire load, is therefore necessary to know the way how the key fire parameters of the wood are changing with its age.

Wood ageing is a process of change that takes place in the wood under the impact of constantly changing action of oxygen, moisture, temperature, UV radiation and biological agents [1-2]. This process results in a change in the chemical composition of wood [2-3].

Chemical changes during wood ageing, depend, in particular, on properties of the wood (chemical composition, the type and amount of accompanied substances, bulk density, surface treatment and possible chemical or modifying protection) and external conditions, in which the ageing process takes place. Among the external conditions which influence the chemical changes in wood most significantly belong in particular the type (state) of an environment (air, water or soil) affecting the wood, then temperature, humidity, electromagnetic radiation (its wavelength and in-

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tensity), the presence of various chemical substances, respectively their mixtures (e.g. sea salt) and presence of various biological agents (mold, fungi and insects) [4-8]. Significant impact on changes in wood during its ageing, under certain conditions, can also have the moisture content at the time of incorporation in the structure (although in most cases this does not show high variability). Effect of initial and final moisture content of wood to its selected properties is described in scientific work [9].

On selected chemical (or even physical) changes of wood the age can have the same effect as temperature increased, respectively increased temperature can accelerate the wood ageing. E.g. according to [10] the ten hours lasting exposure of Fir wood to temperature of 60 ° C causes the decrease of terpenes amount to approximately the same value as was reported in the 108 years old Fir wood, not subjected to thermal modification.

The fire parameters of virtually all temperate wood species are already known and described in several scientific papers, e.g. [11-13]. But, only a few scientific studies have focused on the exact assessment of changes of key fire parameters (heat release rate and yield of carbon monoxide) of wood and wood based materials due to their ageing. The aim of the presented paper is therefore to assess the impact of Oak wood ageing on the change of its key fire parameters (average and maximum heat release rate, yield of carbon monoxide and the average rate of mass loss due to the thermal loading).

2. Material and methods

In research were used the samples of Oak wood (*Quercus robur* L.) with dimensions of 100 x 100 x 20 mm. The samples were divided into two groups. The first group consisted of samples of Oak wood that were dried immediately after the felling to absolute moisture content of 12% and subsequently stored in laboratory conditions (temperature of 20 ± 1 ° C and relative humidity of 50 ± 5%) over 5 years. The second group consisted of Oak wood samples obtained from the wall roof beam of roof truss structure localized in Southern Slovakia (Levice district). The age of the wall beam of roof was 160 years. Before testing, the samples were dried to zero absolute moisture content at temperature of 103 ± 2 ° C. The average density of the first group of samples was 730 kg m^{-3} and the second group of samples of 692 kg m^{-3}.

The heat release rate, yield of carbon monoxide and the specific rate of mass loss of the samples were measured on a cone calorimeter by the test procedures in accordance with ISO 5660-1:2002 [14]. The samples were loaded with a heat flux density of 20 and 30 kW m^{-2} during the test.

3. Results and discussion

Rate of heat release and the specific rate of mass loss of samples tested is shown in Fig. 1. The maximum and average heat release rate and the yield of carbon monoxide illustrate Tab. 1.

The results obtained show that the ageing of Oak wood caused a considerable decrease of the maximum and the average rate of heat release during the test on a cone calorimeter. Due to ageing also the dependence of the maximum rate of heat release rate of the Oak wood on the density of an external heat flux was decreasing. A similar impact on the change of the maximum and the average rate of heat release has the thermal modification of wood. During the thermal modification, as well as in the ageing process, it comes to the partial degradation of thermally most unstable components that are under test conditions in a cone calorimeter decomposed to volatile flammable products in the phase of flame burning. The thermal decomposition of the most unstable components during ageing is the main cause of significant reductions in the maximum rate of heat release from a sample of 160 year old Oak wood. Assumption about the degradation of thermally most unstable samples during ageing of a sample is also supported by the results of scientific work [10], according to which the ten hours lasting exposure of Fir wood to temperature of 60 ° C is causing a decrease in the amount of terpenes to approximately the same value as in the 108 years old Fir wood that was not subjected to a thermal modification. Those conclusions are confirmed by the results of scientific work [15], according to which is the rate of thermal degradation of wood at temperatures below 100 ° C so low that there cannot be determined the lowest temperature at which the thermal degradation begins. Similar conclusions are also provided in the scientific work [16-18], according to which the chemical composition of wood, under conditions of increased humidity or decreased pressure, is also changing at temperatures below 100 °C. Cited results, together with here obtained data showed that in tested 160 years old Oak wood occurred chemical changes that were demonstrated by the decrease in average, and also the maximum rate of heat release. Impact on the average heat release rate was not as much significant as in the case of the maximum rate of heat release. Lower average rate of heat release in case of older wood was largely influenced by the duration of the test (30 minutes), therefore the results points out a lower burning rate of older wood, but not a lower total heat release.

The data in the Tab. 1 shows that in burning of 160 years old Oak wood is emitted less carbon monoxide than in the burning of the 5 year old Oak wood. Lower yield of CO from older wood is related to its lower average specific rate of mass loss (as is clear from Tab. 1). Higher average rate of mass loss of 5 years old wood was the cause of higher average equivalent ratio (between fuel and air), in which the combustion process took place and hence also higher CO yield. In addition to the average equivalent ratio also the other factors (mainly moisture of the samples) have influence on the yield of CO. In the this case, however, the moisture content of the sample did not have any impact on the CO yield, since all samples were to zero absolute moisture content dried before testing. Another reason for the lower yield of CO in case of 160 years old wood samples was the fact that there later occurred a flameless combustion (glowing), since in wood and wood based materials burning the most CO is released just at this stage of combustion.

The oak wood in age 160 years after felling showed better fire parameters despite lower density, while according to [19-21] the higher density value has a positive impact on the higher thermal resistance of wood and wood based materials.

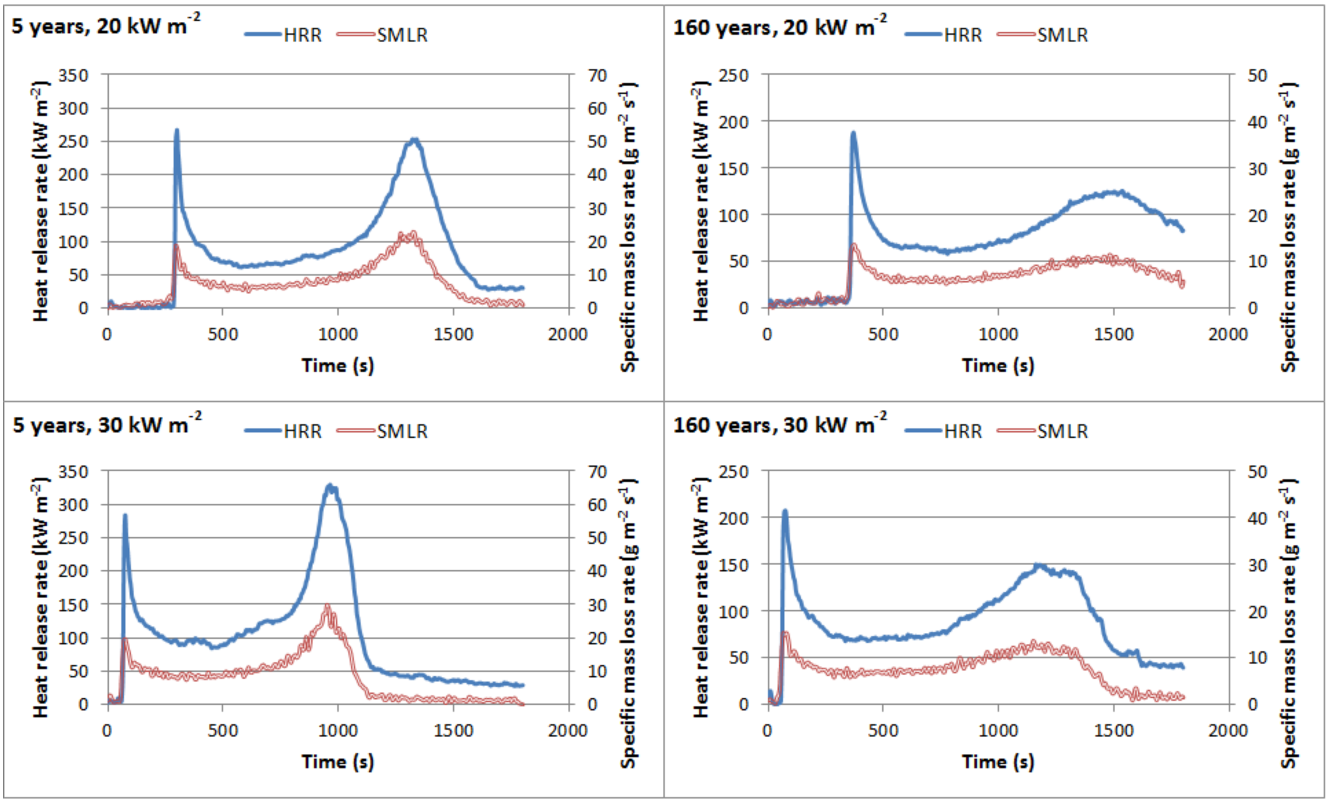

Figure 1 Heat release rate and specific mass loss rate of 5 years old and 160 years old Oak wood

Table 1 Impact of the age of Oak wood and heat flux density on selected fire parameters

Years (-)	Heat flux (kW m^{-2})	Peak HRR (kW m^{-2})	Average HRR (kW m^{-2})	Average SMLR (g m^{-2} s^{-1})	CO yield per mass loss (g kg^{-1})	CO yield per heat release (g MJ^{-1})
5	20	267	83	7.5	16.3	1.46
	30	330	101	8.1	21	1.32
160	20	188	74	6.6	10.3	0.98
	30	208	88	7.4	17.8	1.29

Note: HRR – Heat Release Rate, SMLR – Specific Mass Loss Rate

4. Conclusion

Increase in age of oak wood has a significant impact on the decrease of the maximum and average heat release rate, average rate of mass loss and carbon monoxide yield based on the mass loss of the sample and the heat released. Impact of Oak wood ageing on the decrease in the maximum and average heat release rate is increasing with increasing heat flux density. And conversely, the impact of ageing on the decrease in the average rate of mass loss and CO yield (related to the mass loss and heat released) is decreasing with increasing heat flux density. The dependency of those fire parameters of Oak wood on the age is significant enough to have an influence on the development of the internal dynamics of fire in the structure fire zone, of which a substantial part of the fire loading is formed by the materials tested.

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Toxic metals pollution due to industrial effluents released along Dombivali Industrial Belt of Mumbai, India

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ABSTRACT

The paper deals with understanding the pollution discharge scenario of the effluents released from different manufacturing industries situated along the Dombivali Industrial Belt of Mumbai, India. The study was performed from June, 2012 to May, 2013 to quantify the potentially toxic metals like Cu, Ni, Cr, Pb, Fe and Zn which are present in the industrial effluents. On the basis of average annual concentrations of the above toxic metals, it was observed that the effluents released from dyeing industries were having high concentration of Cu (22.53 mg L^{-1}) and Pb (13.14 mg L^{-1}), amounting to 21.95 % and 65.24 % of the total Cu and Pb respectively. The effluents from fine chemical industries were found to have high Fe (51.14 mg L^{-1}) and Zn (9.49 mg L^{-1}) which corresponds to 28.45 % and 26.65 % of the total Fe and Zn respectively. The concentration of Ni (1.10 mg L^{-1}) was maximum in the effluents discharged from textile industries, while Cr content (4.83 mg L^{-1}) was maximum in the effluents released from oil and surfactant industries. It was observed that the majority of the above mentioned average annual concentration of potentially toxic metals (except Ni) were above the maximum tolerable limit set for the discharge of industrial effluents in the inland surface water. It is feared that the existing situation if neglected may cause severe long term damage to the surrounding population as well as to the ecosystem.

Keywords: Industrial effluents • Toxic metals • Waste water • Dombivali Industrial Belt

1. Introduction

In India most of the industries are situated along the river banks for easy availability of water and also disposal of the wastes. These wastes often contain a wide range of contaminants such as petroleum hydrocarbons, chlorinated hydrocarbons and toxic metals, various acids, alkalis, dyes and other chemicals which greatly change the pH of water. The waste also includes detergents that create a mass of white foam in the river waters. All these chemicals are quite harmful or even fatally toxic to fish [1-3] and other aquatic populations [4]. It is found that one-third of the total water pollution in India comes in the form of industrial effluent discharge, solid wastes and other hazardous wastes. Most of these defaulting industries are petrochemical industries, sugar mills, distilleries, leather processing industries, paper mill, agrochemicals and pesticides manufacturing industries and pharmaceutical industries. For such industries the surface water is the main source for waste disposal. Untreated or allegedly treated effluents have increase the level of surface water pollution up to 20 times the safe level in 22 critically polluted areas of the country. It is found that almost all water bodies in India are polluted by industrial activities [5-7]. Although all industries in India function under the strict guidelines of the Central Pollution Control Board (CPCB) but still the environmental situation is far from satisfactory. Different norms and guidelines are given for all the industries depending upon their pollution potentials. Most major industries have treatment facilities for industrial effluents. But this is not the case with small scale industries, which cannot afford enormous investments in pollution control equipment as their profit margin is very slender. As a result there are sufficient evidences available related with the mismanagement of industrial wastes [8-15]. Consequently, at the end of each time period the pollution problem takes menacing concern. Some of the previous studies in the Arabian Sea have shown that the petroleum hydrocarbons ranged from 1.8 to 11.1 mg L^{-1} in water, 1.84 to 5.81 mg g^{-1} dry wt in sediments and 0.33 to 3.67 mg L^{-1} wet wt in fish [16],

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while the total DDT in zooplankton samples in the Arabian Sea [17] varied from 0.083 to 0.563 mg L^{-1}. The problem of water pollution has become still worse due to toxic metals. Although some trace metallic elements are important for proper functioning of biological systems, their deficiency or excess could lead to a number of disorders [18]. With the increased use of a wide variety of metals in industries and in our daily life, there is now a greater awareness of toxic metal pollution of the environment. The increasing trend in concentration of toxic metals in the aquatic environment has attracted considerable attention amongst ecologists globally during the last decades and has also begun to cause concern in most of the major industrialized cities. The major reason for the concern over the pollution due to toxic metals in aquatic environment is their non biodegradable nature, accumulative properties and long biological half lives. It is also difficult to remove them completely from the environment once they enter into it. Untreated or allegedly treated industrial effluents containing variable amounts of toxic metals have the potential to contaminate crops growing under such irrigation. Toxic metal pollution is an ever increasing problem of aquatic bodies. These metals not only pollute the water bodies but also pose a threat to the aquatic biota [1-2]. In India, incidence of toxic metal accumulation in fish, oysters, sediments and other components of aquatic ecosystems have been reported regularly [1-2]. These toxic metals have a marked effect on the aquatic flora and fauna which through biomagnification enter the food chain and ultimately affect the human beings as well. The increase in residue levels of toxic metal content in water, sediments and biota, will result in decreased productivity [19] and increase in health risk in case of human beings [20-25].

With the ever increasing pace of industrialization in Maharashtra state of India, the price of industrial development is heavily borne by most of aquatic bodies in the state. A report of the Central Pollution Control Board (CPCB) shows that the state has the largest number of polluted river water stretches in the country. Hence there is a need for extensive monitoring of discharged industrial effluents which has the potential of polluting the nearby water bodies like rivers or creeks. It is expected that such type of study will help to understand the trend in discharge pattern over a period of time which is an essential component of any pollution control management. The present study along the Dombivali Industrial Belt of Mumbai city of Indian state of Maharashtra was therefore carried out to understand the discharge scenario of toxic metals in the effluents released from different industrial sectors.

2. Experimental

2.1. Study area

The Dombivali industrial area was established by Maharashtra Industrial Development Corporation (*M.I.D.C*) in 1964. The industrial belt occupies an area of about 347.88 hectares, is located in south of Ulhas River and about 45.00 km from Mumbai international airport. There are about 30 highly polluting small/ medium/ large scale chemical industries located in this industrial belt. Quantity of industrial effluent generated in the industrial area is about 14 million litres per day, which is finally discharged into the creek through open drainages which was passing through residential area [26].

2.2. Climatic condition

Dombivali enjoys a tropical climate with mean annual temperature of 24.3 ^{o}C (min) to 32.9 ^{o}C (max). The hottest and driest part of the year is April-May, when temperature rises to 38.0 ^{o}C. The humidity is usually in the range of 58 to 84% and sea breeze in the evening hours is a blessing to combat the high temperature and humidity during summer months. The average southwest monsoon rainfall is in the range of 1850 mm to 2000 mm. The average annual rainfall in the region is the range from 1286 to 1233 mm [26].

2.3. Requirements

All the chemicals and reagents used for analysis were of analytical reagent grade. The glassware's used in the analysis were washed with distilled de-ionized water; the pipettes and burette were rinsed with the experimental solution before final use.

2.4. Industrial effluent sampling and preservation

The industrial waste water effluent samples were collected randomly twice in a month in morning, afternoon and evening session from different industries like pharmaceutical, textile, oil and surfactant, agrochemical, metallurgical, dyeing and fine chemical industries of Dombivali Industrial belt of Mumbai. For each type of industry three representative units were selected. The samples were collected every month from June, 2012 to May, 2013. Polyethylene bottles of 2.5 L were used to collect the grab water samples. The bottles were thoroughly cleaned with hydrochloric acid, washed with tape water to render free of acid, washed with distilled water twice, again rinsed with the water sample to be collected and then filled up the bottle with the sample leaving only a small air gap at the top. The sample bottles were finally sealed with paraffin wax.

2.5. Toxic metal analysis by AAS technique

Water samples (500 mL) were filtered using Whatman No. 41 (0.45µm pore size) filter paper for estimation of dissolved metal content. Filtrate (500 mL) was preserved with 2mL nitric acid to prevent the precipitation of metals. The samples were concentrated on a water bath depending on the suspected level of the metals [27]. The analysis for the majority of the potentially toxic metals like *Cu*, *Ni*, *Cr*, *Pb*, *Fe* and *Zn* was done by Perkin Elmer ASS-280 Flame Atomic Absorption Spectrophotometer. The calibration curves were prepared separately for all the metals by running different concentrations of standard solutions. A reagent blank sample was run throughout the method, and the blank readings were subtracted from the samples to correct for reagent impurities and other sources of errors from the environment. Average values of three replicates were calculated for each determination.

3. Results and discussion

The experimental data on toxic metal content in the industrial waste water effluent samples collected from pharmaceuticals, textile, oil & surfactants, agrochemical, metallurgical, dyeing and fine chemicals industries of Dombivali industrial belt of Mumbai, India is presented in Table 1 and the contribution of individual toxic metal from different industrial sector is presented in Figures 1-6.

Trace elements are those elements which are present in relatively low concentration of less than few mg L^{-1}. Among the special group of trace elements are the potentially toxic metals like *Cr*, *Ni*, *Zn*, *Cu*, *Pb* and *Fe* which are having the potential to create health hazards among humans, plants and other aquatic biological life. The *Cu* content was found to be minimum of 4.36 mg L^{-1} in the effluents released from pharmaceutical industries which account for 4.24 % of the total *Cu* content (Figure 1). The maximum *Cu* content was found to be 22.53 mg L^{-1} in the effluents released from dyeing industries, accounting for 21.95% of the total *Cu* content (Figure 1). The observed values were above the maximum permissible limit of 3.00 mg L^{-1} set for industrial effluents discharged in the inland surface water [28]. Similar results were obtained in our previous study performed along the Taloja Industrial belt of Mumbai, India in which the *Cu* contents in the effluents of pharmaceutical and dyeing industries were reported as 17.60 mg L^{-1} and 33.30 mg L^{-1} respectively [29]. Previous researchers have reported that as compared to other toxic metals (except *Hg*), *Cu* is highly toxic to most fishes, invertebrates and aquatic plants. The adverse effect of *Cu* is generally reflected by reduced growth and reproduction rate in both plants and animals. The *Cu* is observed to be chronic in the level of 0.02–0.2 mg L^{-1} [30]. It is observed that absorption of *Cu* by the aquatic plants is three times more in comparison to the plants growing on dry lands [31]. In plants, excess of *Cu* may cause root damage, the growth of roots get inhibited, development of number of short, brownish coloured secondary roots and also results in destroying the normal cell membrane structure. Since *Cu* is readily accumulated in organisms, its toxicity arises when the absorption rate is more than the excretion rate. Hence it is very important to keep check on the concentration levels of *Cu* in waste water.

The *Ni* content reported in the present investigation was found to vary between 0.34 mg L^{-1} in the effluents released from pharmaceutical industries, to 1.10 mg L^{-1} in the effluents released from textile industries (Table 1).Thus pharmaceutical industries contribute to 6.36% (minimum) of the total *Ni* contribution, while textile industries contribute to 20.70% (maximum) of the total *Ni* contribution (Figure 2). The observed values were within the maximum permissible limit of 3.00 mg L^{-1} set for industrial effluents discharged in the inland surface water [28]. The values obtained in the present investigation were very much below the values reported in our previous study performed along the Taloja Industrial Belt of Mumbai, India in which the *Ni* contents in the effluents of pharmaceutical and textile industries were reported as 33.60 mg L^{-1} and 20.20 mg L^{-1} respectively [29]. There are no reports on the impact of *Ni* on human health due to short-term exposure, however it may results in loss of body weight, damage to heart and liver as well may results in skin irritation on long time exposure [32]. A previous report also suggests the carcinogenic action of nickel carbonyl on rat [33].

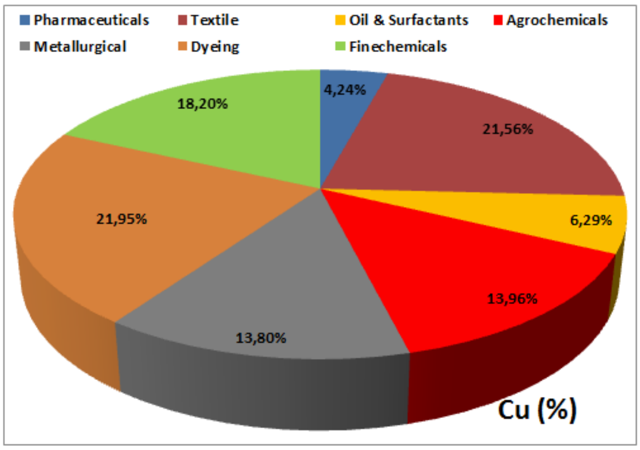

Figure 1 Percentage of *Cu* contributed out of total *Cu* released from the effluents of different industries located along the Dombivali Industrial Belt of Mumbai

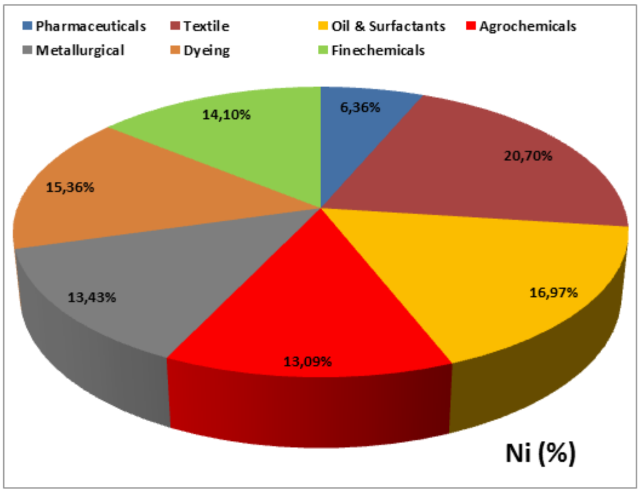

Figure 2 Percentage of *Ni* contributed out of total *Ni* released from the effluents of different industries located along the Dombivali Industrial Belt of Mumbai

The *Cr* content in the industrial effluent samples was found to be minimum of 0.51 mg L^{-1} in the effluents released from pharmaceutical industries which account for 3.22 % of the total *Cr* content (Figure 3). The maximum *Cr* content was found to be 4.83 mg L^{-1} in the effluents released from oil & Surfactant industries, accounting for 30.61 % of the total *Cr* content (Figure 3). The *Cr* content in the effluents released from fine chemicals and metallurgical industries was found to be 4.73 and 2.11 mg L^{-1} respectively (Table 1). The *Cr* content in the effluents released from oil & Surfactant, fine chemicals and metallurgical industries were above the maximum permissible limit of 2.00 mg L^{-1} set for industrial effluents discharged in the inland surface water [28]. Similar results were obtained in our previous study performed along the Taloja Industrial belt of Mumbai, India in which still higher *Cr* content (27.50 mg L^{-1}) exceeding the maximum permissible limit was reported in the effluents released fine chemical industries [29]. Among the invertebrates the acute toxicity of *Cr* was found to vary depending on the species of invertebrates [30]. The compounds of *Cr* are known to cause cancer in human beings [34] and the toxicity was found to increase at higher temperature. In plants the toxicity of *Cr* is indicated by small roots, narrow leaves with exhibition of reddish brown discoloration with small necrotic blotches [31].

The *Pb* content reported in the present investigation was found to vary between 0.36 mg L^{-1} in the effluents released from pharmaceutical industries, to 13.14 mg L^{-1} in the effluents released from dyeing industries (Table 1). Thus pharmaceutical industries contribute to 1.80% (minimum) of the total *Pb* content, while dyeing industries contribute to 65.24 % (maximum) of the total *Pb* content (Figure 4). The observed values were above the maximum permissible limit of 0.10 mg L^{-1} set for industrial effluents discharged in the inland surface water [28]. Similar results were obtained in our previous study performed along the Taloja Industrial Belt of Mumbai, India in which still higher *Pb* contents of 21.70 and 24.00 mg L^{-1} were reported in the effluents released from pharmaceutical and dyeing industries respectively [29]. In aquatic plants the acute toxicity of *Pb* is generally observed in the concentration range of 0.1–5.0 mg L^{-1}. *Pb* is observed to enhanced growth in plants at initial concentration while at the concentration of 5 mg L^{-1} onwards severe growth retardation, decolouration and morphological abnormalities are observed. High concentration of *Pb* will have negative influence on photosynthesis, respiration and other metabolic processes. In vertebrates, the acute toxicity of *Pb* is observed in the concentration of 0.1–10 mg L^{-1} [30]; still higher concentration of *Pb* will create threat to the fishes.

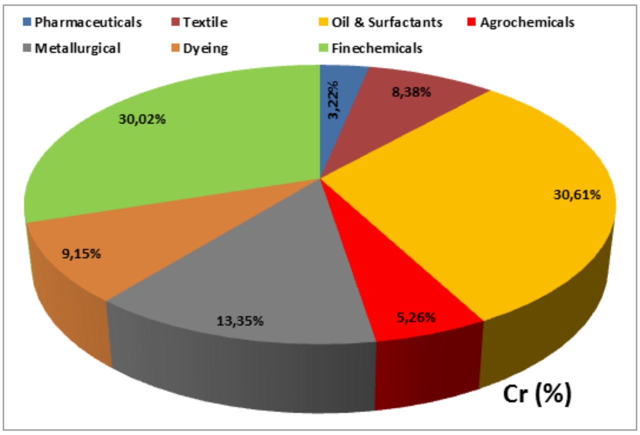

Figure 3 Percentage of *Cr* contributed out of total *Cr* released from the effluents of different industries located along the Dombivali Industrial Belt of Mumbai

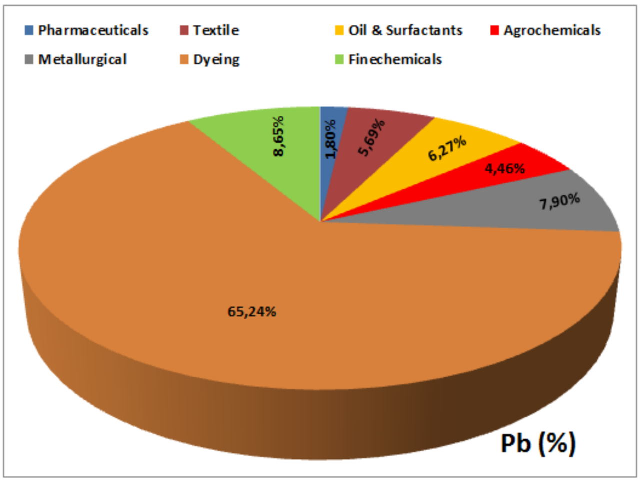

Figure 4 Percentage of *Pb* contributed out of total *Pb* released from the effluents of different industries located along the Dombivali Industrial Belt of Mumbai

The *Fe* content in the industrial effluent samples was found to be minimum of 7.68 mg L^{-1} in the effluents released from pharmaceutical industries which account for 4.27 % of the total *Fe* content (Figure 5). The maximum *Fe* content was found to be 51.14 mg L^{-1} in the effluents released from fine chemical industries, accounting for 28.45 % of the total *Fe* (Figure 5). Similar results were obtained in our previous study performed along the Taloja Industrial belt of Mumbai, India in which the *Fe* contents in the effluents released from pharmaceutical and fine chemical industries were found to be 10.40 mg L^{-1} and 7.70 mg L^{-1} respectively [29]. The observed level of *Fe* in the industrial effluents discharged from different industries were above the permissible limit of 3.00 mg L^{-1} set for effluents released in the inland surface water [28]. It is reported that since most of the organisms need *Fe* for their growth, its high concentration may result in hazard due to these pathogenic organisms [32].

Table 1 Toxic metal content in the industrial effluents released from Dombivali Industrial Belt of Mumbai, India (Average values for the assessment year from June, 2012 to May, 2013)

Toxic metals (mg L^{-1}) **Industries**	Cu	Ni	Cr	Pb	Fe	Zn
Pharmaceuticals	4.36	0.34	0.51	0.36	7.68	1.45
Textile	22.13	1.10	1.32	1.15	27.98	4.95
Oil & Surfactants	6.45	0.90	4.83	1.26	9.11	1.79
Agrochemicals	14.33	0.70	0.83	0.90	31.74	3.69
Metallurgical	14.17	0.72	2.11	1.59	14.40	4.85
Dyeing	22.53	0.82	1.44	13.14	37.70	9.39
Fine chemicals	18.68	0.75	4.73	1.74	51.14	9.49
Maximum Tolerable Limit (mg L^{-1})	3.00	3.00	2.00	0.10	3.00	5.00

The concentration of *Zn* reported in the present investigation was found to vary between 1.45 mg L^{-1} in the effluents released from pharmaceutical industries to 9.49 mg L^{-1} in the effluents released from fine chemical industries (Table 1). Thus pharmaceutical and fine chemical industrial effluents contribute to minimum of 4.08 % and maximum of 26.65% of the total *Zn* content (Figure 6). The *Zn* content in the effluents released from dyeing (9.39 mg L^{-1}) and fine chemical industries (9.49 mg L^{-1}) were above the maximum permissible limit of 5.00 mg L^{-1} set for industrial effluents discharged in the inland surface water [28]. The concentration levels of *Zn* obtained in the present investigation were less than that reported in our previous study performed along the Taloja Industrial belt of Mumbai, India in which still higher *Zn* contents of 25.4 and 26.8 mg L^{-1} were observed in the effluents released from fine chemicals and pharmaceutical industries respectively [29]. *Zn* in higher concentration may inhibit plant growth; result in necrosis and chlorosis.

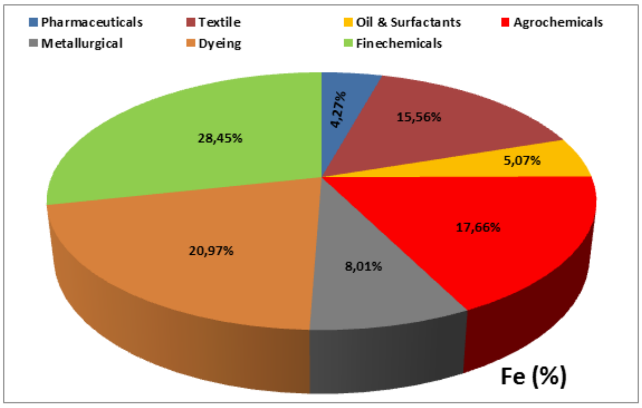

Figure 5 Percentage of *Fe* contributed out of total *Fe* released from the effluents of different industries located along the Dombivali Industrial Belt of Mumbai

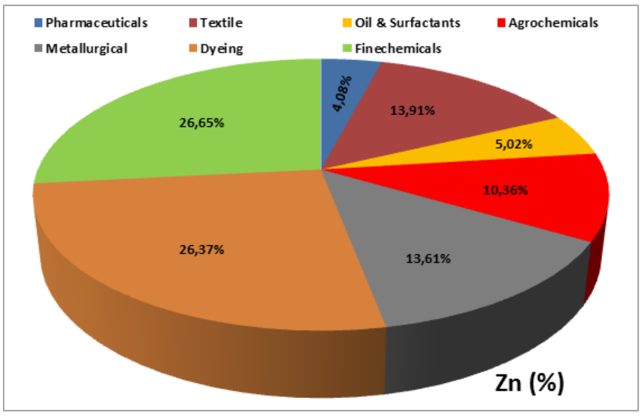

Figure 6 Percentage of *Zn* contributed out of total *Zn* released from the effluents of different industries located along the Dombivali Industrial Belt of Mumbai.

4. Conclusion

Currently, India is considered to be one of attractive destinations for investment in the world economy. Apart from its large domestic consumer base of one billion, it also offers a perfect setting for basing manufacturing and other services to serve the global market owing to its cheap labour. With the Indian Government making an all out effort to increase Foreign direct investment, huge investments can also be expected in manufacturing chemicals, pesticides, textiles and every imaginable product; increase in waste output and spread of toxic hotspots across the country. The growing ecosystem degradation due to rapid industrialization in India is particularly more damaging to the vast population of poor in the country who depend solely on ecosystem services, and are sometimes the principal factor causing poverty and social conflict. The time has come to move towards ecosystem specific discharge standards to maintain the health and productivity of natural resources on which the majority of Indians are dependent. The existing situation if mishandled can cause irreparable ecological harm in the long term well masked by short term economic prosperity due to extensive industrial growth.

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Investigation of activation energy of polypropylene composite thermooxidation by model-free methods

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ABSTRACT

This paper deals with thermogravimetric analysis of polypropylene composite that contains 45 % glass fibre. Samples of 1.06 g ± 0.01 g were thermally stressed by heating rates of 2.84 °C min^{-1}; 5.00 °C min^{-1}; 7.63 °C min^{-1} and 9.72 °C min^{-1} under air flow conditions. As a testing apparatus a hot air furnace was used in accordance with ISO 871:2010 and modified for macrothermogravimetric purposes. Activation energies by Kissinger, Flynn–Wall-Ozawa, Kissinger–Akahira-Sunose and Tang were calculated according to obtained results. The temperature of initial decomposition of the tested composite was determined 237 °C – 257 °C in dependence on the heating rate. Activation energy was rising along with the level of conversion until it reached a value around 106.35 kJ mol^{-1} according to Flynn-Wall-Ozava metnod, 100.82 kJ mol^{-1} by the Kissinger-Akahira-Sunose method and 101.25 kJ mol^{-1} by the Tang method. Calculation by the Kissinger method determined the activation energy value as 106.19 kJ mol^{-1}.

Keywords: Activation energy • Polypropylene • Thermooxidation • Thermal analysis

1. Introduction

These days polymeric materials are widely used due to their extensive level of adaptation achieved by various additives. Polypropylene is one of the most used synthetic polymers. Besides its use as a pure chemical substance, the purpose of nanocomposites is growing as well. Polypropylene just like other similar hydrocarbonates is flammable. Its limiting oxygen index is said to be between 17.4 % - 19 % [1-5].

Enescu et al. state that thermo-oxidative degradation of polypropylene takes place in one step with a small residue at the end of the test, about 1.7 wt% [4].

Its thermal decomposition area was established within temperature range from 300 °C to 450 °C by thermogravimetric analysis in argon atmosphere, whereby char formation was not detected. [6] Gesten et al. present the beginning pyrolysis temperature as 340°C – 391°C and end pyrolysis temperature as 481 °C – 494 °C while they determined the activation energy value to be 250 kJ mol^{-1} [7]. Activation energy while testing in nitrogen atmosphere is not constant but increases with conversion from 105 kJ mol^{-1} to 150 kJ mol^{-1} [8] and in case of decomposition of <500 nm particles the activation anergy was caculated by various methods resulting in 74 kJ mol^{-1} - 300 kJ mol^{-1} [9]. In oxygen atmosphere polypropylene self-ignited at ca. 260 °C. In air it was stable up to about 222 °C. The major products from its oxidative pyrolysis were acetaldehyde, acetone, butan-1-al, and an unsaturated C6 ketone [10]. Thermogravimetry characterized with the heating rate of 10 °C min^{-1} under static air conditions declared the decomposition range of pure polypropylene between 225.3 °C – 378.1 °C [5]. In case of oxidative pyrolysis the overall activation energy was 112.1 kJ mol^{-1} [11]. Chien and Kiang state its value as 67.2 kJ mol^{-1} [10] and for its pyrolysis oxidation products activation energy was declared 94 kJ mol^{-1} by Lyon et al. [12]. Combination of synthetic and natural polymers as composite materials is also an actual theme. Materials that contain thermoplastics and lignocellulosics as main ingredients are called wood plastic composites. Schwarzinger, Leidl and Pultz dealt with thermal decomposition of these materials in their work [13], as well as Arao et al. [6], Jeske et al. [14], or Gregorova et al. [15].

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2. Experimental

2.1. Testing apparatus

Scheme of the used testing apparatus is shown on Fig. 1. To achieve steady heating of the sample a hot air furnace according ISO 871:2010 (2) [16] was used. The mentioned furnace had been specially adjusted for thermogravimetric purposes. Chrebet et al. give a more detailed description of the adjustment in their work. [17]. Before testing each one of the samples was put in a metal crucible (3). The crucible was inserted in the furnace by a designated sample holder (1) in a way that ensures its connection with the scales through a cross connection rod (4).The weight of heated samples was continuously observed and noted in 10 s time intervals by a computer (6). Digital scopes were used for that purpose and placed under the furnace (5). Activation energies were determined by using four thermogravimetric observations for each sample with heating rates ranged from 2.84 °C min^{-1} to 9.72 °C min^{-1}. Constant air flow rate of 6 $dm^3\ min^{-1}$ was used as heating medium.

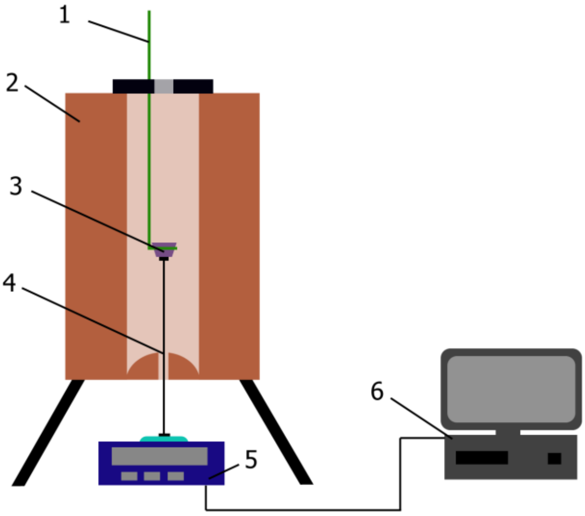

Figure 1 Scheme of the testing apparatus; 1 – designated sample holder, 2 – hot air furnace, 3 – crucible with a testing sample, 4 – cross connection rod, 5 – scales, 6 – computer [18]

2.2. Samples

A polypropylene composite available under commercial name Slovalen PH69 GF45 was tested. It is a modified homopolymer of polypropylene for injection moulding, chemically reinforced with 45% glass fibre and also containing a modifier of mechanical properties [19]. The material was situated in the testing room for three days where the temperature was 21 °C ± 3 °C. The overall weight for used samples was 1.06 g ± 0.01 g. Using an IKA bomb calorimeter we determined the heat of combustion where the average value for three observations resulted in 25.548 kJ g^{-1}.

2.3. Methods for determination of activation energy

One group of the methods used for determination of thermooxidation activation energies of materials are iso-conversional methods also known as model-free methods. These are based on usage of values obtained by thermogravimetric analysis which refer to constant levels of sample conversions. Conversion is in fact an actual weight loss quantity re-calculated as a total weight loss for a sample:

$$\alpha = \frac{m_p - m_a}{m_p - m_k} \tag{1}$$

where m_p is the initial mass of sample (g), m_a is the actual mass (g) and m_k is the mass at the end of observation (g). Model-free methods are based on the Arrhenius equation which form is as follows:

$$k = A.e^{\frac{-E_a}{RT}} \tag{2}$$

where k is a rate constant, A is an pre-exponential factor (min^{-1}), E_a is the activation energy (J mol^{-1}), R is the universal gas constant (8,314 J K^{-1} mol^{-1}) and T is the thermodynamic temperature (K).

Another basic assumption is that the reaction rate in solid phase depends on temperature and conversion level. In this case the kinetic equation can be:

$$\frac{d\alpha}{dt} = k(T)\,f(\alpha) \tag{3}$$

where α (-) is an unitless number that describes the conversion level of the sample and t is time (min).

The main kinetic equation then acquires the following form implied from equations 2 and 3:

$$\frac{d\alpha}{dt} = A.e^{\frac{-E_a}{RT}}.f(\alpha) \tag{4}$$

The Kissinger method represents a simple calculation method based on an assumption that with a change of heating rate the temperature of maximum weight loss rate changes too. Kissinger further assumed that the mentioned change depends only on the activation energy value of the given reaction [20]. The result is a simple value of activation energy. The adjusted form of this equation is nowadays presented as:

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_m} \tag{5}$$

where ϕ is the heating rate (K min^{-1}), T_m the temperature of maximum weight loss rate. The value of activation energy is calculated by this equation:

$$E_a = -aR \tag{6}$$

where a is the trend slope that represents dependence of the left side of equation (5) on an inverted value of T_m.

The Flynn-Wall-Ozawa (FWO) method represents the course of activation energy values for different conversion levels and it describes the chemical reactions kinetics by the equation:

$$\ln\phi = \ln\left(\frac{A_\alpha E_{a\alpha}}{Rg(\alpha)}\right) - 5.331 - 1.0516\frac{E_{a\alpha}}{RT_\alpha} \tag{7}$$

where $g(\alpha)$ is a constant for a given level of conversion and index α means that it is a value relative to a certain level of conversion [21-22].

The following equation can be used for activation energy calculation by such method:

$$E_{a\alpha} = -\frac{bR}{1.0516} \tag{8}$$

where b is the trend slope that represents dependence of natural logarithm of heating rates on an inverted value of T_m for given level of conversion.

Kissinger-Akahira-Sunose (KAS) method is similar to Kissinger method. In fact the point is in its application for different levels of conversion. Thermodynamic temperature for the maximum weight loss rate is replaced by thermodynamic temperature adequate for a certain level of conversion of the sample. The kinetic equation for this type of method is mostly presented as [20, 23]:

$$\ln\left(\frac{\phi}{T_\alpha^2}\right) = \ln\left(\frac{A_\alpha R}{E_{a\alpha} g(\alpha)}\right) - \frac{E_{a\alpha}}{RT_\alpha} \tag{9}$$

Determination of activation energy is similar to previous techniques that means reading the trend line slope that indicates dependence of the left side of equation (9) on an inverted value of T_α.

$$E_{a\alpha} = -cR \tag{10}$$

where c is the mentioned trend line slope.

Tang et al. in their work suggested an equation for the temperature integral in their work that has higher accuracy and reliability [24]. They acquired the following equation:

$$\ln\left[\frac{\phi}{T_\alpha^{1.89466100}}\right] = \left[\ln\frac{AE_{a\alpha}}{\beta R} + 3.63504095 - 1.89466100\ln E_{a\alpha}\right] - 1.00145033\frac{E_{a\alpha}}{RT_\alpha} \tag{11}$$

The activation energy can be calculated from a dependence of natural logarithm of the heating rate and $T_\alpha^{1.89466100}$ ratio on an inverted value of thermodynamic temperature relevant to a certain level of conversion.

$$E_{a\alpha} = -\frac{dR}{1.00145033} \tag{12}$$

where d represents the trend line slope.

3. Results and discussion

On the dependence curve of the conversion level versus temperature (Fig. 2) which was produced during sample heating we can note one major level of decomposition. Until the temperature reached 230 °C no markable weight loss changes were detected on the samples. It was observed the initial rise of conversion between 237 °C – 257 °C margins respectively to individual samples. Samples mass loss by 1 % occured at 253 °C for a heating rate of 2.84 °C min^{-1} and at 315 °C min^{-1} for 9.72 °C min^{-1}. The remaining two samples reached 99% of their initial mass between mentioned temperature intervals. Similar values are presented in literature for pure polypropylene whereby its temperature of decomposition for a heating rate of 10 °C min^{-1} is determined 258 °C and the temperature at 1 % weight loss 315 °C [1].

Further progress of the conversion versus temperature charts is vigorous whereby their slopes rise along with the temperature. At 384 °C – 428 °C most of the polypropylene is depleted and the conversion level attends a linear, almost constant course. Similar progress is shown by thermal degradation of polypropylene copolymer in oxidative atmosphere. When testing in nitrogen atmosphere there was no second segment on the TGA curve [14]. This phase can be therefore explained by reaction of the carbon residue with oxygen. Temperatures for initial weight loss are presented in Tab. 1 along with the maximum weight loss rate.

In Fig. 3 are displayed differential thermogravimetric curves that represent individual heating rates. They all have a similar constantly accelerating vigorous progress that flows into a skew maximum and consequently drops to a next to zero level.

The graph clarifies that with rising heating rates the maximum mass loss rate rises as well and moves towards higher temperatures. Temperature zones described besides dependence on Fig. 2 are visible also. Maximal mass loss rates obtained by thermogravimetry are shown in Tab. 1 along with other values that are characteristic for thermal analysis.

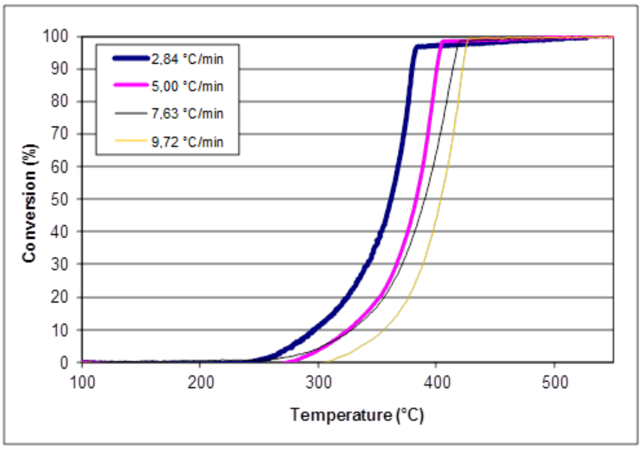

Figure 2 Dependence curve of the conversion level versus temperature during various heating rates

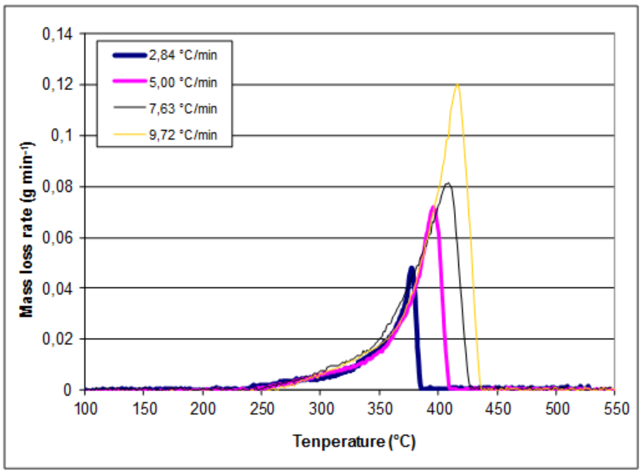

Figure 3 Dependence curve of sample mass loss versus temperature during various heating rates

From results obtained from thermogravimetric analysis activation energies were calculated by chosen non-isothermal or model-free methods. Kissinger, FWO, KAS and Tang methods were selected.

Eq. (6) was used for calculation by the Kissinger method. The trend line slope was determined according to dependence shown by Fig. 4. As can be seen on Tab. 2 the square of the correlation coefficient (R^2) scored 0.9986. This method allows us to determine only one activation energy value for the whole reaction process. In our case it was 106.19 kJ mol^{-1}.

Activation energies for individual conversions were calculated from equations (8), (10) and (12) by FWO, KAS and Tang methods. Graphical dependences inevitable for *b*, *c* and *d* trend line determinations are displayed in Fig. 5-7. For better lucidity only 0.1, 0.3, 0.5, 0.7 and 0.9 conversion dependences were displayed.

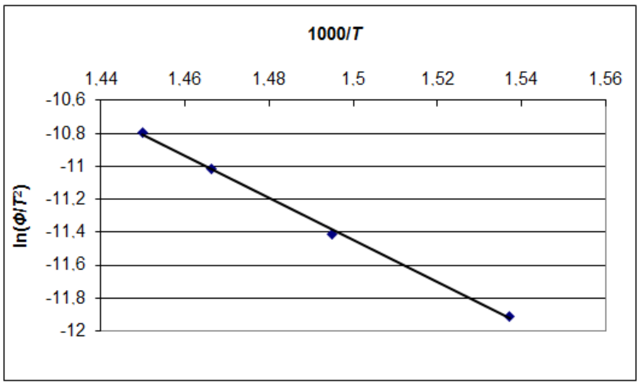

Figure 4 Kissinger plot of Slovalen

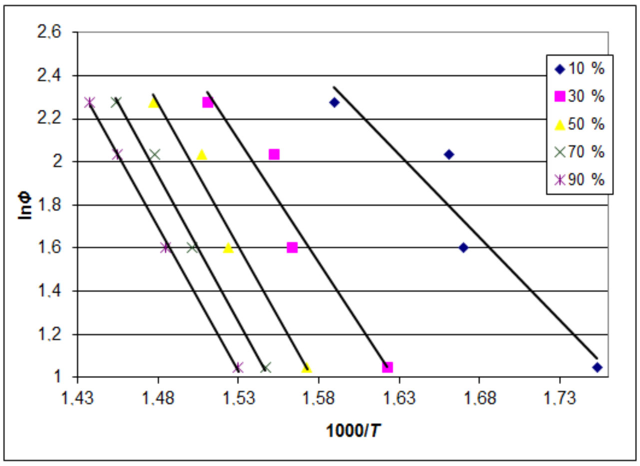

Figure 5 FWO plot of Slovalen for selected values of conversion

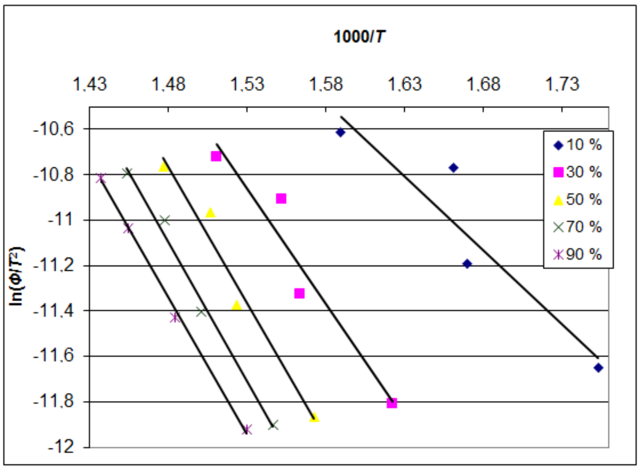

Figure 6 KAS plot of Slovalen for selected values of conversion

Obtained activation energies' results are shown in Tab. 1 and their progress for different conversion values is displayed in Fig. 8. In case of FWO, KAS and Tang method their progress is obviously similar. At the beginning, the activation energy value is rising along with conversion until reaching about 50 % mass loss of the samples. In this zone values of activation energies are ranged between 54.06 kJ mol^{-1} and 105.15 kJ mol^{-1}. In the second zone, the activation energy versus conversion dependence curve is almost constant although its slightly concave shape reaches maximum at 0.7 conversion value with activation energy ranged from 102.15 kJ mol^{-1} to 107.62 kJ mol^{-1}. Squares of correlation coefficient values now reach more than 96 %.

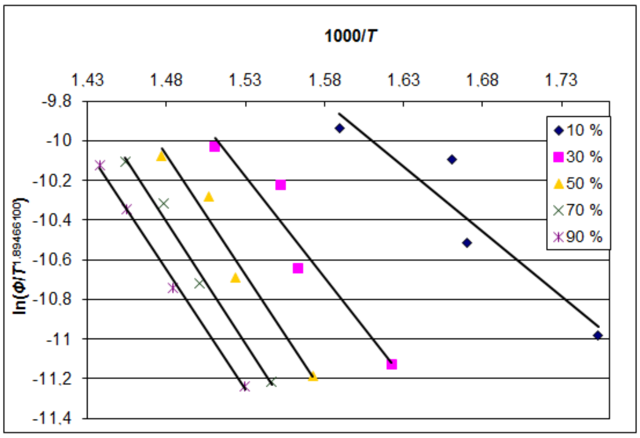

Figure 7 Tang plot of Slovalen for selected values of conversion

For the whole progress FWO curve values are higher than values for KAS and Tang curves which are almost the same. This similarity is caused by similarity between Eq. (9) and (11). The average activation energy of the leveled part of the graph showed on Fig. 8 presents 106.35 kJ mol^{-1}, 100.82 kJ mol^{-1} and 101.25 kJ mol^{-1} by FWO, KAS and Tang methods. These values are near to the value obtained by the Kissinger method.

These achieved results approximately correspond with activation energies of polypropylene stated by the already quoted literature.

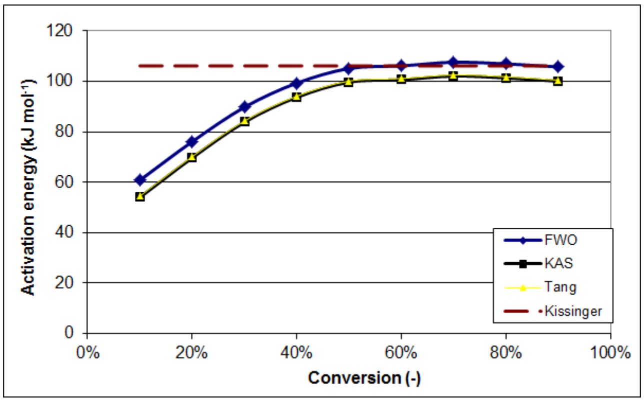

Figure 8 The activation energy as a function of conversion

Table 1 Characteristic values of thermal analysis

Heating rate (°C min^{-1})	T_i (°C)	T_{max} (°C)	T_t (°C)	m_{max} (mg min^{-1})
2.84	237	377	389	48.0
5.00	249	396	415	70.5
7.63	248	409	428	81.5
9.72	257	417	436	120.5

T_i: initial temperature of decomposition; T_{max}: maximal weight loss rate temperature; T_t: decomposition termination temperature; m_{max}: maximal weight loss rate.

Table 2 The activation energy and squares of correlation coefficients obtained by FWO, KAS, Tang and Kissinger method

	FWO		KAS		Tang		Kissinger	
α	E_a (kJ mol^{-1})	R^2	E_a (kJ mol^{-1})	R^2	E_a (kJ mol^{-1})	R^2	E_a (kJ mol^{-1})	R^2
0.1	60.84	0.9095	54.06	0.8768	54.50	0.8789		
0.2	76.12	0.9292	69.73	0.9084	70.17	0.9097		
0.3	89.81	0.9431	83.88	0.9287	84.31	0.9296		
0.4	99.34	0.9562	93.73	0.9461	94.17	0.9467		
0.5	105.15	0.9727	99.72	0.9666	100.15	0.967	106.19	0.9986
0.6	106.19	0.983	100.72	0.9792	101.15	0.9794		
0.7	107.62	0.9913	102.15	0.9894	102.58	0.9895		
0.8	107.01	0.9971	101.43	0.9965	101.87	0.9965		
0.9	105.78	0.998	100.08	0.9976	100.53	0.9976		

4. Conclusion

This work presents results of thermogravimetric analysis of composite material based on polypropylene that contains 45 wt% glass fibers. Sample decomposition took place in first major step followed by the second almost unnoticeable one. The initial decomposition temperature was established between 237 °C - 257 °C. With rising heating rate the maximal weight loss rate was rising also and moving towards higher temperatures at the same time.

Results obtained by thermogravimetric analysis were used for activation energy calculation by non-isothermal, model-free methods. Kissinger, FWO, KAS and Tang methods were chosen. As the Kissinger method only uses maximal weight loss rate temperature for calculations the result is only one value for the entire reaction progress. In case of the used samples it was rated 106.19 kJ mol^{-1}. The rest of the methods allow us to create activation energy versus level of conversion dependence graph. Based on its progress we can state that at first the activation energy rises until it stabilizes approximately at 50 % of the sample weight. In this stabilized state the values were between 99.76 kJ mol^{-1} and 107.62 kJ mol^{-1}. For the whole progress of activation energy versus conversion dependence we can claim that by FWO method slightly higher results were obtained in comparison with KAS and Tang methods which from mathematical point of view are very alike.

Acknowledgements

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Emission of pollutants from torrefaction of wood

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ABSTRACT

The torrefaction of biomass is carried out in order to obtain homogenous material with a low water content. This process can also be called mild pyrolysis. The paper focuses upon an experimental study of emissions released in the torrefaction process of deciduous wood types beech (*Fagus sylvatica*) and linden (*Tilia cordata*). Torrefaction was carried out in a reactor from Parr Instrument Company, USA. The reactor was heated to a temperature of 300ºC which was maintained for three hours. Concentrations of pollutants CO, CO_2 and CH_4 were ascertained in the emissions. For beech, concentrations of CO and CH_4 increased with temperature up to a concentration of 12500 ppm and 2.59% at a temperature of 300ºC. For linden, concentrations of CO_2 decreased with increasing temperature to 2.63% at a temperature of 300ºC.

Keywords: Emissions • Pyrolysis • Torrefaction • Wood

1. Introduction

Due to worldwide excessive use of fossil fuels and related global warming, the use of renewable resources is become more and more interesting. From a CO_2 viewpoint, the CO_2 process in the burning of biomass is neutral. Biomass fuel has worse properties in comparison with fossil fuels. Unlike fossil fuels, they have a low bulk density, a high humidity content and low calorific value. These biomass properties therefore cause technical problems when processing biomass and such operations are then less competitive. Therefore, before using as energy, various methods of pre-preparation of biomass are recommended. One method is the torrefaction of biomass.

Torrefaction is the thermal processing of biomass for 10 - 60 minutes at a medium-high temperature of 200 - 300ºC at atmospheric pressure, without the access of oxygen. It is carried out in order to obtain homogenous material with a low water content. The whole process consists of drying, torrefaction and cooling phases. This process can also be called mild pyrolysis during which approximately 70% of the original weight and 80 to 90% of the original energy content remains [1-2].

During torrefaction, we distinguish between three temperature phases depending upon time. The torrefaction reaction time is defined as the sum of the heating time from 200ºC to the required temperature, the time for which torrefaction temperature is maintained (torrefaction phase of approximately 30 minutes) and the time necessary for cooling from torrefaction temperature to 200ºC [3-4].

During the pyrolytic process, we may observe a range of processes depending upon the achieved temperature. For simplification, we may divide these processes into three temperature intervals:

1. Within a temperature of up to 200 ºC, there is a process of drying and the creation of water vapour via the physical separation of water. These processes are strongly endothermic.
2. Within temperatures from 200 to 500 ºC, there is an area of so called dry distillation. Here there is a major separation of side chains from high molecular organic compounds and transformation of macromolecular structures into gas and liquid organic products and solid carbon.
3. In the gas creation phase within 500 to 1200 ºC, products created by dry distillation are further split and transformed. Then, stable gases such as H_2, CO, CO_2 and CH_4 are created from the solid carbon as well as from liquid organic compounds.

The aim of the work is an experimental study of emissions released in the low temperature pyrolysis process of deciduous wood types beech *(Fagus sylvatica)* and linden *(Tilia cordata).*

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2. Material and methods

The torrefaction of two types of deciduous wood, linden and beech, was carried out under laboratory conditions using a 4570/80 reactor from Parr Instrument Company, USA. Twenty blocks with dimensions of 8 x 2 x 2 cm of the appropriate wood type, with a total mass of approximately 380 g, were placed into the reactor. The material was placed in the vessel in the shape of a grid so a sensor for measuring temperatures could be placed in the centre.

Torrefaction took place without air access and the temperature in the reactor was gradually increased to 320 ºC. The temperature in the reactor was read from the display on the reactor's control unit. After fitting and sealing the reactor head, the gas was transferred via an outlet to apparatus consisting of Erlenmayer glass flasks through a closing valve and a high pressure hose.

Pach et al. [2] observed the creation of emissions from Birch, Pine and Bagasse in an N_2 inert atmosphere at temperatures of 230 °C, 250 °C and 280 °C. This temperature was kept for various time intervals (1, 2 or 3 hours). The gas was extracted through a cooler where the tar and water condensed. The gas was then led through a cotton filter through a gas gauge and was gathered in collection sacks for gas. The gas content was analysed using gas chromatography for CO_2, CO, N_2, CH_4, and C_2, carbohydrates (ethane, ethene and acetylene) content.

In our case, the first Erlenmayer flask was filled with water, the second contained a 1M HCl solution and the third contained 1M $NaHCO_3$. After the apparatus, there was a filter for trapping humidity and a three-way valve via which it was possible to redirect the gas mixture to individual measuring sensors.

The following types of sensors were used for measuring the gas components from low temperature pyrolysis:

- Detcon Model IR-700-CO_2 sensor designed to detect and monitor carbon dioxide gas in air using miniature non-dispersive Infrared Optical (NDIR) sensor technology. The sensor is calibrated by the producer for measuring a concentration range from 0 to 5% CO_2.
- An MQ7 semiconductor sensor for measuring CO, by Sandbox Electronics. The sensor is calibrated by the producer for measuring a CO concentration range from 10 to 10000 ppm.
- A MadIR D01 is a single-chamber infrared sensor designed for continuous measurement of methane (CH_4) in gas mixtures. The range of measuring the methane concentration in gas mixtures is 0 - 5% of CH_4.

3. Results and discussion

Concentrations of the pollutants CO, CH_4 and CO_2 were measured at temperatures of 230, 250, 280 and 300 °C. Concentrations of pollutants found for beech and linden at individual temperatures are shown on Fig. 1 to 3.

Concentrations of the pollutants CO, CH_4 and CO_2 were measured at temperatures of 230, 250, 280 and 300 °C. Concentrations of pollutants found for beech and linden at individual temperatures are shown on Fig. 1 to 3.

Concentrations of CO and CH_4 increased with increasing temperature (Fig. 1 and Fig. 3) in both tested types of wood. Fig. 2 shows that, on the other hand, CO_2 concentration decreased with increasing temperature. The highest concentration of CO - 12500 ppm - was found during torrefaction of beech at 300ºC and the lowest for linden - 6700 ppm.

The intensity in the creation of pyrolysis gases and their development during low temperature pyrolysis differed for individual types of wood. The development of pyrolysis gases as well as the intensity of their development could also be monitored visually in Erlenmayer glass flasks.

As shown when measuring the concentration of individual gases, the semiconductor sensors are not the suitable for monitoring gas components of low temperature pyrolysis, where often the semiconductor sensor range was exceeded and its saturation took place at low temperature in the reactor during the drying phase. Exceeding the range of a particular type of sensor at a certain temperature depended upon the type of wood used and also perhaps upon its humidity.

Kiel [5] states the following content of gas emissions from the torrefaction of willow in a nitrogen atmosphere at 260 ºC for 32 minutes: CO 0.1%, CO_2 3.3%, H_2O 89.3%, acetic acid 4.8%, furfural 0.2%, methanol 1.2%, formic acid 0.1%, remainder (CH_4, C_xH_y, toluene and benzene) 1%. Analysis of the content of emissions was carried out using gas chromatography.

Pach et al. [2] monitored emissions from the torrefaction of birch in a nitrogen atmosphere at various temperatures and various torrefaction times. The greatest amount of CH_4, C_2 and CO_2 was created at 280 °C and two hours of torrefaction, which were 0.3%, 0.13% and 24.5%. On the other hand, the greatest amount of CO_2 was created at 250 ºC and a torrefaction time of one hour, which was 81.2%.

To date, there have only been a few studies on the influence of pressure upon the creation of gas emissions. Mok and Antal [6] investigated pyrolysis at a pressure of 0.6 MPa and at a temperature of 500 ºC. They discovered that an increase in pressure results in an increase in the yields of biochar and CO_2. On the other hand, a decrease in the production of CO, CH_4, C_2H_6 a C_3H_6 was discovered.

The woody biomass used in study autors [7] was *Leucaena leucocephala*, the fast growing tree which normally considered as one of the most potential energy crops in Thailand. Leucaena has been torrefied at low temperature at atmospheric pressure and under pressure up to 4 MPa in inert atmosphere. The torrefaction temperature is an important factor influencing coal yield. It was discovered that the solid proportion of the yield decreases with an increasing calcination temperature. For example, at atmospheric temperature, the coal yield was 88. %, 82.2% and 73.9% at temperatures of 200 °C, 225 °C and 250 °C. With an increase in pressure, coal yield increased, e.g. 88.2% at *t* = 200°C and with a pressure of 4 MPa it increased to 89.9%. On the other hand, at 225 and 250 ºC, it was discovered that the coal yield had already decreased when increasing pressure by 1 MPa [7].

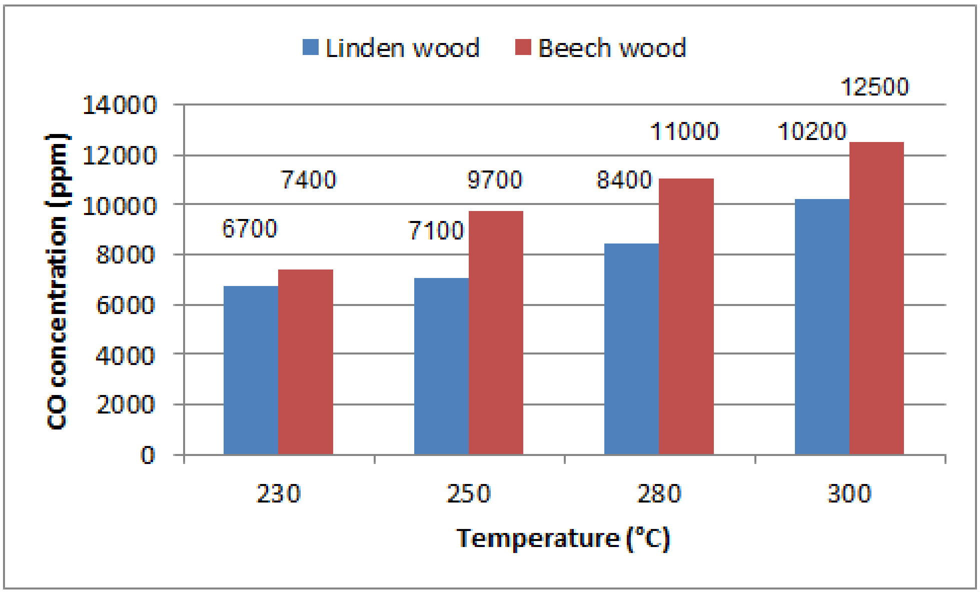

Figure 1 Dependence of carbon monoxide concentration on the temperature

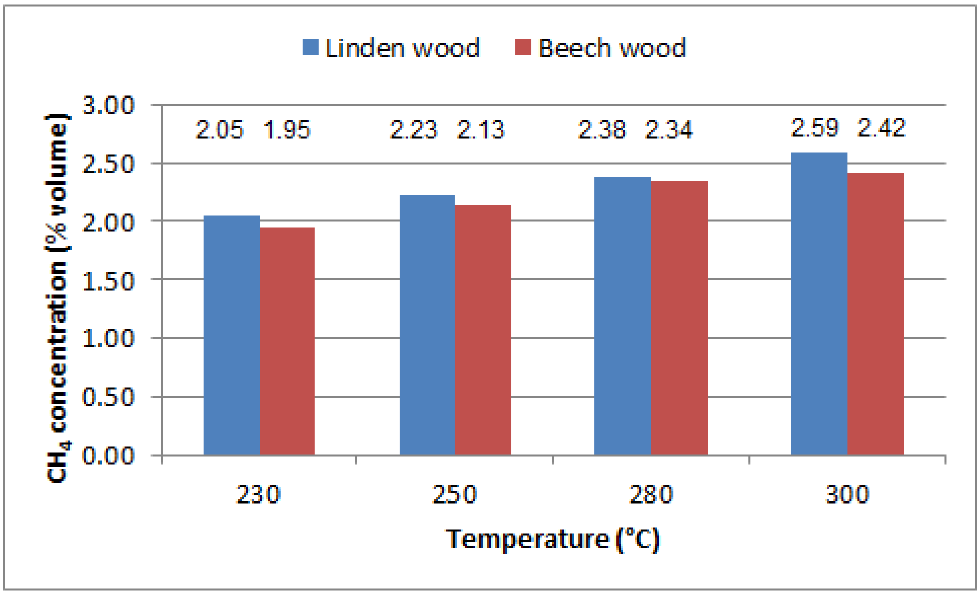

Figure 2 Dependence of methane concentration on the temperature

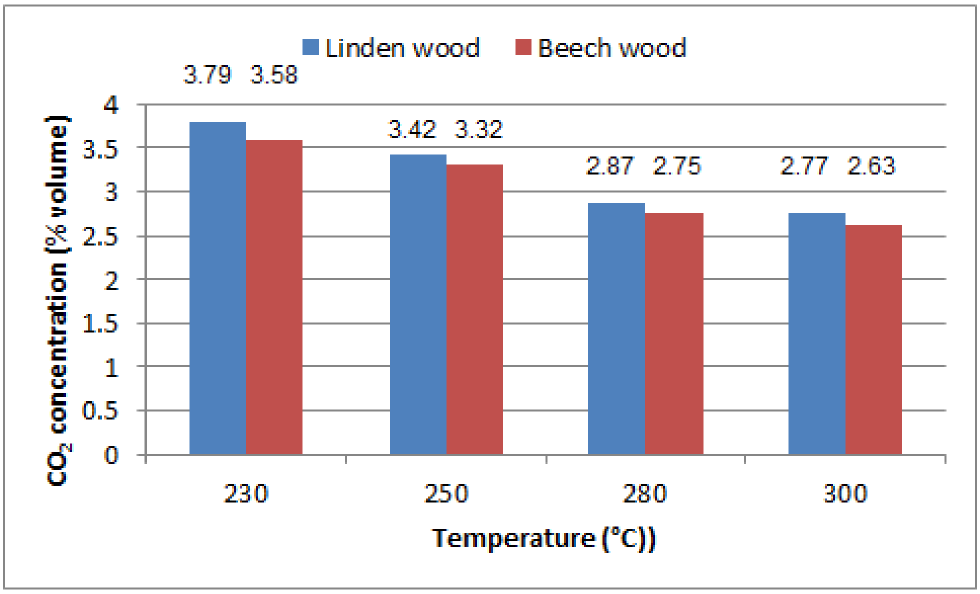

Figure 3 Dependence of carbon dioxide concentration on the temperature

4. Conclusion

Torrefaction is currently considered to be attractive technology. It takes place at relatively low temperatures, resulting in lower emissions of potential pollutants in comparison with pyrolysis or total incineration of biomass. The produced charcoal has hydrophobic properties, thanks to which it can stored for a long period, it is easier to crush in order for further pressing, e.g. into pellets. Pellets obtained in this way have lower seasonal changeability in terms of their physical and energy properties. It was discovered within the work that infrared sensors are suitable for measuring concentrations of pollutants. The following concentrations of CO were measured at 230, 250, 280 and 300 °C for beech at 7400, 9700, 11000, 12500 ppm and 6700, 7100, 8400 10200 ppm for linden. Concentrations of CO_2 at 230, 250, 280 and 300 °C for beech at with % of: 3.58, 3.32, 2.75, and 2.63 and for linden with % of: 3.79, 3.42, 2.87 and 2.77. Concentrations of CH_4 for 230, 250, 280 and 300 ºC were measured for beech *(Fagus sylvatica)* with % of: 1.95, 2.13, 2.34 and 2.42 and for linden *(Tilia cordata)* with % of: 2.05, 2.23, 2.38 and 2.42.

Acknowledgements

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