FAST PYROLYSIS – EFFECT OF WOOD DRYING ON THE YIELD AND PROPERTIES OF BIO-OIL

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The composition and properties of the products of fast pyrolysis of hardwood, obtained in a two-chamber (drying and pyrolytic) ablation type reactor in the temperature range 450-600ºC, were investigated. It has been found that, upon the additional drying of wood at 200ºC and subsequent pyrolysis, the quality of bio-oil is improved owing to the decrease in the amount of water and acids. It has been shown that the increase of the drying temperature to 240ºC decreases the yield of the main product. Optimum parameters of the drying conditions and the temperature of the pyrolysis of wood, at which the bio-oil yield exceeds 60% and its calorific value makes up 17-20 MJ/kg, have been determined.

Keywords: Pyrolytic oil, Wood, Fast pyrolysis, Drying, Ablation type reactor

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INTRODUCTION

The annual world's stock of plant biomass increases by 117 billion tons (in terms of the weight of oven dry material), including by 80 billion tons in forests, which is equivalent to 40 billion tons of petroleum (Zaykov 2002).

The application of renewable plant biomass resources for energy production is becoming increasingly urgent worldwide, because it becomes evident that the sources of fossil fuel energy can be exhausted dramatically with increasing industrial, transport, and agricultural outputs. As resources, low-grade wood and other forms of biomes, for example, peat, straw and bark may be used. One of the methods for utilizing waste wood for energy purposes is thermal processing.

Along this line, technologies for fast pyrolysis of wood are progressing rapidly, which enables the conversion of solid wood biomass into a liquid product – bio-oil, which can be used as a fuel or as a raw material for producing valuable chemicals. As a fuel, bio-oil is neutral with respect to the release of carbon dioxide. Upon its burning, a low amount of nitrogen oxide is released, and no sulphur dioxides are formed. Bio-oil can be stored, pumped over, and transported in the same manner as petroleum products. However, its corrosive activity (pH 2.0-2.5), high viscosity, and possible stratification, which depend strongly on temperature, should be taken into account (Bridgwater 1999). Bio-oil can be burned directly in boilers, gas turbines, and diesel engines for heat and power supply (Bridgwater et al. 2001; Czernik and Bridgwater 2005).

The composition of pyrolysis oil is similar to the biomass composition. In comparison with wood, it has a somewhat higher heat capacity, namely, 15-20 MJ/kg. The products' composition depends on the pyrolysis conditions and the wood type. Pyrolytic oils, in comparison with other fuel oils, have a similar density and a low content of ash elements (Oasmaa and Meier 2002).

In realizing the fast pyrolysis of wood, a raw material with the water content 8-10% is commonly used (Oasmaa and Meier 2002). However, the water content in pyrolytic oil is equal to 25% on average, as it includes pyroligneous water, which is formed mainly upon the dehydration of carbohydrates. The high content of water in bio-oil has an adverse effect on the calorific value of the end product. To decrease the amount of water in bio-oil, wood with a low moisture content should be used for pyrolysis. However, the temperature range of wood drying is limited by the possibility of the development of thermal-oxidative reactions, which lead to a more cross-linked condensed system of components and a higher thermal stability of the wood complex (Domburg et al. 1980).

The objective of the present work was to investigate the effect of the drying process parameters and subsequent fast pyrolysis of hardwood on the properties, chemical composition and yield of bio-oil.

EXPERIMENTAL

Raw Materials

Mixed hardwood chips (fraction 0.1-1.0 mm, moisture 8.5-9%) were used.

Pyrolysis

Fast pyrolysis was carried out using a two-chamber pyrolytic laboratory device that allows changing of the pyrolysis and drying temperatures and the duration of drying. The program "Maple10" was used for plotting the dependencies, based on multiple regression analysis.

The equipment's capacity was 150 g of the raw material in one cycle. The main constituent parts of the reactor (Fig. 1) are as follows:

- A drying chamber with a mixer and an autonomous heating and temperature control system (1).
- A pyrolysis chamber with a mixer, and an autonomous heating and temperature control system (2). The main constituent part of the pyrolysis chamber is a pan, which is heated to a definite temperature (450-700ºC). When opening a hatch, which connects chambers 1 and 2, the wood particles get onto the heated surface of the pan, where pyrolysis proceeds within 30 sec in an atmosphere of the gases formed.
- The volatile products' cooling and condensation systems (3). Condensation proceeds using a water cooling system, which consists of 2 coolers and a collector.
- Char collector.

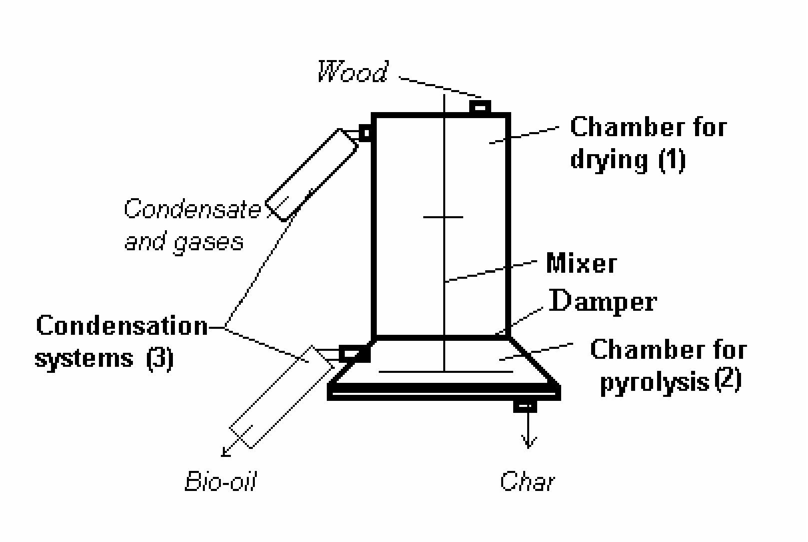


Figure 1. Schematic diagram of the laboratory pyrolytic device.

Gas Chromatography – Mass Spectrometry (GC-MS)

The pyrolytic oil was characterized with a Shimadzu GC/MS – QP 2010, capillary column RTX-1701, 60 m x 0.25 mm x 0.25 µm film. The injector temperature was 250°C, and the ion source was 250ºC with EI of 70 eV. The MS scan range was m/z 15-350. The carrier gas was helium at a flow rate of 1 ml min^{-1}, and the split ratio was 1:30. The oven program was 1 min isothermal at 60ºC, then 6ºC/min to 270ºC, and finally 10 min at 270ºC. The mass spectral database Library MS NIST 147.LI13 was used, and authentic reference compounds were found for substance identification.

Water Content in Bio-oil

A titrator Karl Fischer-270, and solution HYDRONAL-Conlomat AG were used.

Heat Capacity

Heat capacity was determined in compliance with ISO 1928-76, using an Oxygen Bomb Calorimeter-1341.

RESULTS AND DISCUSSION

To investigate the influence of drying conditions of wood, the sample was heated in the upper chamber of the reactor (1) at the temperature 200°C during 90 min, and the volatile products were cooled and condensed (Fig. 1). The results of the analysis have shown that the main component of the condensate is water, whose relative content according to GCMS data is 80% (Table 1). Acids, ketones, and furans were present in the condensate. Among monomeric compounds, acetic acid, hydroxipropanone, and furfural were found in major amounts. The formation of these compounds is typical for low-temperature degradation of wood hemicelluloses (Kislitsin 1990).

To study the effect of wood drying on the composition of bio-oil, pyrolysis was carried out at 550°C, using wood samples with the moisture content 8.5-9% and with drying at 200°C during 90 min. The bio-oils obtained as a result of pyrolysis were analysed by GCMS. The results show that the relative content of water in the composition of the bio-oil obtained upon pyrolysis of dried wood decreased by 7.6% (Table 1). Besides, the content of acids decreased mainly at the expense of acetic acid, and the content of compounds with carbonyl groups and anhydrosaccharides increased.

Table 1. Chemical Composition of Volatile Products, Obtained upon Drying and Pyrolysis of Wood (relative content from GCMS, %)

Compounds	**Content in volatile products, relative %**		
	Drying (200°C, 90 min)	**Pyrolysis (550°C)**	**Drying (200°C, 90 min) and pyrolysis (550°C)**
H_2O	80.1	22.0	14.4
Acids, Esters	11.6	20.2	17.8
Alcohols, Aldehydes	0.9	9.3	11.9
Ketones, Lactones	3.1	15.0	16.0
Pyrans	0.0	1.5	1.5
Furans	1.7	6.6	7.4
Levoglucosan	0.0	1.6	3.7
Phenols, lignin derivatives	0.8	23.5	24.2

The amount of water in bio-oil, determined by titration according to the Fischer method, decreased to 19-20% upon pyrolysis of dried wood in comparison with the 25-28% in bio-oil, obtained upon pyrolysis of a moist wood sample (Table 2).

The results of the analysis of the heat capacity of pyrolytic oils showed an increase in this parameter from 14 MJ/kg (without drying) to 17-20 MJ/kg, when the wood was dried and then pyrolysed (Table 2). Obviously, the main factor that influences this parameter is the decrease in the amount of water in the bio-oil.

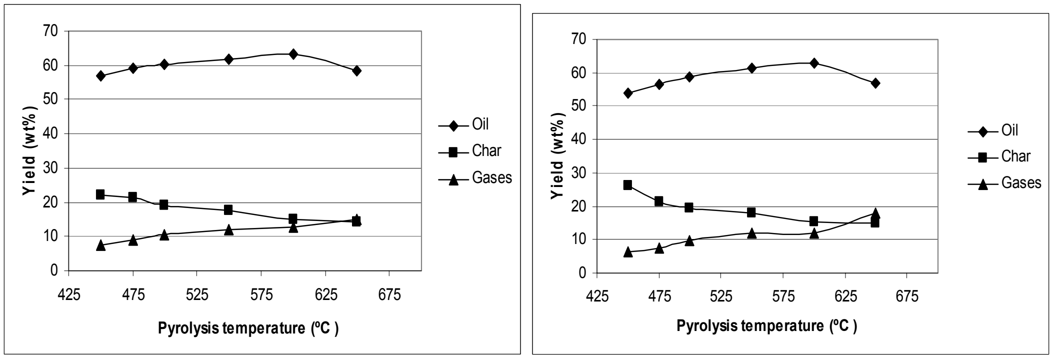
An increase in pH (Table 2) during the two-stage process has been observed. It can be explained by the release of acetic acid in the first stage of the process. This factor is very important, taking into account the high corrosive activity of pyrolytic oils, which also determines the required construction material of the reactor.

Table 2. Properties of pyrolytic oil*

Characteristics	**Pyrolysis at 550°C**	
	Without drying	**Drying at 200°C, 90 min**
Heat capacity, MJ/kg	14	17-20
Water amount, %	25-28	19-20
pH	2.3 –2.5	3.0-3.2
Bio-oil yield, %	62-64	63

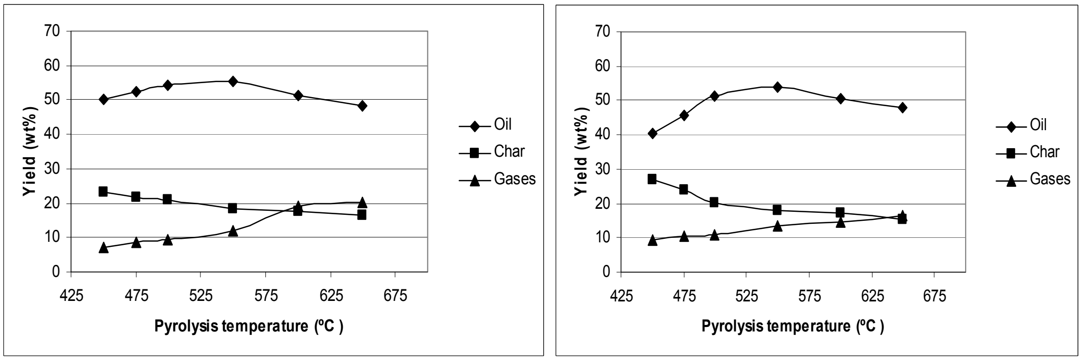
* 4 replicates of experiments were made

To elucidate the effect of the temperature and duration of drying on the yield of liquid, solid, and gaseous products, pyrolysis of wood dried at different temperatures was carried out (Figs. 2, 3).



a b

Figure 2. Change in the yield of oil, char and gases *versus* the temperature of pyrolysis of wood (drying temperature 200ºC (a) 45 min, (b) 90 min).



c d

Figure 3. Change in the yield of oil, char and gases *versus* the temperature of pyrolysis of wood (drying temperature 240ºC (c) 45 min and (d) 90 min).

The results of the pyrolysis of wood samples, dried at temperatures of 200 and 240ºC, have shown that the increase in the drying temperature influenced the yield of pyrolysis products, while the increase in the drying time from 45 to 90 min did not affect it (Figs. 2 (a, b), 3 (c, d)). Upon pyrolysis of the wood dried at 200ºC, the bio-oil yield grew with increasing temperature from 450ºC to 600ºC, reaching 63% (Fig. 2 (a, b)). Further rise in temperature led to a decrease in the bio-oil yield and an increase in the amount of non-condensing gases.

Upon pyrolysis in the temperature range 450-650ºC of wood samples, whose drying was performed at 240ºC (Fig. 3 (c, d)), the bio-oil yield was lower. Its maximum value was reached at a lower temperature, in comparison with the case of the samples dried at 200ºC. At increasing pyrolysis temperature above 550ºC, no additional amount of liquid products was formed. Obviously, upon drying of wood at 240ºC, the formation of new, thermally more stable bonds occurs (Chirkova et al. 2006), which results also in a higher yield of the char residue and an increase in the amount of non-condensing gases upon pyrolysis of these samples.

The results of modelling of the pyrolysis process show that the yield of pyrolytic oil changed upon varying both drying temperature and pyrolysis temperature (Fig. 4). The optimum conditions for the formation of bio-oil were a drying temperature of 200^{o}C and a pyrolysis temperature of 550^{o}C. The maximum yield of bio-oil was 63% of the dry raw material. The decrease in the drying temperature below the optimum level influenced the bio-oil yield only insignificantly.

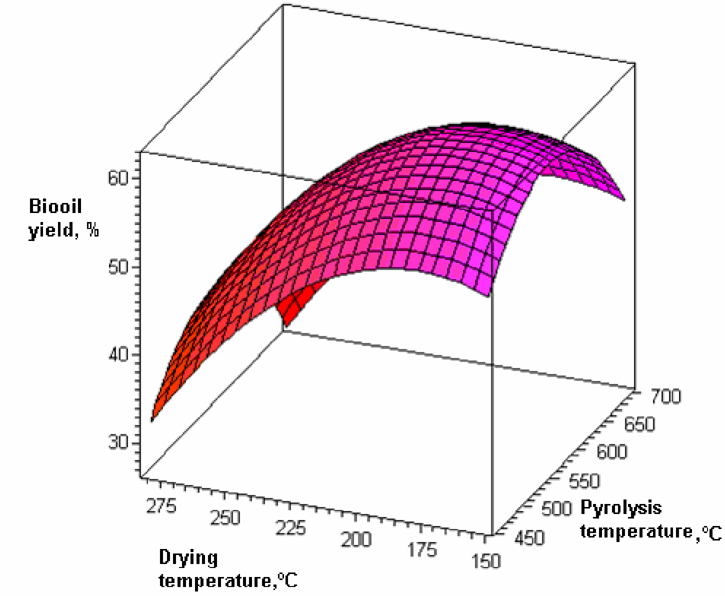


Figure 4. Change in the yield of bio-oil upon pyrolysis of wood *versus* the temperature of drying and pyrolysis (drying time 90 min).

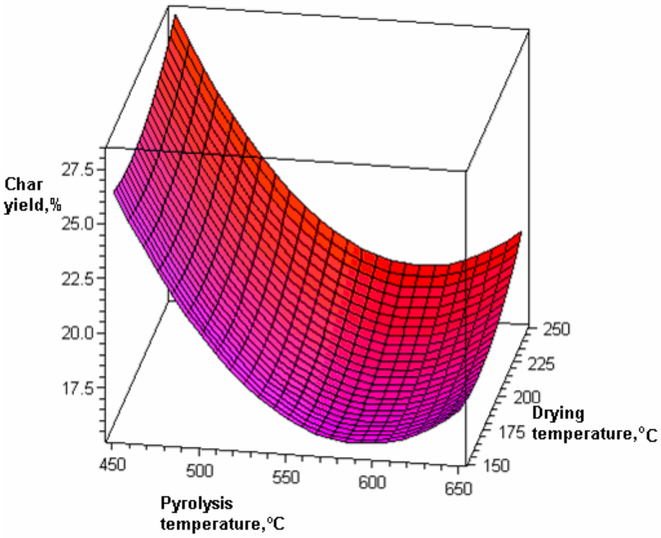


Figure 5. Change in the yield of char upon pyrolysis of wood *versus* the temperature of drying and pyrolysis (drying time 90 min).

At the same time, the increase in the drying temperature and the changes in the pyrolysis temperature below and above the optimum levels had an equal adverse action on the bio-oil yield. The latter decreased and reached about 40% at the drying temperature 275°C.

The drying temperature practically did not influence the formation of char (Fig. 5).

The lowest quantity of char was formed under pyrolysis conditions that were optimum for obtaining bio-oil. At a temperature of 450°C, the char yield was the highest, namely, 27%.

CONCLUSIONS

1. The process of fast pyrolysis of hardwood using a two-chamber ablation type reactor has been investigated, depending on the drying conditions and pyrolysis temperature.
2. It has been found that the drying of the raw material at 200ºC and pyrolysis at 550ºC resulted in improving of the quality of bio-oil. The improvements included a decrease in the water content to 19-20%, increased pH, and a calorific value of 17-20 MJ/kg.
3. It has been found that the drying of wood at the temperature 240ºC obviously led to condensation reactions and cross-linking of wood components, as well as a decrease in the yield of bio-oil.
4. The maximum yield of bio-oil (above 60%) was obtained under the conditions of drying at 200ºC and pyrolysis at 550ºC. The lowest quantity of char was formed under pyrolysis conditions that were the optimum for obtaining bio-oil.
5. Drying of wood at a higher temperature (above 200°C) decreased the yield of liquid products of pyrolysis.

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