

PYROLYSIS OF WOODY MATERIAL

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Abstract

This work aimed to study the recovery of beech wood by the process of pyrolysis. The effects of experimental conditions in products yield and composition were studied. The thermal behaviour of forestry biomass was studied in a batch reactor at temperatures ranging from 350°C to 450°C. The reaction time of wood thermal degradation took 95 min. The main objective was the identification of the oxygenates and carbonaceous species generated by pyrolysis of beech wood. The products of wood cracking were classified into three groups : 25.1 %wt. of gas, 44.3 %wt. of liquids and 30.6 %wt. of carbon solid residues. There is considerable experimental evidence that suggests that there is competition between gas, liquids and char during wood pyrolysis which depends on the heating conditions.

Keywords: Pyrolysis; beech wood; gas; liquids; char.

1. Introduction

Global warming and its ecosystem implications (e.g., ice melting at the poles and rising of ocean levels) are taking place beyond doubt and are causing increasing concerns worldwide. The CO₂ level is sky high (at ~ 380 ppm) and has steadily risen by 40% since the beginning of the industrial revolution, mainly because of anthropogenic action [1]. Emissions, such as particulates and nitrogen oxides NO_x (in particular from diesel engines), pose serious environmental and health challenges. Rapidly increasing energy demand, associated with increase in population especially in developing countries in Asia, and the global economy, in conjunction with declining energy reserves (of fossil fuels) require new strategies for production and utilization of energy.

Biomass is contemporaneous (non-fossil) and complex biogenic organic-inorganic solid product generated by natural and anthropogenic (technogenic) processes, and comprises : (1) natural constituents originated from growing land- and water-based vegetation via photosynthesis or generated via animal and human food digestion; and (2) technogenic products derived via processing of the above natural constituents. The general classification of biomass varieties as fuel resources can be divided preliminary and roughly into several groups and sub-groups according to their distinct biological diversity and similar source and origin [2].

Natural biomass is a renewable energy source, while biomass fuel is still an incomplete renewable energy resource. Since it is considered that the biomass system and respective biofuels as sub-systems do not contribute to the greenhouse effect due to the CO₂ neutral conversion, extensive investigations have been carried out worldwide to enhance the biomass use by substituting fossil fuels for energy conversion [3,4].

Assessments and projections in various reports and from several indicate that there would not be a single solution for our energy problem: rather, multiple technologies will be developed and implemented. For example, increased utilization of renewables will not be sufficient to meet the increasing energy demand. Alternative production routes, including nuclear, will also be necessary. According to a recent report, 'fossil fuels will be a major part of the world's energy portfolio for decades to come ...' [1]. It is therefore imperative that utilization of fossil fuels is done in the most efficient and environmentally benign

manner. Aside from exploring underutilized energy sources, increased efficiency will be a key in meeting this challenge and securing a sustainable society.

It is well-known that "the methodology and logic from coal experiments can be applied to biomass" [5]. Surprisingly, it was found that the long term experience and knowledge achieved for the most studied solid fuels (coal, peat, petroleum coke, municipal solid waste, and refuse-derived fuel or char) and their products have not been implemented very successfully in the field of biomass.

Biomass is expected to be a major source of sustainable energy in the future as the World transitions from traditional carbon-based fuels such as coal, petroleum and natural gas to carbon-neutral fuels to combat global warming and fossil fuel depletion. As recognized in Ref. [6], biomass-derived bio-fuels are the only current sustainable source of liquid hydrocarbons required for transportation. However, an economic way of making them has not yet been devised despite the fact that lignocellulosic biomass costs significantly less than crude oil (about \$ 15 per barrel of oil energy equivalent). The US forests, crops, and urban wood wastes can produce 1,3 billion dry tons of renewable biomass per year without land use change [7]. Land use change is an important consideration because using good cropland for the production of bio-fuels exacerbates the very global warming problem they attempt to solve [8].

Barriers to usage of this biomass are (i) It is voluminous-resulting in low energy density, (ii) It is distributed over large and remote areas. (iii) The cost of transportation from remote locations to a central processing facility is high. (iv) It is chemically diverse making biochemical fermentation techniques difficult, and (v) The method of waste disposal (minerals, ash, etc.) that is generated during processing at a central facility is important for sustainable forests and crops.

Currently available pyrolysis methods for conversion of this biomass to liquid transportation fuels require small particle size (~1 mm) and several times the amount of catalyst [9]. This is clearly not possible with the widely distributed 1.3 billion dry tons of renewable biomass supply available per year [6].

Wood pyrolysis is a complex process. Thus, from a thermal perspective, wood pyrolysis is a combination of successive endothermic and exothermic reactions. Similar observations have been reported by other researchers in the literature [10-14] but the current wood pyrolysis models do not account for this phenomenon. Nevertheless, it is important for determining the energy required to convert solid wood to liquid bio-fuels and from the point-of-view of internal pressure generation that may split the particle [15].

Fast pyrolysis has been studied to produce a liquid product from woody materials, with adequate fuel properties ("bio-oil") in contrast to the typical slow pyrolysis method of carbonization to produce char. However, some properties of this bio-oil restrict its direct use in a diesel engine, so research is still undergoing to improve the properties (bio-oil upgrading). In addition, there has been some investigation on the formation of liquid products with commercial interest, such as levoglucosan, furfural or pyrocatechol [16].

Thermal degradation of wood is a complex research topic because wood contains different fractions. On microscopic scale, wood cells are composed of so-called microfibrils, bundles of cellulose molecules 'coated' with hemicellulose. In between the microfibrils (and sometimes within the amorphous regions of the microfibril lignin) is deposited. These wood fractions show different thermal behaviour. Three zones may therefore be distinguished in weight loss curves of wood: hemicelluloses, the most reactive compounds, decompose at temperature in the range of 225-325°C, cellulose at 305-375°C and lignin gradually over the temperature range of 250-500°C [17-18]. This research addresses specifically the first zone i.e. decomposition of hemicellulose in the relatively low temperature range of 225-300°C, a process also known as torrefaction [19-24]. The solid product of such a process, roasted or so-called torrefied wood, has found application as a barbecue fuel and firelighter [21]. It may be attractive in future as [20] a renewable fuel with increased energy density (compared to raw wood) for gasification and/or co-combustion [17,24].

In a previous work [25] thermal cracking of the model seven components mixed plastics (HDPE, LDPE, LLDPE, PP, PVC, PET, PS) into oils/waxes were pyrolyzed to study the effect of the experimental condition on products yields and composition. In the present work, was pyrolyzed forestry biomass with the aim of studying the experimental conditions that maximized liquid yields. The aim of next research of mixing plastic and forestry biomass will be to improve the liquid fraction of the oils/waxes, and to evaluate the H-donor effect of the plastic type, as plastic wastes pyrolysis will produce a liquid medium, which may facilitate mass and heat transfer and consequently biomass pyrolysis reactions. A mixture PE and

PP, the major plastic components of the Municipal Solid Wastes was used in the previous study [25]. Beech wood was the biomass species selected for this work, because it is the most abundant variety in Slovak forestry. On the other hand, the presence of plastics might also improve liquid properties and its behavior as a fuel. Because, certain bio-oil properties such as its low heating value, incomplete volatility, acidity, instability, and incompatibility with standard petroleum fuels significantly restrict its application [26]. The undesirable properties of pyrolysis oil result from the chemical composition of bio-oil that mostly consists of different classes of oxygenated organic compounds. The elimination of oxygen is thus necessary to transform bio-oil into a liquid fuel that would be broadly accepted and economically attractive.

2. Experimental

2.1. Biomass

Beech wood sawdust were used as biomass. Some characteristics of the used wood material are given in Table 1 [31]. The particle size of the wood material was from 0,1 to 5 mm (sawdust). The beech wood used in our work was obtained from the Slovak Republic. The ash content of beech wood amounts only 0,34 mass [31].

Table 1 Some characteristic of the beech wood

Elemental coposition (%wt.) ^a	
C	45.9
H	6.0
N	0.2
S	0.2
O ^b	47.7
Wood components distribution (%wt.) ^a	
Cellulose ^b	46.4
Lignin	25.3
Hemi cellulose	22.4
Water soluble	5.1
Ether soluble	0.8

a Dry ash-free basis, *b* By differences

2.2. Thermal decomposition

We used a similar apparatus as in our previous work [27], without cooler operating at 90°C. We fed the batch reactor with 17g of beech wood sawdust and closed it. The experiments were run in inert atmosphere. The flow of nitrogen (inert) gas was 50 ml.min⁻¹. The time of wood thermal degradation took 95 min. The final temperature at thermal decomposition of wood was 450°C. The following program for thermal cracking of wood was used: heating rate 16.5°C min⁻¹ to 350°C, 8 min temperature stabilization, heating rate 9°C min⁻¹ up to 440°C, heating rate of 7.5°C min⁻¹ up to 480°C. However, final real temperature in the reactor was 450°C. The temperature was controlled by thermocouples. Detailed description of thermal cracking is given in literature [27].

2.3. Analysis of gaseous and liquid products

Analysis of the gases obtained from pyrolysis of wood was performed with gas chromatograph Hewlet Packard HP 6890⁺. The three-PLOT chromatographic column system consist of two parallelly installed detectors FID and TCD and of three switching valves. Helium was used as a carrier gas. The temperature in the injection chamber was 150°C. The time of analysis was about 40 min.

The liquid obtained from pyrolysis were analyzed with the gas chromatograph CHROM 5. The gas chromatograph system consist of the DB-PETRO column and of the FID detector. Helium was used as a carrier gas. The temperature in the injection chamber was 240°C. The time analysis was about 80 min. The analytical procedure was described in detail in [27,28].

3. Results and discussion

The main objective is the identification of the oxygenous and carbonaceous species generated by pyrolysis of wood. The thermal decomposition of woody material was performed under atmospheric pressure at 450°C. The thermal degradation products of wood were classified into three groups: gas, liquid (hydrocarbons, oxygen derivatives and water) and solid residue. Table 2 shows the yields of thermal decomposed products.

Pyrolysis of the beech wood resulted in 25.1 %wt. of gas, 44.3 %wt. of liquids and 30.6 %wt. of carbon solid residues. Material balance of pyrolysis beech wood was performed within the period of heating in the temperature interval 350-450 for 95 min. There is considerable experimental evidence [15] that suggests that there is competition between gas, liquids and carbon solids (char) during wood pyrolysis which depends on the heating conditions. For long intraparticle volatile residence time, gas yield increases at high pyrolysis temperatures, whereas, char yield increases at low temperature. The gas producing reaction must be one of the primary competing reactions rather than the secondary decomposition of the intermediate solid. The intermediate solid is converted only to char and gas is produced directly from the virgin wood by a primary reaction.

Table 2 Product distribution of pyrolysis of the beech wood at 450°C

Product yields	Weight, [g]	%wt.
Gas	4.3	25.1
Liquid	5.2	44.3
Solid residue	7.5	30.6

The changes in composition of gaseous pyrolytic products were inspected during heating of wood to the final temperature. The representative composition of liquid pyrolytic products was stated by gas chromatography, after completing the pyrolytic process. The overall material balance of the wood pyrolysis, at the end temperature 450°C (Tab. 2), was stated by subtracting the mass of the solid residue and the mass of the liquid product from the mass of the sample of the wood, which operation gave the theoretical mass of the liberated pyrolytic gases. The samples of the liberated gases were taken in the case of the end temperature 450°C, then at 350, 400 and 450°C.

Table 3 Product distribution (%wt.) of components in gases obtained by pyrolysis of beech wood at 450°C

Temperature, °C	350	400	450	450	Average composition of gas, %wt.
Time of experiment,	17	28	37	95	
Components, %wt.	Composition, %wt.				
Carbon dioxide	54.9	52.8	50.0	42.2	51.5
Carbon monoxide	34.9	34.7	35.6	34.4	34.9
Hydrogen	-	-	0.2	0.4	0.2
Methane	5.0	6.2	8.2	10.2	7.4
Ethane	1.2	1.5	1.9	2.2	1.7
Ethylene	0.9	1.0	1.2	1.2	1.1
Propane	0.5	0.5	0.6	0.7	0.6
Propene	1.0	1.1	1.2	1.1	1.1
Methylpropane	0.02	0.02	0.02	0.03	0.02
Butane	0.08	0.09	0.08	0.10	0.09
trans-2-Butene	0.1	0.1	0.1	0.1	0.1
1-Butene	0.2	0.2	0.2	0.2	0.2
Methylpropene	0.2	0.2	0.2	0.2	0.2
cis-2-Butene	0.09	0.1	0.08	0.09	0.09
1,3-Butadiene	0.09	0.09	0.06	0.05	0.07
trans-2-Pentene	0.02	0.03	0.01	0.02	0.02
3-Methyl-1-Butene	0.01	-	-	-	tr.*
1,3-Pentadiene	0.03	0.04	0.02	0.03	0.03
2-Methyl-2-butene	0.04	0.04	0.02	0.04	0.04
C ₄ -hydrocarbons	0.03	0.01	0.01	0.01	0.03
Pentane	0.02	0.02	0.01	0.02	0.02
C ₅ -hydrocarbons	0.06	0.5	0.05	0.07	0.2
1-Pentene	0.02	0.03	0.02	0.02	0.02
2-Methyl-1-butene	0.03	0.04	0.02	0.03	0.03
1-Hexane	0.2	0.2	0.2	0.1	0.2
Isoprene	0.02	0.02	0.01	0.01	0.02
Benzene	0.3	0.5	0.1	0.5	0.3

* tr. - traces

From the gas chromatography analysis of gases it can be seen that the gaseous product evolved at pyrolysis of wood consist mainly of carbon oxides (Tab. 3), alongside with low-molecular hydrocarbons, such as methane, ethane, ethylene, propane, propylene, C₄ and C₅⁺. Hydrogen occurs at the highest temperature. The gases carbon dioxide and carbon

monoxide are present in gases in the amount as high as 82.7, even 90 %wt.. It is of interest that while production of carbon monoxide is approximately constant (around 35 %wt.), the concentration of carbon dioxide in gases slightly decreases with rising temperature (from 54,9 to 48.2 %wt.). During heating (with growing temperature and reaction time) production of methane rises from 5 %wt. to 10.3 %wt. Ethane rises from 1.2 to 2.2. %wt., while ethylene (around 1.1. %wt.), propane (around 0.6 %wt.) and propylene (around 1.1% %wt.) do not change in any considerable way. Hydrocarbons C4 and C5 are present only in tenths of %. Traces of benzene are also present.

The formation of carbon dioxide may be explained by decarboxylation of acid groups in the wood. However, the formation of carbon monoxide cannot be explained by dehydration or decarboxylation reactions. The carbon monoxide formation is reported in literatures [24, 29] as reaction of carbon dioxide and steam with porous char to carbon monoxide with increasing temperature. Mineral water may catalyze such reactions, especially since the gases formed in the torrefaction experiments using straw contained a relatively higher amount of carbon monoxide than the pyrolysis experiment using wood (which contains much less mineral matter). It was found (Table 3) that the ratio of carbon dioxide to carbon monoxide decreases with temperature and time (from 1.6 to 1.2), in line with the theory that carbon monoxide is formed in a secondary reaction.

The volatiles consist of a condensable fraction and a non-condensable fraction. Table 4 shows the yields of condensable and non-condensable product for beech wood, at experimental conditions.

Table 4 The yields of gaseous and liquids components from pyrolysis of beech wood at 450°C

Temperature, °C	450		
Time of experiment, min.	95		
Conversion to gases and liquids, %	0.694		
Component	Yields, %wt.	Component	Yields, %wt.
Carbon dioxide	12.9	cis-2-Butene	0.02
Carbon monoxide	8.7	1-Pentene	0.01
Hydrogen	0.04	2-Methyl-1-butene	0.01
Methane	1.9	C ₅ -hydrocarbons	0.05
Ethane	0.4	2-Methyl-2-butene	0.01
Ethylene	0.3	1-Hexene	0.04
Propane	0.1	Benzene	0.09
Propene	0.3	Methanol	0.6
Methylpropane	0.1	Acetic acid	4.3
Butane	0.02	Formic acid	4.7
trans-2-Butene	0.03	Furfural	2.4
1-Butene	0.06	Lactic acid	1.0
Methylpropen	0.04	Levogluosan	0.4
1,3-Butadiene	0.02	Others (including unknowns)	30.9
trans-2.Pentene	0.01	Carbon solid (char)	30.6
1,3-Pentadiene	0.01		

Acetic acid and formic acid are the main liquid pyrolysis products of beech wood, while smaller quantities of methanol, furfural lactic acid and levogluosan. The amount of water is formed (13 –15 %wt.). Šimkovic et al. [30] who used TG/MS to study thermal decomposition of xylan have also observed these compounds. Thus the products found stem mainly from the decomposition of the hemicellulose fraction. The hemicellulose of deciduous woods has acetoxy- and methoxy- groups attached to the polysugars (in particular to xylose units) which form acetic acid and methanol when the wood is heated to temperatures around 200°C [29]. The amount of acetic acid formed is 4.3. %wt. and amount of methanol formed is 0.6 %wt. at 450°C.

The pyroliquid taken from the drip after completing the experiment, contained 44.4 %wt. depending of the feedstock. At laboratory temperature (22°C), the pyroliquid separated into two layers. On heating at 60°C both layers got homogenized to one layer. Both layers have the same composition and both are soluble in tert-butanol. After separating them in

separatory funnel the upper layer presented 14.9 %wt. and the bottom layer was at 29.5 %wt.. Even if the two layers got combined after being heated, and were dissolved in *tert*-butanol, the upper layer cannot be considered to be hydrocarbon (oil) and the bottom layer to be polar (water). After being heated and dissolved in *tert*-butanol on gas chromatography analysis, the pyroliquid has a similar composition as the two layers, separated from each other (upper and bottom layers). After corresponding standards were used, the same profiling oxidative substances were identified in both analyses.

The standards used were: methanol, acetic acid, formic acid, furfural, and lactic acid. The pyroliquid from wood contained rather a large amount of acetic acid, formic acid and furfural. These compounds evolve from oxidative components of wood during pyrolysis.

Py-GC/MS analysis [31] showing water, carbon dioxide, pyruvic acid, and glykolaldehyde as dominant markers for all studied samples. For hardwood samples (beech and oak) much more glycolaldehyde was observed. For beech the greatest amount of syringol was observed while this compound was not observed in pine and spruce wood. Also the amount of 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (HDPO) was very high and dianhydropentose was absent. In beech wood together with syringol also prop-2-enol-syringol and trans-sinapyl alcohol were present while they were also absent in pine and spruce.

Table 4 shows that the yield of the organic condensable fraction is in all cases dominated by the amount of "others", predominantly unknown components. These constitute 70% of the total organic fraction. Carboxylic acids (mainly acetic and formic acids) are the most abundant species in the remaining 22.5% of identified components. They constitute 10% of the total organic fraction. The overall yields of methanol, furfural and phenols are highest for beech. This may be ascribed to the lesser thermal stability of the deciduous lignin when compared to the coniferous and herbaceous lignin of the spruce and-possibly-straw [32]. It also indicates that both the phenolic compounds and methanol have lignin as their common origin. In general, the lignin in deciduous woods contains a mixture of predominantly guaiacyl and syringyl units, while the lignin from coniferous woods is almost exclusively built up from guaiacyl units. The total amounts of C₂-C₄ oxygenated degradation products are generally 1-2 %wt. of the dry feedstock with acetol (1-hydroxy-2-propanone) and 1-hydroxy-2-butanone as main products [35].

Yields of the predominantly hemicellulose-derived furans are generally 2.4. %wt. with furfural as main constituent. The amount of the cellulose-derived levoglucosan does not exceed 0.5 %wt. of the feedstock. The results of pyrolysis of beech wood at 350-450°C are corroborated by recent work of Branca et al. who conducted a conventional fixed-bed pyrolysis with beech wood [33]. This agreement illustrates the fact that the auger facility can be regarded as a slowly moving, fixed bed pyrolysis reactor [32]. The results of the bubbling fluidized bed experiments with beech seam similar to the results of the auger experiments [32].

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is a major component of this tar fraction and considered as an important intermediate in cellulose pyrolysis especially at > 300°C. Consequently, the secondary reaction of levoglucosan is expected to effect the following pyrolysis and the final product composition. In vapor-phase, levoglucosan was selectively converted to the non-condensable gas (mainly CO and CO₂) while char and others condensable low molecule-weight products (furfural, 5-hydroxymethyl furfural, glycolaldehyde, hydroxyacetone, acetic acid and formic acid) were formed more selectively in liquid /solid phase [34]. The vapor-phase gasification of levoglucosan proceeds in a radical-chain mechanism.

4. Conclusion

This paper describes experimental proof of principle activities for staged decomposition a simple and elegant thermochemical conversion option to valorize lignocellulosic biomass. Due to the overlapping thermal stabilities of the main biomass constituents, pyrolysis of the feedstock during a continuous step-wise temperature ramp in a batch reactor, leads to complex mixture of pyrolysis products, with each staged pyrolysis mixture consisting of small amounts of pyrolysis products that originate from all three main biomass constituents. Except for carbon dioxide, carbon monoxide and water, yields of individual chemicals are generally below 5%. However, certain groups of thermal decomposition like acetic acid (4.3.%wt.), formic acid (4.7 %wt.), lactic acid (1.0 %wt.), furfural (2.4 %wt.), methanol (0.6 %wt.) and levoglucosan (0.4 %wt.) are formed in higher yields up to 5 %wt.

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