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Fractionation of Bio-Oil from Flash Pyrolysis

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Biomass is the world's largest source of renewable energy and can replace part of the fossil sources. Main components of biomass are cellulose, hemicelluloses and lignin, which are compounds of C, H and O and represent high energy content. Fast pyrolysis (flash pyrolysis) at temperatures up to 500 °C for a time of few seconds gives a high yield of bio-oil to around 80 %, containing hundreds of components, such as alkanes, alkenes, cyclic hydrocarbons, aromatics, phenols, also ketones, esters, ethers, sugars, alcohols and others. Bio-oil can be directly used as fuel in boilers or after upgrading as motor fuel and a source of chemicals. By upgrading, the catalytic cracking in the presence of zeolites and hydrogenation are mainly used. The paper describes the results of fractionation of bio-oil by aqueous extraction. The yield and composition of the obtained fractions are given.

1. Introduction

Bio-oil, dark brown liquid product with similar elemental composition as biomass, is obtained by thermochemical liquefaction of lignocellulosic biomass materials. Besides bio-oil the gaseous and solid products are produced. Bio-oil is very complex mixture of organic compounds of different size molecules from depolymerisation and fragmentation reactions of the main three components of biomass: cellulose, hemicelluloses and lignin and contains oxygenated hydrocarbons and heterocyclic substances with an appreciable proportion of water from both the original moisture and reaction product. Also solid char may be present. Bio-oil obtained from fast pyrolysis of biomass has the potential to substitute fossil liquid fuels after it is upgraded by catalytic hydrogenation, catalytic cracking or steam reforming. Bio-oil can also provide a source of valuable and useful chemicals by using separation technologies such as distillation and/or extraction. There have been more than 400 compounds identified in bio-oil derived from biomass fast pyrolysis. The developmental focus in this field has been on recovering products from whole bio-oil or from the major, relatively easily separated fractions (Ringer et al., 2006).
The aim of thermal decomposition method, namely fast or also called flash pyrolysis, is to maximize the liquid yield. The maximum yield of bio-oil can occur between 480 and 520 °C depending on feedstock. Biomass is heated rapidly and the liquid product is condensed to bio-oil. Various technologies have been deployed for large scale biomass fast pyrolysis. They include bubbling fluidized beds, circulating fluidizing beds, ablative pyrolysis, vacuum pyrolysis and rotating cone pyrolysis reactors (Ringer et al., 2006).
Bio-oil could, in principle, provide low cost renewable liquid fuel. However, it is characterized by poor physical and chemical properties in general and from fast pyrolysis in particular. It is its corrosiveness, chemical instability, relatively high viscosity, the high presence of oxygen, presence of char particles, etc. The economic viability of bio-oil production depends on finding appropriate methods to upgrade it to a higher quality liquid fuel at a sufficiently low cost.
There are many approaches to improve the quality of liquid fuels: esterifying and acetalization the bio-oil with alcohols like ethanol and butanol (Mahfud et al., 2007); emulsifying the bio-oil in diesel fuels using suitable surfactants (Chiaramonti et al., 2003); deoxygenation of uncondensed bio-oil over zeolite catalysts to direct production of low molecular weight aromatics like BTX (benzene, toluene, xylene) (Carlson et al.,

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2008); gasification of the bio-oil and/or the char co-product to syngas and subsequent Fischer-Tropsch synthesis of long chain hydrocarbons or olefins from the syngas in a so-called Biomass To Liquids (BTL) process (Henrich et al., 2009); direct hydroprocessing of bio-oil to convert it to stable oxygenates or hydrocarbons (Elliott et al., 2007).

Catalytic hydroprocessing of bio-oil has declination to polymerize the oil under heating above about 100 °C, leading ultimately to the formation of extraneous solids or coke at temperatures above about 140 °C, with consequences like reactor plugging and catalyst deactivation (Elliott et al., 2007).

These difficulties can be partially solved by hydroprocessing of thermally resistant portion of the bio-oil only. Thus by adding water to bio-oil it can be separated into an aqueous phase and usually between 20 and 30 % of a viscous higher density phase, so-called pyrolytic lignin as it is largely derived from the lignin fraction of the biomass pyrolysis feedstock. Since pyrolytic lignin is rich in phenolic material it has much greater thermal stability than the carbohydrate derived portion of the bio-oil and consequently is easier to catalytically hydroprocess without solids formation (Piskorz et al., 1989). However in this case one must confront the problem of what to do with the greater, water soluble, portion of the bio-oil.

In order to hydroprocess whole bio-oil, Elliott et al., (2007) proposed to minimize these problems by a two-stage process in the first stage of which the overall thermal stability of the bio-oil is enhanced by catalytic hydrogenation at a low temperature (under 280 °C).

Phenolics can be recovered from bio-oil mainly as fractions, because of the presence of a high number of phenolic derivatives. Phenolics are weak Lewis acids with small dissociation constants, whose hydrophilicity is reinforced in alkali solution. They also have a limited solubility in water; therefore this property can be used for isolation purposes. An addition of water, aqueous $NaHSO_3$ or alkali solution to the bio-oil causes an existence of a two phases - an apolar bio-oil phase enriched on phenolics, low and high molecular mass lignin derivatives and an aqueous phase rich on acids, sugars, alcohols, ketones, aldehydes. The addition of water or slight aqueous basic solutions was used and discussed by some authors to upgrade the pyrolysis oil and to neutralize the fraction (Effendi et al., 2008). Similar procedure was used also by Kelley et al. (1997).

In the past, almost all conventional separation or purification technologies to isolate bio-oil, such as liquid chromatography, extraction, centrifugation and distillation were applied. At present, also molecular distillation seems to be suitable method for such purpose. Bio-oil is a complex mixture of many compounds with a wide range of boiling points. It is heat-sensitive and easily undergoes reactions such as decomposition, polymerization, and oxygenation. Molecular distillation is not limited by these disadvantageous circumstances and is suitable for the separation of bio-oil (Guo et al., 2009).

After evaluating possible approaches to bio-oil fractionation it was proved to be effective and technologically a viable procedure, using different solubility of bio-oil components in water. The objective of this study was to test the possibilities of bio-oil fractionating by phase separation induced by the addition of water to the bio-oil.

2. Materials and methods

The bio-oil (Table 1) was obtained by fast pyrolysis from the company BTG-BTL (Josink Esweg 34, 7545 PN Enschede, Netherlands). Moisture content of given bio-oil was 27.3 % wt. The origin bio-oil was used for experiments without any additional treatment.

Table 1: Typical properties of wood derived crude bio-oil

Physical property	Moisture content,%	pH	Density, $kg.m^{-3}$	Heating value, MJ/kg	Viscosity, mPa s	Solids, %	Vacuum distillation residue, %
Value	25	2.5	1,200	17	40-100	0.1	up to 50

Water in the excess of 20 % wt. was mixed with the crude bio-oil. The total water content in the system was then 47.3 % wt. After settling the phases (apolar - enriched on phenolic and lignin derivates and aqueous polar - rich on acids, sugars, alcohols, ketones, aldehydes) were separated (Table 2).

Table 2: Elemental analysis of polar and apolar phases

Sample name	Nitrogen, %	Carbon, %	Hydrogen, %	Sulphur, %	Oxygen, %
Polar phase	0	46.3	6.2	0	47.5
Apolar phase	0	64.3	6.3	0	29.4

For cracking of apolar phase, natural non-activated zeolite clinoptilotite (Zeocem, Bystré, Slovak Republic) was used as catalyst with S_{BET} = 26.0 m^2/g, V_{micro} = 0.004 cm^3/g, S_t = 18.9 m^2/g, total pore volume V_a = 0.105 cm^3/g, acidity 0.45 mmol NH_3/g. The amount of catalyst has represented of 5 % wt. of the input material.

2.1 Vacuum distillation of polar aqueous phase

Vacuum distillation in semi-continuous short-path evaporator with wiped film type MO-15 (Cvengroš, 1990) was applied to separate aqueous polar phase of bio-oil. Before distillation, water present in the aqueous polar phase was removed using rotary evaporator. The first distillation step was done at 150 °C and 50 kPa to produce the bio-oil fraction D1 with the yield of 17 % wt. relative to the mass of dry bio-oil input. The distillation residue was then subjected to the second distillation step at 150 °C and 2 kPa to produce the bio-oil fraction D2 with the yield of 3 % wt. relative to the mass of dry bio-oil input. The share of distillation residue was 38 % wt. relative to the mass of dry bio-oil input. The condensate D0 from freeze trap obtained at -30 °C formed about 4 % wt. of the input material.

2.2 Thermal cracking of apolar phase

Bio-oil apolar phase was used for thermal cracking in batch reactor up to temperature 450 °C in the presence of nitrogen (Figure 1). A stainless steel batch reactor with 80 mm in diameter, volume of about 400 ml and equipped with stirrer was filled with bio-oil apolar phase (batch of 154 g) and zeolite catalyst (5 % wt.), sealed tight and heated. The temperature of the reactor was measured using two thermocouples. The actual cracking took 20–30 min. Vapours were condensed using a system of condensers with sufficient capacity. In the next text, this material will be marked as a liquid condensate. Gaseous products, containing mainly CO_2 and CO, little CH_4, C_2H_6 and C_2H_4 and almost no hydrogen were not collected. For the balance, the yield of gases and losses were calculated. The cracking residue was solid bulky foamed mass.

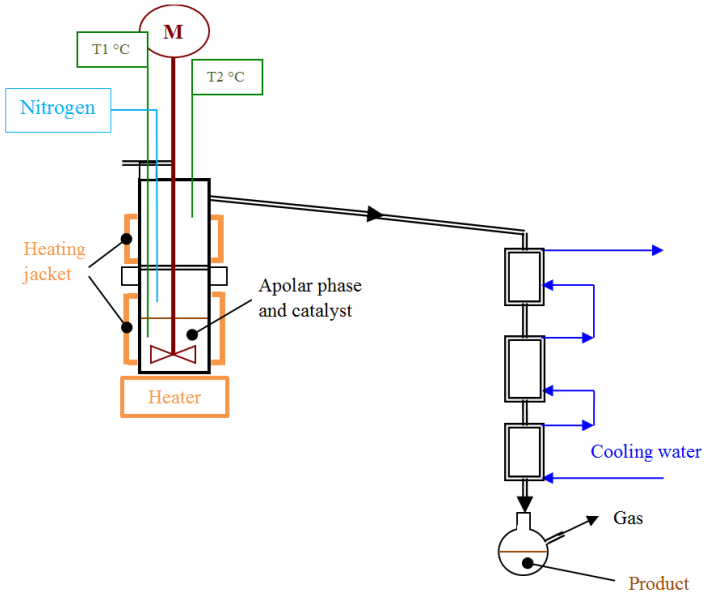

Figure 1: Scheme of batch reactor for cracking.

2.3 GC-MS analysis of products from polar aqueous phase and apolar phase

The fractions obtained by distillation of aqueous polar phase and from apolar phase were analysed by GC–MS. The measurements were performed on an Agilent Technologies 6890N gas chromatograph equipped with a 5973 Network mass-selective detector. The 1 µl of sample was injected at 300 °C in the split injection mode with a split ratio 200:1. Chromatographic separation of fractions was performed using a DB-5 capillary column (30 m × 0.25 mm I.D.) coated with a 5 %-phenyl-methylpolysiloxane film of 0.25 µm thickness as stationary phase (Agilent Technologies, CA, USA). Helium carrier gas was used. Mass spectral data were obtained in the SCAN mode in range 33-450 amu. The identity of the components in the samples was assigned by the comparison of their mass spectra fragmentation patterns with mass spectra in MS library database NIST11.

3. Results and Discussion

3.1 GC-MS analysis of fractions D1, D2 and D0

Fraction D1

GC-MS chromatogram of fraction D1 is shown in the Figure 2. The number of present components is more than 60. In the fraction acids of C1 - C3 (acetic acid, formic acid, propane acid) in the amount of 10 % with the retention time up to 2.5 min are present. They are the most volatile components in the fraction. Aldehydes and ketones are also present here, mainly 1-hydroxy-2-propanone (7 %; 2.518 min.), 2-furanon (4 %; 4.764 min.), 2-hydroxy-3-methylcyklopentanone (5.5 %; 6.163 min.), 1,3-dioxalan (2.3 %; 4.304 min.), isomer of hydroxymethylfurfural (3.6 %; 8.536 min.) and furfural (1.5 %; 3.827 min.). Less volatile components in this sample are phenolic compounds originating from lignin, e. g. cresols (more than 8 %; 6.701 min.; 7.870 min.; 8.035 min.), guaiacol (6.2 %; 6.846 min.), catechol (2.7 %; 2.668 min.), 4-ethyl-guaiacol (2.4 %; 8.954 min.), eugenol (about 2.4 %; 9.777 min.) and vaniline (4.4 %; 10.302 min.).

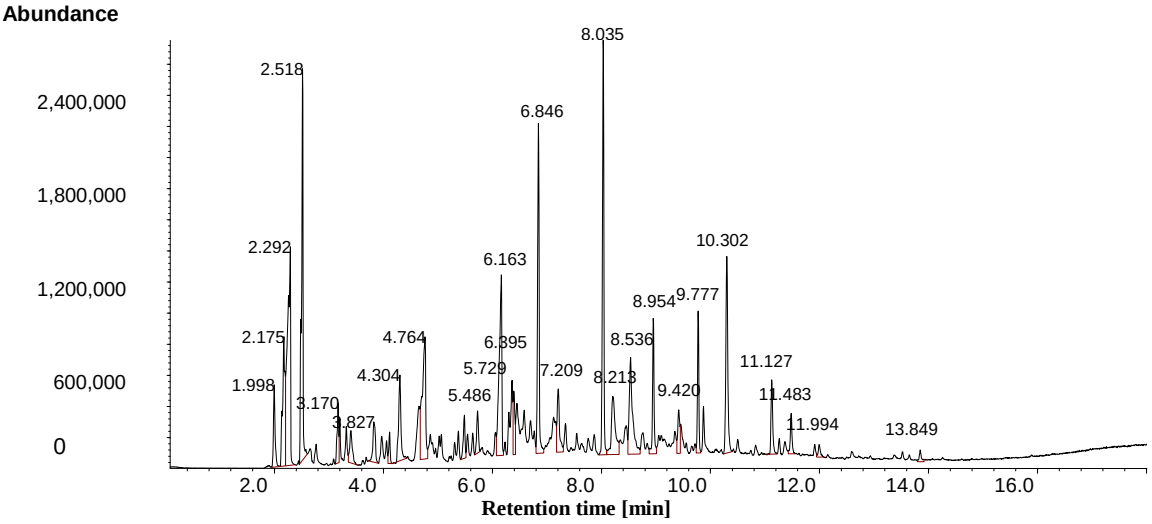

Figure 2: GC-MS chromatogram of fraction D1.

Fraction D2

GC-MS chromatogram of fraction D2 obtained from distillation of aqua phase is shown in the Figure 3. The number of the present components is more than 70. With increasing retention time, the presence of the components with higher molar mass is evident. Vaniline derivate originating from lignin is the main component of the fraction D2. It is present in the amount of 10 % (10.367 min.). Also the group of lower fatty acids up to 3 % is present but in smaller amount in comparison with fraction D1. The group of aldehydes and ketones is not very numerous (e.g. 1,3-dioxalan, 2.5 %; 4.301 min.). According to our expectations the content of phenolic compounds in this fraction is higher compared with D1 fraction (vaniline, catechol 7.6 %; 8.235 min., cresols – more than 5 %; 6.710 min.; 8.033 min.). Levoglucosan (2.8 %; 11. 635 min.) originating from the cellulose is also present.

Fractionation in the vacuum film evaporator has limited efficiency as well as the water extraction to separate polar (62 % wt. relative to the mass of dry bio-oil) and apolar (38 % wt. relative to the mass of dry bio-oil) phases. Despite this, the difference in the share of lighter and heavier components according to the chromatogram is evident. The share of the D2 fraction is significantly lower than that of fraction D1, so the parameters of the coupled distillate will be determined by the properties of fraction D1. The high portion of distillation residue remains as a problem.

Fraction D0

GC-MS chromatogram of fraction D0 obtained by distillation of aqueous phase as a condensate in freeze-trap. The number of components is more than 35. C1-C4 acids (acetic acid 29 %; 2.308 min.) and isomers

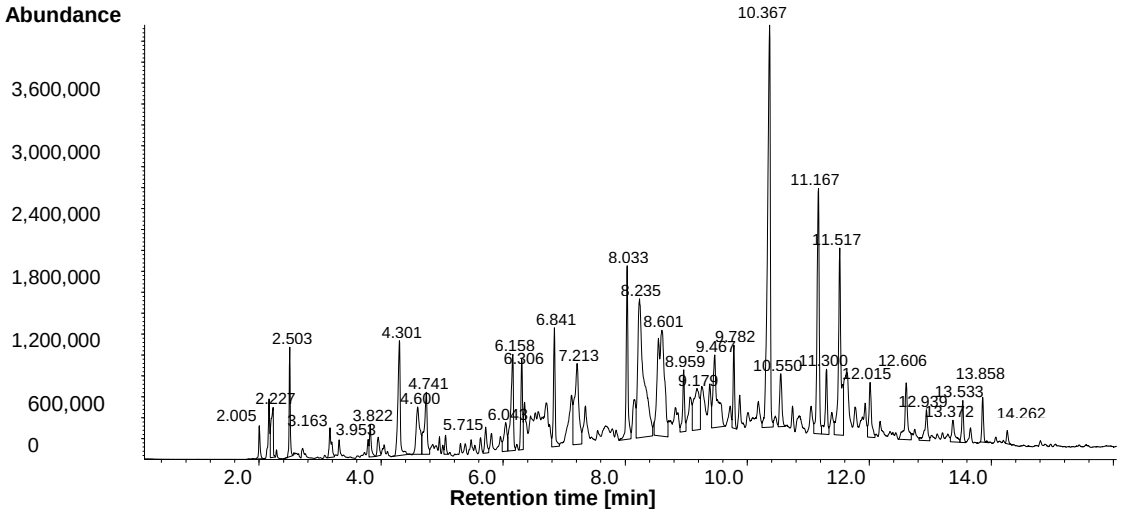

Figure 3: GC-MS chromatogram of fraction D2.

of hydroxy-2-propanone (22 %; 2.485 min.; 2.527 min.) are present in the highest share. The amount of this fraction (4 % wt. relative to the mass of dry bio-oil) is negligible to the whole fractionation process. It can be expected that the amount of formic acids is higher as is shown from the analysis because of lower normal boiling point (100 °C) and it is entrained into the vacuum system. The neutralization should be used to stop these volatile compounds in the form of the salts.

3.2 Thermal cracking of apolar phase and GC-MS analysis

The apolar phase, represented by 38 % wt. relative to the dry bio-oil, underwent the thermal cracking according the Chapter 2.2. The share of liquid condensate, cracking residue and gas together with the losses was 40 % wt., 40 % wt. and 20 % wt., respectively, relative to the input apolar phase. Cracking residue was bulky solid foamed mass. After atmospheric distillation of liquid condensate at 110 °C the distillate in the amount of 50 % wt. relative to the input material or 20 % wt. relative to the dry bio-oil was obtained. This distillate was mild yellow coloured liquid surfaced with the small amount of organic darker layer. It is composed of water and methanol. The distillate residue was moderately viscous liquid. The GC-MS analysis of distillation residue is shown on Figure 4. According to the chromatogram, the products from cracking after distillation treatment contain components from cellulose and hemicelluloses decomposition as well as aromatics from lignin degradation. The acids C1-C3 are also present – mainly acetic acid (4.2 %, 2.258), formic acid (0.5 %, 1.984) and propane acid (0.4 %, 2.659). The group of predominant peaks belongs to aromatic products from lignin with the retention time from 6.238 up to 10.139 min: quaiacol (7.1 %, 6.376), cresols (about of 16%, 6.238, 7.256, 7.438), catechol (4 %, 7.523), etylquaiacol (6.7 %, 8.232), eugenol (4.3 %, 8.953), 2-methoxy-4-propylphenol (4.9 %, 9.039) and 2-methoxy-4(1-propenyl)phenol (3,2 %, 9.793). These components are present also in the chromatograms of polar aqueous fractions D1 and D2 (Figure 2 and Figure 3).

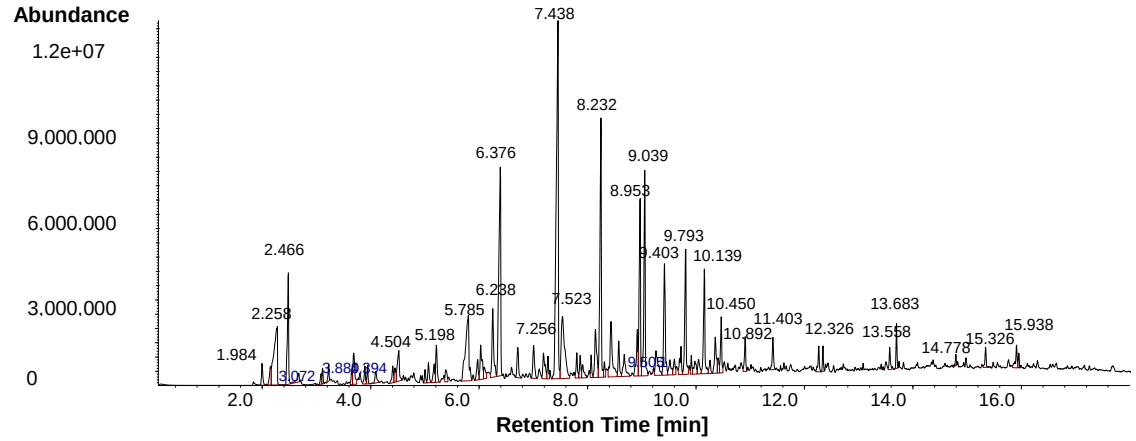

Figure 4: GC-MS chromatogram of fraction from apolar phase.

4. Conclusions

The basic separation step, the addition of water to the bio-oil, caused cleavage of originally homogeneous system into two liquid phases - polar with a yield of 62 % wt. relative to the mass of dry bio-oil and apolar with a yield of 38 % wt. After two-stage distillation treatment of the polar phase in the film evaporator the fraction D1 with a share of 28 % wt. of the polar phase (share of 17 % wt. of dry input bio-oil) and fraction D2 with a share of 5 % wt. of the polar phase (3 % wt. of dry input bio-oil) were obtained, respectively. The condensate from the cold trap in the amount of 6 % of the polar phase (share of 4 % wt. of dry input bio-oil) was recovered.

The distillation residue was represented by 61 % wt. of the polar phase (38 % wt. of dry input bio-oil). Although the efficiency of aqueous separation of polar and apolar phases is relatively low, the difference of chromatograms between D1 and D2 fractions is clear. A higher recovery of non-polar fraction of about 38 % wt. indicates the presence of polar components. Fraction D1 includes both polar components from degradation of cellulose and hemicelluloses as well as non-polar components derived from the decomposition of lignin. In fraction D2 is evidently more components with higher molar mass originating from decomposition of lignin. Yield of fraction D2 to the fraction D1 is five times lower; therefore fraction D1 is for balance of components crucial.

The liquid condensate with the share of 20 % wt. relative to the dry bio-oil was obtained after cracking of apolar phase based on lignin. The volatile components evaporated up to 110 °C were in the amount of 10 % wt. relative to the dry bio-oil. Distillation residue contained mainly phenolic compounds from the decomposition of lignin. The main components in this fraction were cresols (16 %).

The aqueous extraction of bio-oil is a suitable technology for first step of upgrading. Due to the seasonality of the biomass and the bio-oil variability it is necessary to extend tests of bio-oils from other sources and from different producers.

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