



Pyrolysis oil upgrading by high pressure thermal treatment

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ABSTRACT

High pressure thermal treatment (HPTT) is a new process developed by BTG and University of Twente with the potential to economically reduce the oxygen and water content of oil obtained by fast pyrolysis (pyrolysis oil), properties that currently complicate its co-processing in standard refineries. During the HPTT process, pyrolysis oil undergoes a phase split yielding a gas phase, an aqueous phase and an oil phase. In this study, HPTT experiments were carried out at different operating conditions in a continuous tubular reactor. Experimental results showed that, with increasing temperature and residence time, the release of gases (mainly CO₂) and the production of water increased, reducing the oxygen content of the oil phase and hence increasing the energy content (from 14.1 to 28.4 MJ/kg) having the temperature a larger effect when compared to the residence time. Using gel permeation chromatography (GPC), an increase of the molecular weight of the oil phase, probably due to polymerisation of the sugars present in pyrolysis oil, was observed. When water was added as solvent to dilute the feed oil, a decrease of the molecular weight of the resulting oil phase was observed. This indicated that the concentration of organic components had a direct effect on the formation of high molecular weight components. In conclusion, during HPTT an oil with lower oxygen and water content with higher energy value was produced, but adverse formation of high molecular weight components was also detected.

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1. Introduction

Biomass is one of the renewable energy carriers and currently the only renewable source of chemicals. Its use can contribute to the reduction of the green-house-gas emissions because the CO₂ that is produced during the utilisation of biomass can be re-absorbed by new growing biomass, thereby closing the CO₂ cycle. Due to its wide availability, biomass can contribute to securing the energy supply and, when organised in an efficient way, it can stimulate employment especially in developing countries.

Fast (or flash) pyrolysis is a process to thermo-chemically convert solid biomass into a liquid oil. In this process, dry biomass is rapidly heated (residence times of a few seconds) to temperatures around 450–500 °C in the absence of oxygen and at atmospheric pressure. In the past many studies have been carried out to find the operation conditions for which the oil yield can be maximized [1]. In the temperature range mentioned and using residence times of up to 2 s oil yields of up to 70–80 wt.% were obtained [2]. Besides pyrolysis oil - present as condensable vapours at reactions conditions-, also char (~5–10 wt.%) and gases (~20–30 wt.%) are produced. After the reactor, the vapours are rapidly quenched cre-

ating a dark brown oil named pyrolysis oil (also know as bio-oil or bio-crude).

Pyrolysis oil is a mixture of hundreds of different components that are formed during the decomposition of the holocellulose and the lignin present in the feedstock. It has a high water content (15–30 wt.%) and contains a large amount of oxygenated compounds, including acids, aldehydes, alcohols and others (total oxygen content excluding water is 20–40 wt.%) [2]. Due to this high water and oxygen content, the heating value of the oil (HHV ~17 MJ/kg) is low as compared to fossil fuels (HHV 45 MJ/kg). Moreover, because of its high oxygen content and acidity, pyrolysis oil is not miscible with fossil fuels and is corrosive to engines and archetype refinery units, respectively. Another of the problems related to pyrolysis oil is its instability, especially during storage (referred to as “aging” [2]). This aging leads to an increase of viscosity and a possibly unwanted change in chemical composition of pyrolysis oil.

For some applications such as combustion in boilers, the quality of the product obtained via pyrolysis might be sufficient for direct use [3]. However, its direct usage in a diesel engine is difficult due to reasons mentioned in the previous section and above that the tendency of char formation of pyrolysis oil, which can, for example, cause blockage of nozzles in the engines [3]. An option to introduce pyrolysis oil in the transportation fuel market is to co-process it in existing petroleum refineries. Several studies have been carried out

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¹ In memory of Michiel Groeneveld.

Nomenclature

η_i (wet)	wet yield of phase i (wt.%)	H/C	dry molar H/C ratio
η_i (dry)	dry yield of phase i (wt.%)	O/C	dry molar O/C ratio
$\eta_{\text{water produced}}$	water produced yield (wt.%)	HHV	higher heating value (MJ/kg)
M_i	mass phase i (kg)	HPTT	high pressure thermal treatment
H_2O_i	water content phase i (wt.%)	FCC	fluid catalytic cracking
$C_{\text{dry},i}$	C content phase i , dry basis (wt.%)	HDO	hydrodeoxygenation
$H_{\text{dry},i}$	H content phase i , dry basis (wt.%)	GPC	gel permeation chromatography
$O_{\text{dry},i}$	O content phase i , dry basis (wt.%)	THF	tetrahydrofuran
MW_j	Molecular weight element j (g/mol)	OFWA	oil fraction obtained by water addition

towards the direct processing of pyrolysis oil in (lab-scale) FCC units but the results show an excessive char formation resulting in unacceptably low overall gasoline yields [4]. Because of this, an intermediate step, in which pyrolysis oil is upgraded prior to its co-processing, is necessary [5].

One of the possible upgrading processes that have been studied is hydrodeoxygenation (HDO) of pyrolysis oil. This process, in which pyrolysis oil reacts with H_2 in the presence of a catalyst, led to a product with low oxygen content (<5 wt.%) but it has the drawback of high H_2 consumption (up to 900 NI/kg pyrolysis oil, see Elliott [6]) and thus costs.

Biomass Technology Group-BTG, The Netherlands, and in a later stage in collaboration with the University of Twente, developed a process in which pyrolysis oil was thermally treated at high pressures (High Pressure Thermal Treatment, HPTT, Rep et al. [7]). The oil was processed at temperatures of 300–340 °C with a residence time of several minutes at 140 bar. The products obtained after this treatment were an oil phase (which contained ~79% of the initial pyrolysis oil energy) and an aqueous phase (with some organic components containing ~18% of the initial energy). About 5 wt.% of the oil was converted to gas (mainly CO_2) and a small amount of char was produced. The pressure needed to be high to keep the water in liquid state, because evaporation of water led to extensive charring of the oil. After the HPTT process, the oxygen content of the oil phase was reduced from 40 wt.% to 23 wt.% (on dry basis) due to the formation of gaseous CO_2 and water and because several oxygenated compounds were transferred to the aqueous phase. Basically, HPTT was shown to be a cheap deoxygenation process (no need of catalyst or hydrogen) in which the energy of pyrolysis oil was concentrated due to the reduction of the oxygen and water content.

In this paper, new results of the HPTT of pyrolysis oil in a continuous reactor operated at different conditions (temperature, residence time and water dilution ratio) are presented. The aim was to find an operating regime in which an upgraded oil can be obtained that has a higher energy content and lower oxygen content. Ultimately, the goal of this research is to obtain an oil that can (directly or after further upgrading by hydrodeoxygenation) be co-fed to a standard refinery.

2. Experimental section

2.1. Pyrolysis oil

The pyrolysis oil used for this research was produced by VTT Technical Research Centre of Finland using pine wood as feedstock. More details about the properties of the wood can be found elsewhere [8]. The oil received was analysed and put in bottles of the size needed for one run (250 ml). These bottles were frozen (–16 °C) to avoid “aging” of pyrolysis oil. The day before an experiment, a bottle was taken out of the freezer. When the oil was at

room temperature, it was filtered (paper filter 6 μm) to remove possible remaining solids (char, ash, sand. . .) from the oil. A summary of the pyrolysis oil properties is shown in Table 1 (analyses performed by VTT).

2.2. Experimental set-up and procedure

A tubular reactor was built with the aim of studying the HPTT of pyrolysis oil with a fully controllable temperature profile along the reactor and to obtain good mass balance closure. Fig. 1 shows a flow diagram of the set-up.

The feeding system consisted of a HPLC pump that supplied pyrolysis oil (or 2-propanol for cleaning purposes) with flows between 1 and 10 ml/min. A pre-heater was placed before the reactor. It consisted of a cartridge heater with a steel capillary (length: 350 mm, internal diameter: 2 mm) coiled around it which ensured that the oil was entering the reactor at reaction temperature. The heating up time in the pre-heater was typically ~10% of the residence time in the reactor. Preliminary experiments without the pre-heater showed that half of the length of the reactor was needed to reach the desired operation temperature. The reactor itself consisted of a 82 cm long steel tube with an internal diameter of 4 mm. It was heated using an oven with three independent zones that were controlled using the signals of the thermocouples placed inside the reactor at different positions. Along the reactor, 7 temperature indicators were placed to log the temperature profile. In a typical experiment, the temperatures registered by the thermocouples were equal to the desired reaction temperature ± 5 °C. When the oil exited the reactor, it was cooled down but kept at 100 °C to keep the viscosity low. At that point, a back-pressure valve was present to be able to regulate the pressure of the system

Table 1
Pine pyrolysis oil properties (supplied by VTT).

Property	Pine wood pyrolysis oil
Water (wt.%)	23.9
Solids (wt.%)	0.011
Ash (wt.%)	0.03
Carbon (wt.%)	40.6
Hydrogen (wt.%)	7.6
Nitrogen (wt.%)	<0.1
Sulphur (wt.%)	0.01
Chlorine (ppm)	64
Sodium (ppm)	<5
Potassium (ppm)	34
Oxygen (as difference) (wt.%)	51.7
pH	2.7
Density 15 °C (kg/l)	1.206
Viscosity 20 °C (cSt)	58
Viscosity 40 °C (cSt)	17
Viscosity 80 °C (cSt)	4
Flash point (°C)	53
Pour point (°C)	–36

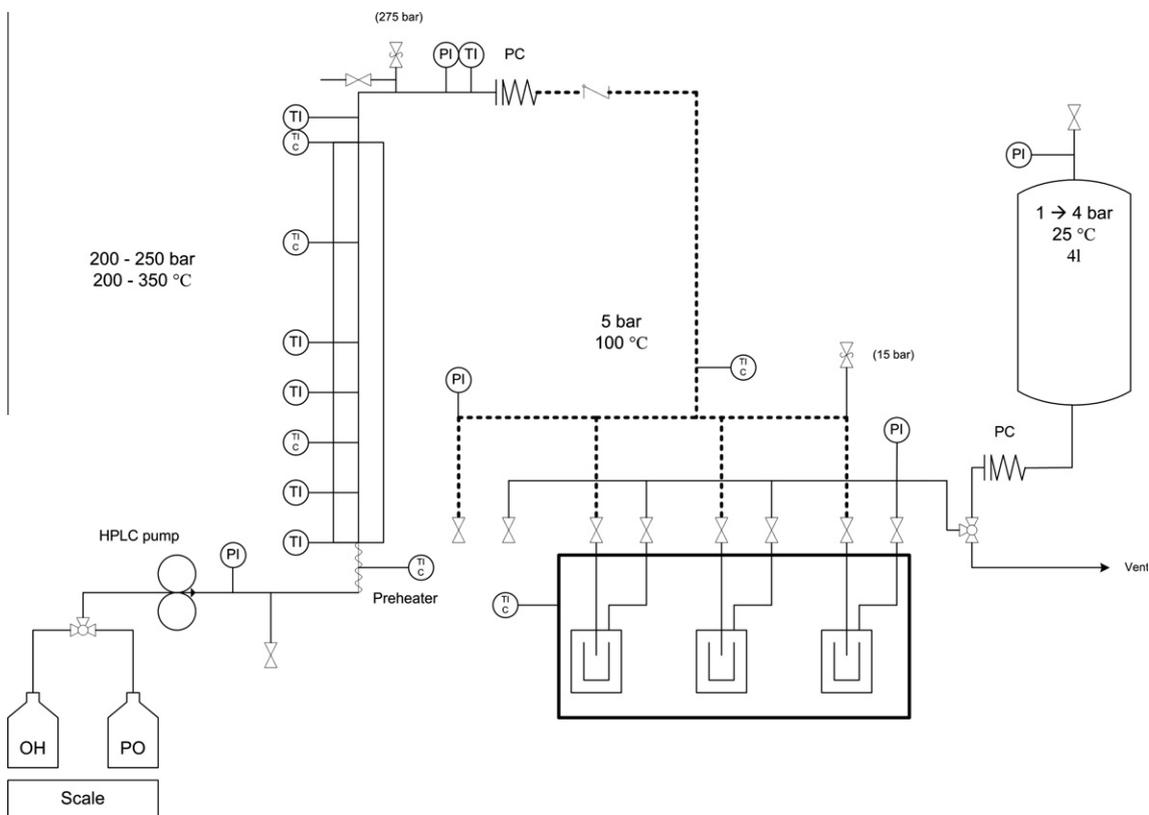


Fig. 1. Flow diagram of HPTT set-up.

(typically 200 bar). After the valve, the products could be directed to 3 product collection vessels. The first one was used to collect the products during warming-up and cooling-down, and the second and third ones, to collect the product during steady-state. The collection vessels consisted of 1.2 l steel vessels that were kept at 100 °C with the use of an oven (to keep the viscosity low and help with the desorption of produced gases from the oil phase). Inside these vessels, 1 l glass jars actually collected the liquid products and could be easily taken out after an experiment to facilitate the reliable quantification of the yields. In these vessels the gases produced during the process were separated from the liquid. The

gases produced during heating-up and cooling-down were vented and gases produced during steady-state were collected in a gas collection bottle for analysis. Between the liquid collection vessels and the gas collection bottle, a back-pressure valve kept the pressure at 5 bar to keep the water in the collection vessels in the liquid state. At the end of each experiment, after cooling-down, the pressures of the gas collection bottle and the liquid collection vessel (the one with the steady-state product) were written down and samples of these gases were taken for GC analysis. Next, the set-up was opened to obtain the liquid products. Typically the liquid product consisted of an aqueous phase on top and viscous oil phase

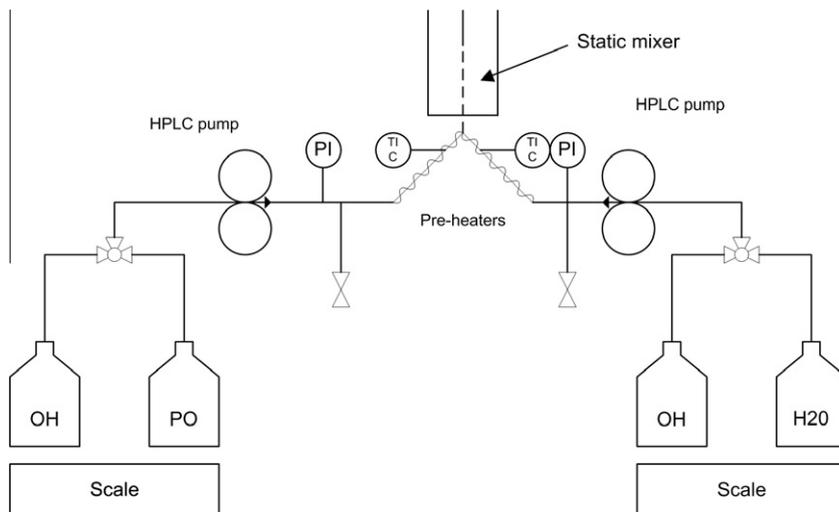


Fig. 2. Modification of the set-up to enable solvent addition to the feed.

at the bottom. The two phases were separated, weighted and analysed.

At a later stage during the research, a second HPLC pump was added to be able to supply a solvent to dilute the pyrolysis oil feed. The solvent used was water. To avoid phase splitting due to cold water addition, a second pre-heater and a static mixer were installed as shown in Fig. 2.

2.3. Analytical equipment and procedures

2.3.1. Gas phase

The gas samples were analysed in a gas chromatograph (Varian Micro GC CP-4900 with two analytical columns, 10 m Molsieve 5A and 10 m PPQ, using Helium as carrier gas). The exact volume of the gas collection bottle was known. The gas volume of the liquid collection vessel was calculated from the total volume minus the volume of the liquid product measured after each experiment. With these measurements and pressure read-outs, the amount and composition of the gas could be calculated.

2.3.2. Liquid phase

To determine the elemental composition of all the liquid phases, a Fisons Instruments 1108 EA CHN-S was used. Each sample was analysed at least twice. If the reproducibility was within $\pm 1\%$, the results were considered good and the average values were taken.

A HPLC system with gel permeation chromatography (GPC) columns was used to determine the molecular weight distribution of the liquid products. This type of analysis was initially performed by the Johann Heinrich von Thünen Institute (vTI), Germany, but in a later stage of this study these analysis could be carried out in-house. The analyses performed by vTI were carried out using an Agilent 1100 HPLC system, using 3 GPC PLgel3micrometer MIXED-E columns connected in series. The column temperature was 40 °C and the solvent used was THF. Calibration was performed using solutions of polystyrene with molecular weight ranging from 162 to 29,510 g/mol. The HPLC equipment at the University of Twente (Agilent 1200 HPLC) was a similar but updated version of the equipment of vTI. The columns, solvent and temperatures used by the UT were the same. These differences in equipment caused small differences in results, especially in the analysis of the feed oil. Because of this, only analyses from the same equipment were compared with each other. The HPLC equipment from vTI was used for the analysis of the products of the HPTT experiments carried out at different temperatures and residence times. The HPLC from the UT was used for the analysis of the products of the HPTT experiments with solvent addition.

A 787 KF Titrino was used to quantify the water content of the original pyrolysis oil and the produced liquid phases (aqueous and oil). The solvent used was a solution of methanol (Aldrich) and dichloromethane (Aldrich) (volumetric ratio 3:1). The titrant used was Hydranal Composite 5 (Riedel-deHaën).

The solvent fractionation technique developed by VTT was used to separate the whole bio-oil and the products of HPTT in major fractions. The fractions obtained by this technique are shown in Fig. 3. More details about this fractionation can be found in the article of Oasmaa et al. [9].

2.4. Definitions

In the results presented, the yields of the products (η_i (wet), in wt.%) have been defined as:

$$\eta_i(\text{wet}) = \frac{M_i}{M_{\text{feed}}} \cdot 100 \quad (1)$$

being i : aqueous, oil or gas phase products and M_i and M_{feed} : the total mass of product phases and feed, respectively.

Knowing the water content of the samples, the dry yields (η_i (dry), in wt.%) could also be calculated. These dry yields of the aqueous and oil phase refer to the yields of organics in these respective phases with respect to the organics in the feed (dry feed):

$$\eta_i(\text{dry}) = \frac{\eta_i(\text{wet}) \cdot (1 - (\text{H}_2\text{O}_i/100))}{1 - (\text{H}_2\text{O}_{\text{feed oil}}/100)} \quad (2)$$

with H_2O_i and $\text{H}_2\text{O}_{\text{feed oil}}$ being the water content (in wt.%) of the product phases and feed, respectively.

To complete the specification of the products on a dry basis, the yield of water produced ($\eta_{\text{water produced}}$, in wt.%) per 100 grams of dry feed oil has to be incorporated:

$$\eta_{\text{water produced}} = \left(\frac{\sum_j (\eta_j(\text{wet}) \cdot \text{H}_2\text{O}_j) - \text{H}_2\text{O}_{\text{feed oil}}}{1 - (\text{H}_2\text{O}_{\text{feed oil}}/100)} \right) \quad (3)$$

being j : aqueous or oil phase products

From the elemental analysis (wet), the dry elemental composition could be calculated by subtracting the contribution of H and O originating from the water:

$$C_{\text{dry},i} = \frac{C_{\text{wet},i}}{1 - (\text{H}_2\text{O}_i/100)} \quad (4)$$

$$H_{\text{dry},i} = \frac{H_{\text{wet},i} - (\text{H}_2\text{O}_i \cdot (2 \cdot \text{MW}_H / (2 \cdot \text{MW}_H + \text{MW}_O)))}{1 - (\text{H}_2\text{O}_i/100)} \quad (5)$$

$$O_{\text{dry},i} = \frac{O_{\text{wet},i} - (\text{H}_2\text{O}_i \cdot (\text{MW}_O / (2 \cdot \text{MW}_H + \text{MW}_O)))}{1 - (\text{H}_2\text{O}_i/100)} \quad (6)$$

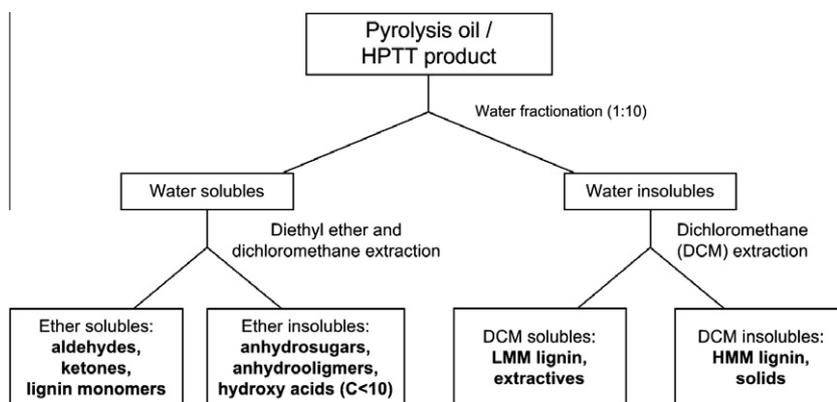


Fig. 3. VTT's solvent fractionation technique applied to pyrolysis oil or an HPTT product. LMM lignin and HMM lignin stand for Low and High Molecular Mass lignin, respectively [9].

with C_{dry} in wt.% and being MW_H , MW_O and MW_C the molecular weight of atomic hydrogen, atomic oxygen and atomic carbon, respectively.

From these dry elemental values, the molar H/C and O/C ratios of the organics in the liquid product phases were calculated:

$$H/C = \frac{H_{dry,i}}{C_{dry,i}} \cdot \frac{MW_C}{MW_H} \quad (7)$$

$$O/C = \frac{O_{dry,i}}{C_{dry,i}} \cdot \frac{MW_C}{MW_O} \quad (8)$$

From the dry elemental composition and the water content, the higher heating value (HHV) was calculated using the Reed's formula [10]:

$$HHV_{Reed,i}(wet) = (1 - H_2O_i/100) \cdot (0.341 \cdot C_{dry,i} + 1.322 \cdot H_{dry,i} - 0.12 \cdot O_{dry,i}) \quad (9)$$

In the original formula, factors concerning the amount of nitrogen, sulphur and ash are also present. However, since pyrolysis oil contains very little of them (<0.1 wt.%), they were not taken into account.

3. Experimental results and discussion

Experiments carried out under different operating conditions were performed to determine their influence on product quality and phase yields. The parameters studied were temperature (200–350 °C), residence time (1.5–3.5 min) and the addition of a solvent (water:pyrolysis oil, vol. 1:1).

It is known that pyrolysis oil remains one liquid phase under HPTT conditions [11] and the liquid phase split occurs during cooling-down (approximately around 200 °C). After the process, the aqueous phase product was typically black for experiments at relatively low temperature (~200–260 °C) and light brown (becoming translucent) at higher temperatures (>300 °C). The oil phase was always black and its visual viscosity increased with reaction temperature.

After the experiments, char was observed at the walls of the reactor (<1 wt.%). The extent of char formation increased with temperature, at higher temperature (>300 °C) even clogging the pre-heater line (internal diameter of 2 mm) and sometimes forcing the end of the experiment.

Comparing the known amount of pyrolysis oil fed to the system during steady-state (values obtained from the weighing scale under the feeding bottle) and the sum of the mass of aqueous and oil phases and the mass of the gases produced, the mass balance could be determined. For all the experiments described in this paper, the mass balance closure was between 96 and 101% (being between 94 and 102% when the dry yields and water production are used). The wet elemental balances were 100–107 wt.% (carbon), 93–103 wt.% (hydrogen) and 91–99 wt.% (oxygen).

3.1. Effect of temperature

The minimum temperature during the experiments was 200 °C as below this temperature HPTT reactions could not be observed. A maximum temperature of 350 °C was used to avoid water in the super critical state (374 °C) and prevent excessive char formation/product deterioration. During these experiments the other operating conditions like residence time and pressure were kept (approximately) constant with the following values:

- Residence time: 3.3–3.5 min (less than 10% of this residence time was used to heat up the oil in the pre-heater).
- Pressure: 200 bar.

The results shown for the experiment at 350 °C correspond to an experiment carried out at 240 bar. This was done because at a pressure of 200 bars and 350 °C, the lines clogged by char.

The properties (elemental composition and water content) of the liquid products are shown in Table 2. It can be seen, that for the oil phase the water content was reduced as compared to the original pyrolysis oil. The oxygen content also decreased considerably with the temperature.

The dry yields of the phases obtained, η_i (dry), and the water produced ($\eta_{water\ produced}$) after HPTT of pyrolysis oil are shown in Fig. 4 as a function of temperature. Although yields are traditionally expressed using wet yields, the graph of the dry yield (as defined in Eq. (2)) gives more insight in the phenomena occurring during the HPTT process. The η_{oil} (dry) went through a maximum at approximately 260 °C. At the same time the dry yield of organics present in the aqueous phase, $\eta_{aqueous}$ (dry) decreased with temperature between 200 and 260 °C but became stable between 260–300 °C. This indicates that, at a temperature between 200 and 260 °C there was net transfer of organics from the aqueous phase to the oil phase accompanied by the formation of some water and gas. At further increasing temperature (260–350 °C), the production of gas steadily increased probably at the expense of the oil yield, as the $\eta_{aqueous}$ (dry) was approximately constant. The gases produced were mainly CO₂ with some small amounts of CO and other gases; the ratio depending on the temperature (Table 3). The $\eta_{water\ produced}$ follows the same trend as the gas yield, although at a somewhat higher absolute level suggesting that de-oxygenation by dehydration can start at milder conditions than de-oxygenation by decarboxylation.

Fig. 5 shows the results of VTT's solvent fractionation technique applied to the aqueous phase products. In this figure, a remarkable decrease of the sugar constituents with increase in temperature can be seen. Knežević et al. [12] showed that during the treatment of aqueous solutions of glucose under similar HPTT conditions, among others, water and a polymerised product were obtained. Combining this information with the current observations that water was produced and the oil yield increased, it is likely that the sugar constituents present in the aqueous phase underwent dehydration and probably polymerisation, and the resulting prod-

Table 2

Liquid product properties after HPTT at different temperature (residence time of 3.4 ± 0.1 min; pressure of 200 bar, except experiment at 349 °C for which the pressure was 240 bar). Elemental composition on dry basis. Oxygen content determined by difference.

T (°C)	200		260		300		350	
	Oil phase	Aq. phase						
C (wt.%)	62.7	52.4	68.4	51.3	71.5	48.6	73.5	47.6
H (wt.%)	6.2	7.1	6.1	8.4	6.3	7.3	6.5	7.7
O (wt.%)	31.1	40.5	25.5	40.3	22.2	42.9	20	43.4
H ₂ O (wt.%)	15.7	36.6	14.9	62.8	9.9	68.3	9.1	70.6

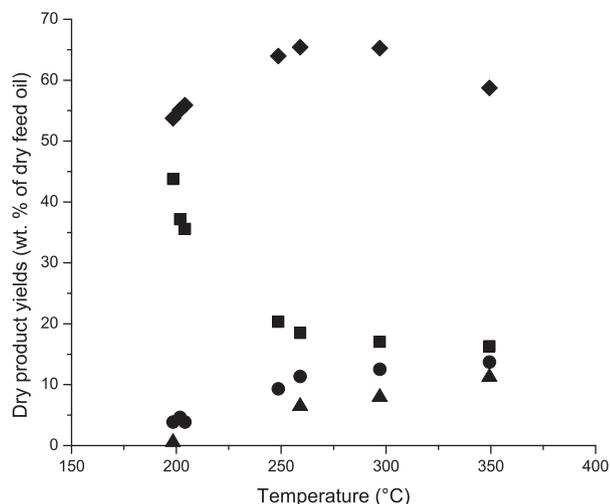


Fig. 4. HPTT product dry phase yields at different temperatures including water production. Oil phase yield (♦), aqueous phase yield (■), water produced yield (●) and gas phase yield (▲).

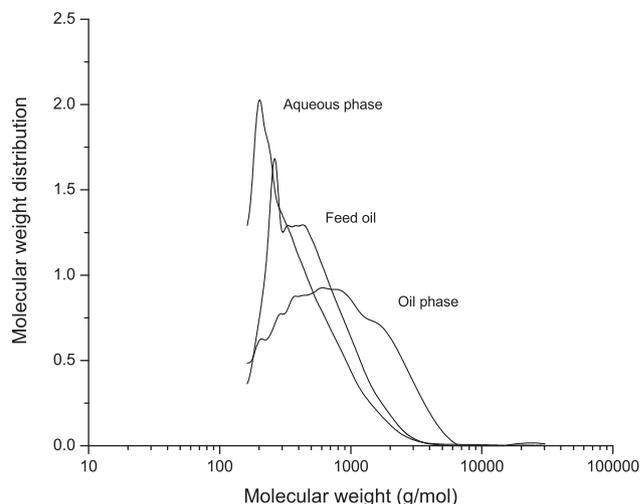


Fig. 6. Molecular weight distribution obtained by GPC analysis of the original pyrolysis oil (feed oil) and the products obtained by HPTT at 200 °C, 3.4 min, 198 bar. Analysis performed by vTI.

Table 3
Gas composition of HPTT experiments at different temperatures.

T (°C)	Gas composition (mol.%)				
	H ₂	CH ₄	CO	CO ₂	C ₂ –C ₃
200	0	0	4.4	95.1	0.5
260	0.8	0.1	5.2	90.3	3.6
300	1.3	0.2	7.7	87.0	3.7
350	1.1	1.2	13.1	79.3	5.3

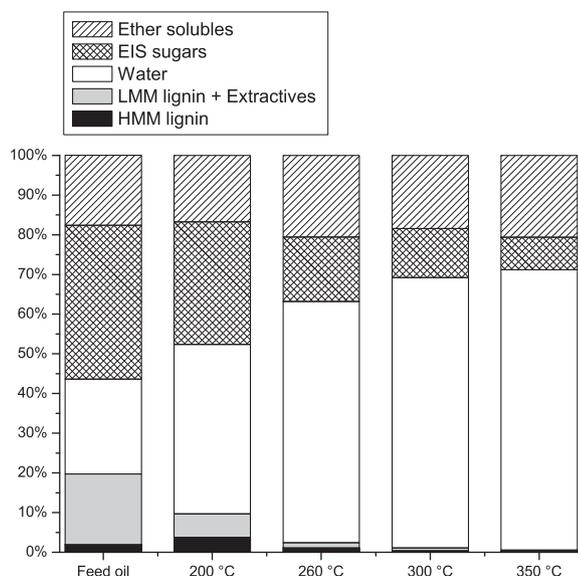


Fig. 5. Results of VTT's solvent fractionation technique applied to the aqueous phase product obtained at various HPTT temperatures.

uct was transferred to the oil phase. To prove that this polymerisation occurred, GPC analyses were performed to the original feed, the oil phase and the aqueous phase (Fig. 6). A considerable increase in the molecular weight of the oil phase as compared to the untreated oil was observed, confirming that polymerisation had occurred during HPTT of pyrolysis oil. Because a part of the

organics from the aqueous phase was transferred to the oil phase (extractives, LMM lignin, HMM lignin and most likely also the HPTT products of the sugars), it can be concluded that for various components in the aqueous phase a change in polarity took place upon HPTT. Besides that, it is likely that also the overall polarity of the organic phase decreased, which can be derived from the lower water content in the oil phase (Table 2).

After HPTT at different temperatures, there were clear differences in physical appearance of the resulting oil phases: at 200 °C it was a viscous liquid and at 350 °C a rubber-like material. However, the comparison of the GPC diagrams of these oil phases did not show any appreciable differences (results not shown). This apparent controversy might be caused by the poor solubility of the very heavy compounds in the solvent used for GPC analysis (THF), keeping these compounds in the filter during sample preparation.

To be able to properly compare the HPTT oil phase and the 'oil phase' of the original feed, water was added to pyrolysis oil at room temperature, forcing a phase split [13]. For this, 25.5 g of water was added to 50.4 g of pyrolysis oil under stirring. The mixture was allowed to settle and two liquid fractions were obtained: an aqueous fraction (60.2 g) and an organic viscous oil fraction (15.6 g). This ratio was chosen because enough water was used to clearly produce two liquid fractions and to avoid producing powder pyrolytic lignin [14]. The oil fraction obtained after water addition (OFWA) was separated from the aqueous fraction and used for comparison with the oil phases obtained after HPTT.

From the elemental analysis and the water content of the oil phase products, dry H/C and O/C molar ratios could be determined (Eq. (7) and (8)). This ratio was also calculated for the original oil and for the OFWA. Fig. 7 shows that after a major reduction of the O/C ratio when pyrolysis oil was processed at 200 °C, higher temperatures did not significantly reduce it. This major reduction of the O/C ratio was most likely caused by phase splitting that occurred during HPTT, as the same decrease in O/C ratio was observed for OFWA (open symbols in Fig. 7). The subsequent reduction of the O/C ratio was due to the production of gases (especially CO₂) and the formation of water by dehydration. The H/C ratio did not vary significantly for the oil phase indicating that the water produced came from the organics present in the aqueous phase.

The reduction of oxygen and water content (see Table 2) in the oil phase had a direct effect on its energy content. Fig. 8a shows the increase of the HHV of the oil phase, calculated using the Reed's

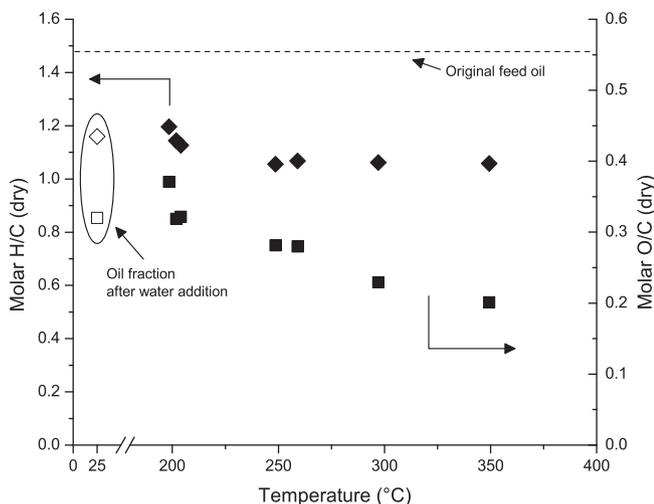


Fig. 7. Molar H/C (◆; left axis) and O/C (■; right axis) ratios of dry oil phase at different temperatures. Empty marks correspond to the values of molar H/C (◇) and O/C (□) for the unprocessed oil fraction obtained by adding water (OFWA) to crude pyrolysis oil and forcing phase split (on dry basis).

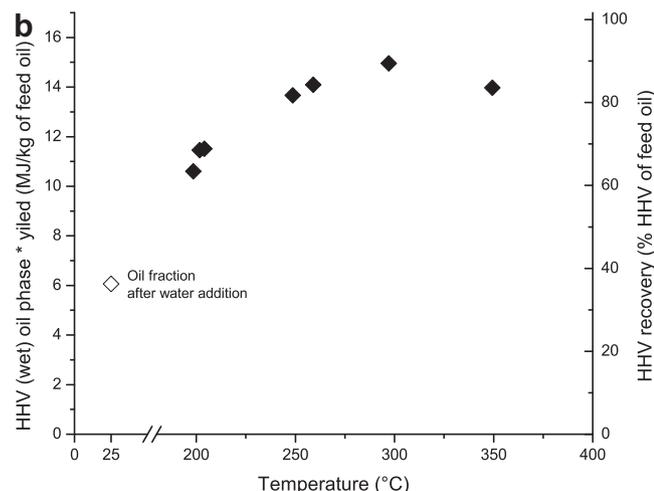
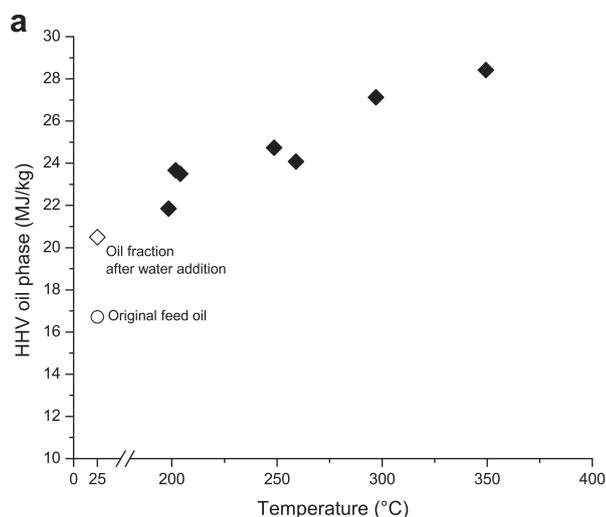


Fig. 8. (a) HHV of the oil phase obtained via HPTT (◆), HHV of unprocessed oil fraction obtained by adding water to crude pyrolysis oil (◇) and HHV of original feed oil (○). (b) HHV oil phases corrected by their yield and HHV recovery of HPTT (◆) and unprocessed oil fraction obtained by adding water to crude pyrolysis oil (◇).

formula (Eq. (9)), with temperature. The HHV of the oil phase was, in all cases, higher than the original oil (value also calculated from Eq. (9)). The yield of the OFWA was very low (31 wt.%) compared to the yield of the oil phase obtained during HPTT (between 50 and 60 wt.%). Fig. 8b shows the HHV corrected by the oil phase yields. It can be seen that while the OFWA just took part of the energy of the feed oil, HPTT concentrated the energy in the oil phase. This is likely to be caused by the transfer of sugar constituents from the aqueous phase to the oil phase, as demonstrated in Fig. 5.

3.2. Effect of residence time

Two series of experiments were carried out at different residence times keeping the temperature constant (first series at 260 °C and a second series was carried out at 300 °C). The residence times applied (including heating up time) were:

- 260 °C: 1.5, 2 and 3.5 min.
- 300 °C: 1.5, 2.2 and 3.5 min.

The η_i (dry) of the two series of experiments are shown in Fig. 9. It can be seen that, in the experiments conducted at 260 °C, the η_{water} produced and η_{gas} (dry) increased with the residence time. On the other hand, at 300 °C, the residence time had almost no influence on the yields. This shows that using longer residence times has the same influence, though to lesser extent, as increasing the temperature.

Elemental analysis of the oil phase products did not reveal a significant dependence on the residence time: H/C ratios of the dry oil phase remained approximately constant and similar in both temperature series (from 1.02 to 1.06 for both series). O/C ratios of the dry oil phase slightly decreased with increasing residence time; this reduction was at 260 °C from 0.33 to 0.28 and at 300 °C from 0.27 to 0.23.

3.3. Effect of solvent addition (water dilution)

Boocock and Sherman [15] studied the influence of the water/wood ratio during the liquefaction of poplar wood in aqueous media at temperatures of 370 °C. Recently, Knežević et al. [12] studied the hydrothermal liquefaction of glucose at similar conditions as used in this study. In their studies, a significant effect of water/

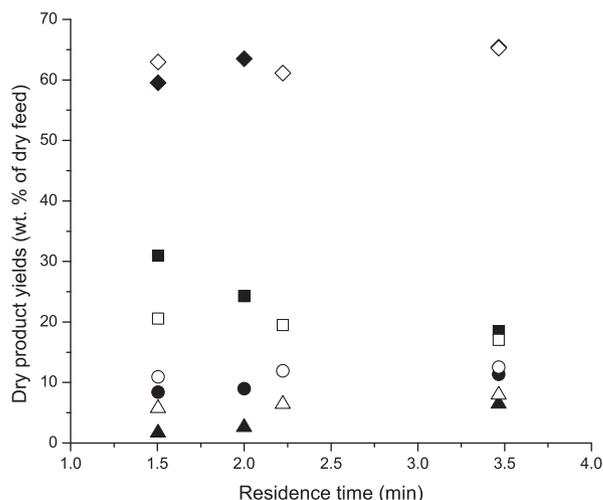


Fig. 9. HPTT product dry phase yields at different residence times including water production. Experiment at 260 °C closed symbols, experiments at 300 °C open symbols. Oil phase yield (◆,◇), aqueous phase yield (■,□), water produced yield (●,○) and gas phase yield (▲,△).

wood ratio and glucose concentration, respectively, was observed. These results from literature indicate that the HPTT product composition can be influenced by dilution of the pyrolysis oil with water.

Assuming that the undesired increase of molecular weight of pyrolysis oil during HPTT (as shown in Fig. 6) was (partly) caused by the polymerisation of sugars, water was added to the feed to decrease the effective sugar concentration in pyrolysis oil and thereby suppress the extent of polymerisation as observed for glucose by Knežević et al. [12]. Details of the experimental set-up are given in Fig. 2.

In this section, results of two experiments with water dilution are shown. Both experiments were carried out at 300 °C and with a volumetric dilution ratio of 1:1 (pyrolysis oil:water). The residence times were 1.7 and 3.8 min, respectively. In Fig. 10, the molecular weight distribution of the product oil is compared to the molecular weight distribution of the oil obtained in two experiments at similar experimental conditions without solvent addition. It can be seen that in the experiments without water addition, the molecular weight distribution was practically the same and independent of the residence time. On the other hand, when water was added to the system, the molecular weight of the products was reduced for both experiments and the effect of residence time appeared to be more significant. At short residence time, less heavy compounds seemed to be formed. These results indicate that dilution has an influence on the overall polymerisation kinetics.

Table 4 shows the production of CO₂ (wt.% of feed) for the same experiments described in the previous paragraph. It can be seen the production of CO₂ (that would reduce the oxygen content in

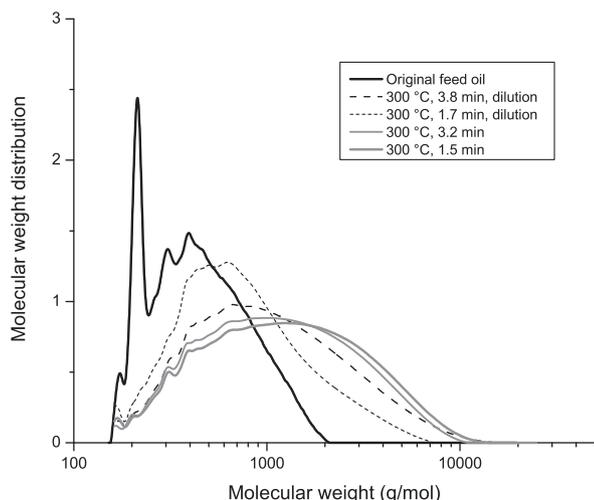


Fig. 10. Molecular weight distribution obtained by GPC analysis of original pyrolysis oil (feed oil) and the oil phase products of HPTT experiments at 300 °C and 200 bar at different residence times. The solid lines correspond to experiments without dilution and the dashed lines correspond to experiments in which pyrolysis oil was diluted 1:1 in volume with water. Analysis performed by University of Twente.

Table 4
Decarboxylation (CO₂ produced for 100 g of feed) of HPTT process at 300 °C and 200 bar at different residence times with and without water addition.

	Residence time (min)	Decarboxylation (wt.% CO ₂)
Without water addition	1.5	3.7
	3.2	4.7
With water addition (1:1)	1.7	1.8
	3.8	4.6

the oil product) also decreased when water was added to the system. This is an undesired effect because the addition of solvent was meant to reduce the rate of formation of heavy compounds, while maintaining the same level of decarboxylation. However, these results suggest that the increase of molecular weight and the production of CO₂ are related. Based on the current results, it is not possible to state whether decarboxylation and polymerisation are indeed the consequence of one (type of) reaction, or the independent result of various decoupled reactions. In the last case only it would be possible to achieve high levels of desired decarboxylation while preventing undesired polymerisation.

4. Discussion

The process temperature has a direct and significant effect on product yields and composition. The yield of the dry oil phase, η_{oil} (dry) went through a maximum between 260 and 300 °C. The increase of η_{oil} (dry) in this temperature range was most likely caused by the polymerisation of the sugar constituents of pyrolysis oil, which otherwise would have remained in the aqueous phase. At temperatures above 300 °C, organics were being converted and transferred to the gas phase, thereby reducing the η_{oil} (dry) again. A significant reduction of the oxygen and water content already occurs due to the (non-reactive) phase splitting of the aqueous and organic phase. However, at increasing temperatures, the oxygen content further reduces, but in a less significant manner than already caused by the phase split. This further reduction in oxygen content was caused by the production of CO₂ and water. The phase split on one hand and the decarboxylation/dehydration on the other resulted in an increase of the energy value of the oil. The oil obtained after HPTT had a higher energy density (wet HHV ranging from 21.8 to 28.4 MJ/kg, depending on the temperature of the process, see Fig. 8a) compared to the original pyrolysis oil (wet HHV 16.7 MJ/kg). Taking into account the yields of HPTT oil obtained, the recovery of energy from the starting oil in the HPTT product oil was 63% at 200 °C, 82% at 260 °C, 89% at 300 °C and 84% at 350 °C. As reference, the energy of the oil fraction obtained by adding water to pyrolysis oil (OFWA) was just 36% of the starting oil. These results, together with the analyses of the aqueous phase products (Fig. 5), indicate that, from 200 °C to 300 °C, there was a transfer of energy from the aqueous phase to the oil phase. At 350 °C, some of the energy was transferred from the liquid phase to the gas phase, possibly induced by high temperature cracking. Therefore, this study indicates that HPTT concentrates the energy of pyrolysis oil substantially making it useful as energy carrier, further reducing the transportation costs as compared to untreated pyrolysis oil. From the organics that remain in the aqueous phase, value added chemicals may be recovered or the whole fraction can be gasified via steam reforming [16,17] or supercritical water gasification [18,19] to obtain hydrogen or synthesis gas.

Dilution of pyrolysis oil with water caused the decrease of the rate of formation of heavy compounds. However, the rate at which CO₂ was formed was also reduced. Therefore, the addition of water had positive and negative effects. At this stage it is not known whether decarboxylation and polymerisation are part of the same type of reaction or can be decoupled.

Although the oxygen and water content of the HPTT oil phase was lowered considerably with respect to untreated pyrolysis oil, miscibility tests showed that it was still completely immiscible with a conventional heavy refinery stream, Long Residue (properties of this oil can be found elsewhere [20]). This shows that oxygen and water content are not the only parameters that determine the quality of the upgraded product with respect to co-refining possibilities but other aspects (one of them most likely being the molecular weight distribution) are probably also of

importance. Further upgrading of the HPTT oil by HDO is an option that can be explored, as one of the obstacles of HDO of untreated pyrolysis oil is its high hydrogen consumption [6]. Since the HPTT oil phase has a much lower oxygen (between 20 and 27 wt.% on dry basis) than the original oil (40 wt.% on dry basis), the stoichiometric amount of hydrogen needed to convert oxygen into water is considerably reduced when using HPTT oil in HDO. Besides that, there are two other possible influences of the pre-treatment of pyrolysis oil via HPTT which might benefit the HDO process:

1. The lower content of light components and water in the oil phase might enable a higher hydrogen partial pressure at the same total reactor pressure thereby possibly reducing the required reaction times.
2. Components that remain in the water phase after HPTT are to a large extent acids and other small molecules (see Fig. 5), which are not likely to yield transportation fuel type components. Hydrogen consumption of these components during HDO is prevented as the aqueous fraction would be excluded from HDO.

One possible problem that has to be investigated is if the higher molecular weight components formed during HPTT are refractive towards further processing by HDO. Especially then, ways to prevent polymerisation during HPTT, like water dilution, are of crucial importance.

5. Conclusions

The current work has shown that the high pressure thermal treatment (HPTT) is an effective way to reduce the oxygen and water content of pyrolysis oil, thereby also substantially increasing the energy density.

The main phenomenon observed during HPTT of pyrolysis oil is a phase split that must be provoked by the change of polarity of various compounds. This is likely to be caused by dehydration, decarboxylation and probably polymerisation reactions. All these reactions are fast: the residence time did not have significant influences between 1.5 and 3.7 min. The process temperature (varied between 200 and 350 °C) did have a much larger influence on product yields and properties. Dilution of the organic components changes the speed of some of these reactions. However, it is not yet clear if the desired decarboxylation and the undesired increase of molecular weight are part of the same or different reaction paths.

Despite the reduction of oxygen and water content, the HPTT oil proved to be immiscible with a conventional heavy refinery stream (Long Residue). Further processing of HPTT oil via HDO, might be an option that could reduce the H₂ consumption during HDO as compared to direct HDO of pyrolysis oil.

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References

- [1] Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. *Renewable Sustainable Energy Rev* 2000;4:1–73.
- [2] Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils-state of the art for the end users. *Energy Fuels* 1999;13:914–21.
- [3] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 2004;18:590–8.
- [4] Samolada MC, Vasalos IA. Catalytic cracking of biomass flash pyrolysis liquids. In: Bridgwater AV, Boocock DGB, editors. *Developments in thermochemical biomass conversion*. London: Blackie Academic and Professional; 1997. p. 657–71.
- [5] Lappas AA, Bezegegianni S, Vasalos IA. Production of biofuels via co-processing in conventional refining processes. *Catal Today* 2008;145:55–62.
- [6] Elliott DC. Historical developments in hydroprocessing bio-oils. *Energy Fuels* 2007;21:1792–815.
- [7] Rep M, Venderbosch RH, Assink D, Tromp W, Kersten SRA, Prins W, et al. De-oxygenation of bio-oils. In: Bridgwater AV, Boocock DGB, editors. *Science in thermal and chemical biomass conversion*. Chippenham: CLP Press; 2006. p. 1526–35.
- [8] Oasmaa A, Solantausta Y, Arpiainen V, Kuoppala E, Sipila K. Fast pyrolysis bio-oils from wood and agricultural residues. *Energy Fuels* 2009; in press: doi:10.1021/ef901107f.
- [9] Oasmaa A, Kuoppala E, Solantausta Y. Fast pyrolysis of forestry residue. 2. Physicochemical composition of product liquid. *Energy Fuels* 2003;17:433–43.
- [10] Domalski ES, Jobe Jr TL, Milne TA. *Thermodynamic data for biomass materials and waste components*. New York: The American Society of Mechanical Engineers; 1987.
- [11] Knezević D, Van Swaaij WPM, Kersten SRA. Hydrothermal conversion of biomass. II. Conversion of wood, pyrolysis oil, and glucose in hot compressed water. *Ind Eng Chem Res* 2010;49:104–12.
- [12] Knezević D, Van Swaaij WPM, Kersten SRA. Hydrothermal conversion of biomass: I. Glucose conversion in hot compressed water. *Ind Eng Chem Res* 2009;48:4731–43.
- [13] Radlein D. The production of chemicals from fast pyrolysis bio-oils. In: Bridgwater AV, editor. *Fast pyrolysis of biomass. A handbook*. Newbury, Berkshire: CLP Press; 1999. p. 164–85.
- [14] Scholze B, Meier D. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC/MS, FTIR, and functional groups. *J Anal Appl Pyrolysis* 2001;60:41–54.
- [15] Boocock DGB, Sherman KM. Further aspects of powdered poplar wood liquefaction by aqueous pyrolysis. *The Can J Chem Eng* 1985;63:627–33.
- [16] Czernik S, French R, Feik C, Chornet E. Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. *Ind Eng Chem Res* 2002;41:4209–15.
- [17] Van Rossum G, Kersten SRA, van Swaaij WPM. Staged catalytic gasification/steam reforming of pyrolysis oil. *Ind Eng Chem Res* 2009;48:5857–66.
- [18] Kersten SRA, Potic B, Prins W, Van Swaaij WPM. Gasification of model compounds and wood in hot compressed water. *Ind Eng Chem Res* 2006;45:4169–77.
- [19] Van Rossum G, Potic B, Kersten SRA, van Swaaij WPM. Catalytic gasification of dry and wet biomass. *Catal Today* 2009;145:10–8.
- [20] De Miguel Mercader F, Groeneveld MJ, Kersten SRA, Way NWJ, Schaverien CJ, Hogendoorn JA. Production of advanced biofuels: co-processing of upgraded pyrolysis oil in standard refinery units. *Appl Catal B: Environ* 2010; in press. doi:10.1016/j.apcatb.2010.01.033.