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## Pyrolysis oil upgrading to transportation fuels by catalytic hydrotreatment

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### **Chapter 3: Insights in the Hydrotreatment of Fast Pyrolysis Oil using a Ruthenium on Carbon Catalyst**

#### **Abstract**

The use of Ru/C (5 %-wt.) as a catalyst for the hydrogenation of fast pyrolysis oil was explored at 350 °C and 200 bar pressure in a batch reactor set-up. The main objective was to determine the effect of the reaction time on the oil yield and elemental compositions of the product phases. Highest oil yields (65 %-wt.) were obtained after 4 h using a 5 %-wt. intake of catalyst on fast pyrolysis oil. Longer reaction times lead to a reduction of the oil yield due to the formation of gas phase components (methane, ethane, propane, CO/CO<sub>2</sub>). A solvent-solvent extraction procedure was applied to gain insights in the molecular processes during the catalytic hydrotreatment experiments. It appears that specifically the carbohydrate fraction is very reactive. The observations are rationalized by a set of reaction pathways for the various product phases.

## **1. Introduction**

Environmental concerns and possible future shortages have boosted research on alternatives for fossil derived liquid transportation fuels. Biomass is considered a promising alternative due to its high abundance and renewability. Various products from different sources of biomass have been proposed. A potentially interesting second generation transportation fuel is fast pyrolysis oil and bio-liquids derived thereof. Fast pyrolysis oils can be obtained from biomass in yields up to 70 %-wt. [1]. As of now, crude fast pyrolysis oil is not suitable for application in internal combustion engines and some upgrading is required. A suitable technology is hydrogenation, through which oils are hydrotreated and (some) bound oxygen can be removed in the form of water. Typically, catalysts and harsh operating conditions (400 °C and 200 bar) are required to obtain reasonable deoxygenation levels [2-5].

The majority of the catalytic and reactor engineering know-how on pyrolysis oil hydrodeoxygenation is derived from the hydrodesulphurization of fossil feeds (HDS). Typical hydrotreatment catalyst such as NiMoS and CoMoS on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are applied and the process is typically performed in packed bed reactor configurations [2-5]. A two stage approach appears necessary for hydrodeoxygenation to avoid severe coking. In the first stage (140-275 °C ) the oil is stabilized while the second stage (350-450 °C at pressures up to 300 bar) is applied to treat the ‘stabilized’ oil to obtain deep oxygen removal. Continuous operation in a downflow mode gave an oil in a yield of 30 to 55 % with an deoxygenation level of 99 % [6,7]. A limited numbers of studies in batch mode have been reported [5,8,9].

Apart from the conventional desulfurization catalysts, also noble metal catalysts have been reported for the hydrotreatment of pyrolysis oil. Gagnon *et al* [8] for example used ruthenium on alumina and NiW on alumina to hydrotreat (stabilized) oil. Elliott *et al.* [10,11] used ruthenium on carbon for the hydrotreatment of fast pyrolysis oil as well as representative model components. Typical conditions are 180-240 °C and hydrogen pressures of 133-142 bar in a down flow operated trickle bed reactor. This approach resulted in a reduction of the oxygen content from 41.3 %-wt. down to 20-27.0 %-wt.

We recently reported a catalyst screening study in a batch set-up with a range of noble metal catalysts (Ru/C, Ru/TiO<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Pt/C and Pd/C) at 250-350 °C and 100-200

bar [12]. Good performance of the Ru/C catalyst with respect to oil yield (up to 60 %-wt.) and deoxygenation level (up to 90 %-wt.) was observed [12]. Model component studies have also been performed using Ru/C to gain insight in the complex chemistry of the HDO of pyrolysis oil components [10,11,13]. Elliott studied the hydrotreatment of alkyl-substituted guaiacols (for example 4-alkyl-2-methoxyphenols) at elevated temperatures (250 °C). These components were converted to alkyl-cyclohexanols and at lower temperatures (150 °C) to alkyl-methoxy-cyclohexanols, indicating substantial hydrogenation activity of the catalyst for aromatic C-C bonds. Recently, Elliott reported the hydrotreatment of model components like acetic acid, guaiacol and furfural using Ru/C at 150-300 °C and pressures of 138 bar for a reaction time of 4 h [10,11]. This study shows that gasification to hydrocarbons and CO/CO<sub>2</sub> occurs to a significant extent. In our group the hydrotreatment (175-250 °C, 100 bar, 4 h) of model compounds (D-glucose, D-cellobiose) representative for the carbohydrate fraction in pyrolysis oil was studied using Ru/C as the catalyst [13]. The experiments show that carbohydrates are converted relatively fast (1 h of reaction time) to a mixture of polyols. In the absence of a catalyst, the carbohydrates are converted for a large part to solids showing that the carbohydrates are a potential source for char formation. An interesting finding was the observation that the solids formed from carbohydrate conversions are not inert and are catalytically converted to liquid and gasphase components [13].

We here report a study on the effect of process conditions, and particularly the reaction time, for the hydrotreatment of fast pyrolysis oil with Ru/C in a batch reactor set-up to determine the optimum time with respect to oil yield. The mass balances were constructed and the resulting gas and liquid products were analysed in detail. In addition, a solvent-solvent extraction approach was used to gain insight in the molecular processes occurring during the hydrotreatment of fast pyrolysis oil. On the basis of the experimental findings an overall reaction scheme for the hydrotreatment of fast pyrolysis oil is proposed.

## **2. Materials and Methods**

### 2.1 Materials

Fast pyrolysis oil was supplied by BTG (Enschede) and was prepared from beech wood. Relevant properties of the oil are given in Table 1. The noble metal catalysts Ru/C was obtained from Sigma Aldrich and contained 5 %-wt. of active metal. Hydrogen and helium were obtained from Hoek Loos (Schiedam) and were of analytical grade (hydrogen 6.0). Nitrogen (technical grade, >98 % purity) was also obtained from Hoek Loos (Schiedam). Tetrahydrofuran and n-decane were obtained from Acros and were of analytical grade (99.99 %).

Table 1. Properties of fast pyrolysis oil used in this study

Property	Value
Water content (%-wt.)	27.8
Elemental composition, dry base (%-wt.)	
C	58.6
H	6.2
O	35.2

### 2.2 Hydrodeoxygenation experiment

Fast pyrolysis oil was hydrotreated in a 100 ml batch autoclave setup (Buchi AG). The maximum pressure and temperature of the set-up are 350 bar and 450 °C, respectively. The temperature of the system is controlled using an electric heating mantle combined with a cooling spiral using water. The reactor content is stirred at 1300 rpm with a magnetically driven gas inducing impeller (Ruston type). Temperature and pressure in the reactor vessel are measured and monitored by a PC.

The reactor was filled with fast pyrolysis oil (25 g) and catalyst (1.25 g, 5 %-wt. on basis of wet pyrolysis oil). Subsequently, the reactor was flushed with nitrogen gas and pressurized with 20 bar of hydrogen at room temperature. The reactor was heated to the reaction temperature (350 °C) with a heating rate of 16 °C/min and kept at that temperature for the intended reaction time. Subsequently, the pressure in the reactor was set to 200 bar by adding hydrogen gas to the reactor. The pressure during a run was kept

constant by continuous feeding of hydrogen. After completion of the reaction the reactor was cooled to ambient temperature. The pressure was recorded for mass balance calculations and the gas phase was sampled using a gas bag. The liquid product, consisting of a water phase and two organic phases, was recovered from the reactor using a syringe and the liquid products weighed. Subsequently, the reactor was rinsed with acetone. The combined acetone fractions with suspended solids were filtered. After filtration, the filter was dried and weighed. The amount of solids minus the original catalyst intake was taken as the amount of solids formed during the HDO process. The deep HDO experiments were conducted in duplicate. The experimental error in the mass balance and elemental composition was between 5-10 %-wt.

### 2.3 Analyses of the HDO oils

#### 2.3.1 GC/MS and 2D-GC analyses

Samples were either injected pure or diluted with tetrahydrofuran (THF) to 50 %-wt. n-Decane was used as an internal standard.

GC-MS analysis were performed on a Quadrupole Hewlett Packard 5972 MSD attached to a Hewlett Packard 5890 GC equipped with a 30 m x 0.25 mm i.d. and 0.25  $\mu\text{m}$  sol-gel capillary column. The injector temperature was set at 250  $^{\circ}\text{C}$ . The oven temperature was kept at 40  $^{\circ}\text{C}$  for 5 minutes then heated up to 250  $^{\circ}\text{C}$  at a rate of 3  $^{\circ}\text{C min}^{-1}$  and then held at 250  $^{\circ}\text{C}$  for 10 minutes.

2D-GC analyses were performed on a trace 2D-GC from Interscience equipped with a cryogenic trap system and two columns, a 30 m x 0.25 mm i.d. and 0.25  $\mu\text{m}$  film of sol-gel capillary column connected to a 148 cm x 0.1 mm i.d. and 0.1  $\mu\text{m}$  film Restek 1701 column. An FID detector was applied. A dual jet modulator was applied using carbon dioxide to trap the samples. The lowest possible operating temperature for the cold trap is 60  $^{\circ}\text{C}$ . Helium was used as the carrier gas (flow 0.6 ml/min). The injector temperature and FID temperature were set at 250  $^{\circ}\text{C}$ . The oven temperature was kept at 60  $^{\circ}\text{C}$  for 5 minutes then heated up to 250  $^{\circ}\text{C}$  at a rate of 3  $^{\circ}\text{C min}^{-1}$ . The pressure was set at 70 kPa. The modulation time was 6 seconds.

### 2.3.2 Elemental composition, NMR analyses and water content

The elemental composition of the HDO oils (C, H and N) was determined using an Euro Vector 3400 CHN-S analyzer. The oxygen content was determined by difference.

<sup>1</sup>H- NMR spectra were recorded on a 500 MHz NMR (Varian). The samples were dissolved in CDCl<sub>3</sub>.

The water content in the samples was determined by a Karl Fischer titration using an Metrohm Titrino 758 titration device. A small amount of product (0.03-0.05 g) was added to an isolated glass chamber containing Hydranal (Karl Fischer Solvent, Riedel de Haen). The titrations were carried out using the Karl Fischer titrant Composit 5K (Riedel de Haen). All measurements were performed in duplo.

### 2.4 Gas phase analyses

The gas phases after reaction were collected and stored in a gas bag (SKC Tedlar 3 Liter Sample Bag (9.5" x 10") equipped with a polypropylene septum fitting. GC-TCD analyses were performed on a Hewlett Packard 5890 Series II GC equipped with a Porablot Q Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> column and a Molecular Sieve (5A) column. The injector temperature was set at 150 °C, the detector temperature at 90 °C. The oven temperature was kept at 40 °C for 2 minute then heated up to 90 °C at 20 °C/min and kept at this temperature for 2 minutes. The columns were flushed for 30 seconds with gas sample before starting the measurement. A reference gas containing H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, ethylene, ethane, propylene and propane with known composition was used for peak identification and quantification.

### 2.5 Solvent-solvent fractionation

The fast pyrolysis oil used in this study was fractionated by a solvent-solvent extraction according to the scheme provided in Figure 1. The various steps will be discussed in the following.

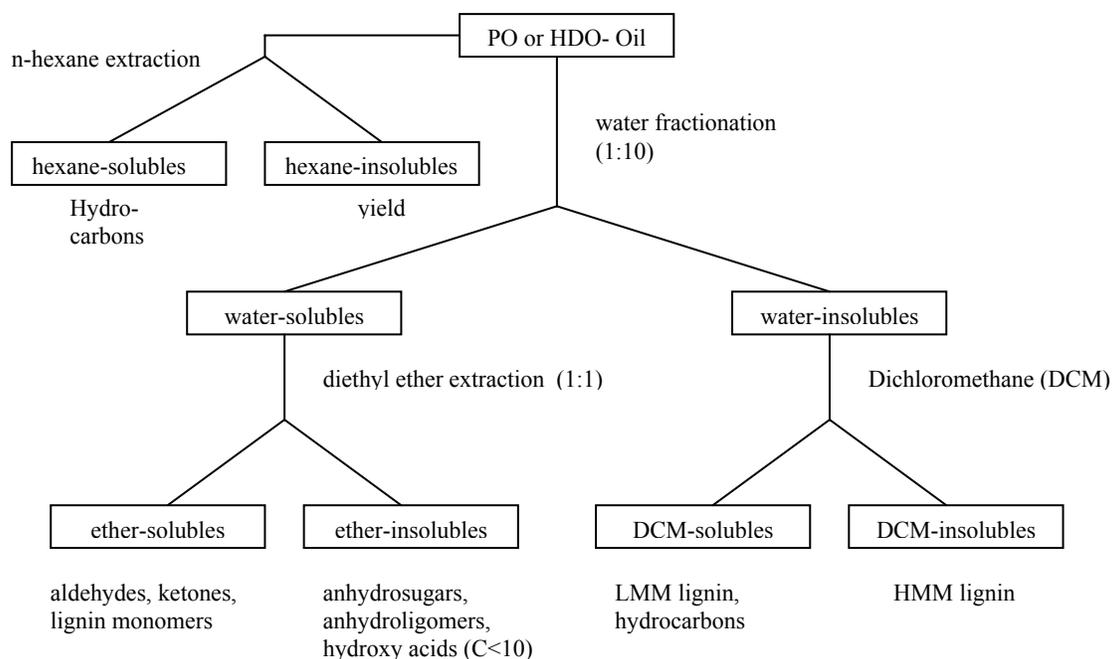


Figure 1. Fractionation scheme applied to pyrolysis oil and HDO oil [14,15].

*Oil extraction using n-hexane as solvent.* A typical pyrolysis oil sample was extracted with n-hexane (1:1). Two phases were formed, a brown liquid top phase (n-hexane solubles) and a viscous black-brown bottom phase (n-hexane insolubles). For determination of the mass balance both samples were dried and weighed. The n-hexane soluble fraction contains large amounts of hydrocarbons and is labeled as hydrocarbons.

*Oil extraction using water as solvent.* An oil sample was extracted with water (1:10). The water was added dropwise into the oil to prevent solids formation. This resulted in two liquid phases, a clear liquid light brown phase (water solubles) and a viscous black phase (water insolubles). Both liquid phases were further extracted using different solvents. For determination of the mass balance the water insoluble fraction was dried in air until constant weight was achieved. The water content of the water soluble fraction was determined using Karl Fischer titration.

*Water solubles extraction using diethyl ether as solvent.* The water soluble fraction was extracted further with diethylether (1:1). This resulted in two phases, a top phase (diethyl ether solubles) and a water phase (diethyl ether insolubles). For determination of the mass balance the ether soluble fraction was dried and weighed. The water content of the ether

insolubles fraction was determined using a Karl Fischer titration. The diethylether soluble fraction contains mainly aldehydes, ketones and lignin monomers and is labeled as such. The diethyl ether insolubles mainly consists of sugars (sugar fraction).

*Water insolubles extraction using dichloromethane as solvent.* The water insoluble fraction was extracted further with dichloromethane (1:1). Two phases were formed, an organic top phase (dichloromethane solubles) and a solid phase (dichloromethane insolubles). For the determination of the mass balance both samples were dried until constant weight. The weight of dichloromethane solubles was corrected for the hydrocarbon content by subtraction of the weight of the hydrocarbon fraction as determined by n-hexane extraction. The dichloromethane soluble fraction contains low molecular weight lignins and is labelled as the DCM soluble fraction. The dichloromethane insoluble fraction is rich in higher molecular weight lignin fragments and is labeled the DCM insoluble fraction.

### **3. Results and Discussion**

The hydrotreatment experiments were carried out in a batch autoclave at constant temperature (350 °C) and pressure (200 bar) with Ru/C as the catalyst. The liquid product after reaction consisted of three different phases, a slightly yellow aqueous phase and two brown oil phases, one with a density higher than water and a density lower than water. Furthermore substantial amounts of solids (coke/char) and gas phase organics were formed as well.

#### *3.1 Effect of reaction time on product yield and deoxygenation level*

The effect of reaction time on the weight of the various phases after reaction was determined in the range of 1 to 6 h and the results are shown in Figure 2.

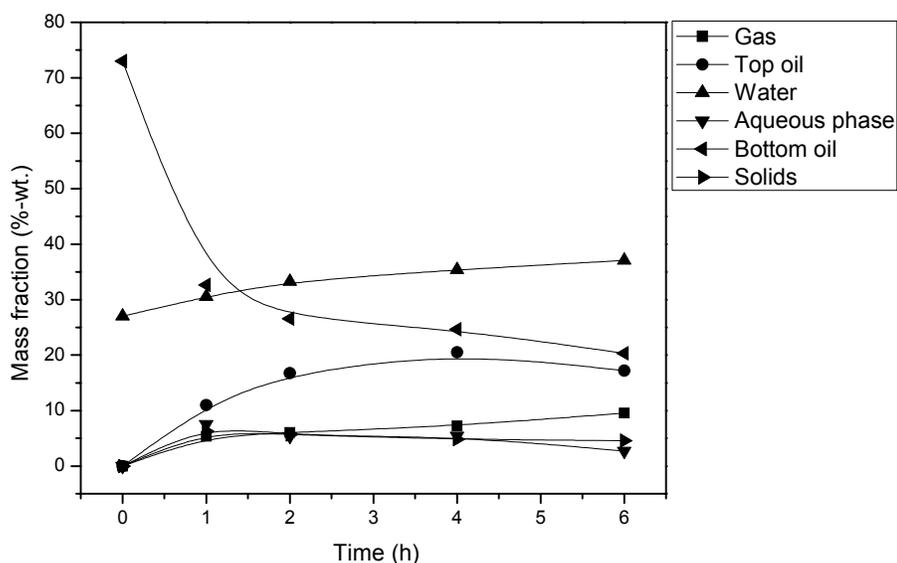


Figure 2. Product distribution for the hydrotreatment of pyrolysis oil (350 °C and 200 bar, Ru/C catalyst) at different reaction times (dry base, except for the aqueous phase)

In general the mass balance closure was very good, ranging from 93 % to 96 %. The amount of bottom oil decreased with time. The amount of top oil increased from 1 to 4 h after which it also decreased in time. For illustrative purposes the total oil yield, being the sum of the top and bottom oil, is provided in Figure 3. The total oil yield increased in time when going from 1 to 4 h reaction time. The highest product yield (65 %-wt.) was obtained at a reaction time of 4 h. At longer reaction time the oil yield was lower. Thus, from a yield perspective, a 4 h reaction time seems preferred.

This decrease in total oil phase when going from 4 to 6 h is associated with an increase the amount of gas phase components (Figure 2). This indicates that the oil phase is further (hydro-cracked) to gas phase components (*vide infra*).

Furthermore, the amount of solids decreased at prolonged reaction times, indicating that solids formed in the course of the reaction are susceptible for further gasification and/or liquefaction. This explanation is supported by recent model studies on the carbohydrate fraction of fast pyrolysis oil [13], which indeed showed that the solids formed upon catalytic hydrotreatment of carbohydrates are not inert.

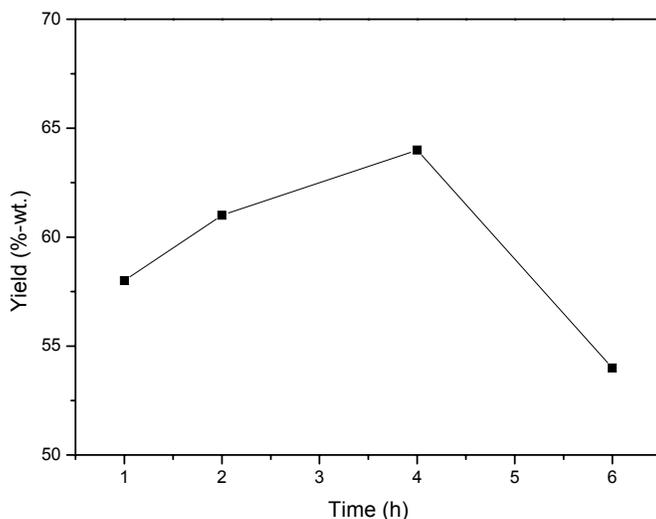


Figure 3. Total oil yield (dry basis) for the hydrotreatment of pyrolysis oil (350 °C and 200 bar, Ru/C) versus reaction time.

The amount of water in the system increased from 28 %-wt. to 37 %-wt. during reaction. A likely explanation is the formation of water due to dehydration (repolymerisation) and hydrodeoxygenation reactions [16].

Figure 4 shows the composition of the gas phase as a function of reaction time. For all experiments, un-reacted hydrogen is still present at the end of the reaction, indicating that hydrogen is not limiting. The main components formed are CO<sub>2</sub> and methane, the latter typically observed while using Ru/C [17]. The amount of methane is about constant (8-12 %-wt.), and appears to be formed in the first hour of reaction only. The amount of methane may be related to the level of Ru dispersion on the support [18], as was shown in a recent investigation by our group [19].

The initial formation of CO<sub>2</sub> and CO are due to various decarboxylation and decarbonylation reactions, respectively [20-23], as it has been observed for uncatalyzed experiments as well (HPTT process) [24]. The amount of carbon dioxide increases from 13 to 19 %-mol during the reaction time. This suggests that, after an initial rapid production, further CO<sub>2</sub> formation by decarboxylation reactions is relatively slow.

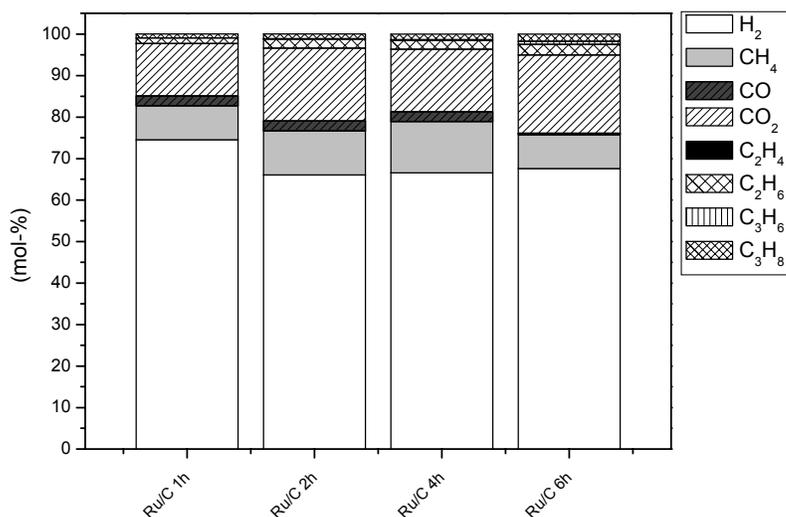
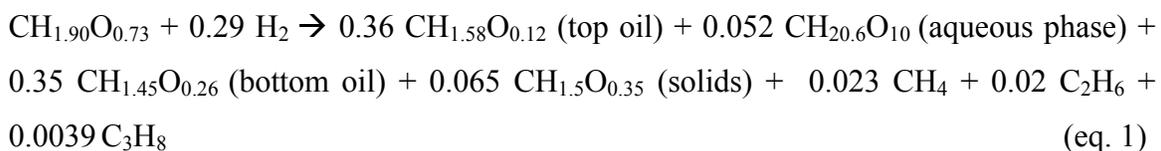


Figure 4. Gas composition for the hydrotreatment of fast pyrolysis oil at different reaction times (Ru/C, 350 °C, 200 bar).

Also of interest is the gradual increase in the amount of higher alkanes (ethane, ethane, propene and propane) in the course of the reaction (from 2.3 to 5.0 %-mol). These could be produced by hydrocracking of larger hydrocarbons formed during the hydrotreatment reaction (*vide infra*).

### 3.2 Hydrogen consumption

Hydrogen consumption during the catalytic hydrotreatment reaction will be a major variable cost contributor for the process [25]. Unfortunately, in the present set-up, it was not possible to accurately determine the hydrogen uptake during the reaction. However, with the mass balances and elemental composition available for each phase, it can be calculated. The reaction stoichiometry as determined from the elemental data (wet base) for the different phases for a typical run (6 h) is shown in eq. 1.



The calculated hydrogen consumption based on this approach for all reaction times are presented in Figure 5.

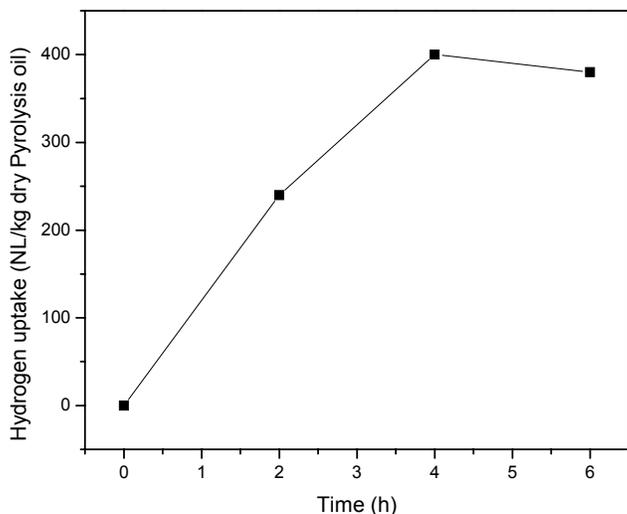


Figure 5. Hydrogen consumption versus time for the hydrotreatment of fast pyrolysis oil (Ru/C, 350 °C, 200 bar.)

Thus, the hydrogen uptake increases with time when going from 1 to 4 h and remains almost constant at prolonged reaction times. An explanation may be catalyst deactivation, however, the composition and amounts of the various phases still changes in the last 2 h of reactions. A more detailed study on catalyst deactivation is reported in a separate chapter [19], showing that deactivation occurs to a significant extent. The ongoing changes in amount and composition of the various phases suggests nevertheless that chemical reactions continue to take place, but are either thermal in nature or do not involve excessive amounts of hydrogen.

A hydrogen consumption of 400 NI per kg dry bio-oil (4 h reaction time) coincides well with data from literature. For example, Elliott *et al.* [26] reported an hydrogen uptake of 461 NI/kg dry bio-oil in a continuous packed bed reactor with two temperature zones (150 °C and 365 °C) to arrive at a deoxygenation level of 92 %.

### 3.3 Carbon distribution as a function of time

Of particular interest is the carbon distribution between the various phases as a function of time. The carbon content of each phase was determined from the mass balances in combination with the elemental composition of each phase. The C-balance closure ranges from 93-100 %. The results are given in Figure 6.

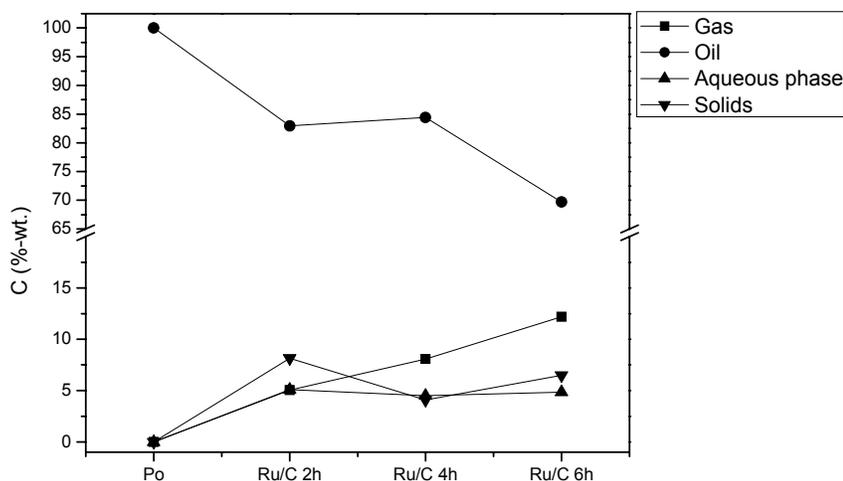


Figure 6. The carbon distribution for each phase as function of the reaction time (Ru/C catalyst, 350 °C, 200 bar).

The carbon content in the oil product decreases to ~84 %-wt. of the original C content of the pyrolysis oil after 2 h reaction time and remains constant at this value till about 4 h. Between 4 and 6 h the carbon content drops down to ~70 %-wt. A considerable amount of carbon is transformed to gaseous components, and the C content in the gas phase increases throughout the reaction to about 10 %-wt. (methane, higher alkanes and CO/CO<sub>2</sub>, *vide supra*). Furthermore, a significant amount of the carbon ends up in the aqueous phase formed during the reaction and in the solids (char/coke). While the carbon content of the water phase is about constant throughout the reaction time (4-5 %-wt.), the solids initially retain a rather high carbon content (8 %-wt) but this is reduced down to 4 to 5 %-wt. after long reaction times.

### 3.4 Composition of the product oils

A useful representation to present the effect of process conditions on the elemental composition of the product oils is the Van Krevelen plot [27]. Figure 7 depicts the weight average elemental data of the two product oils (top and bottom oil) at different reaction times.

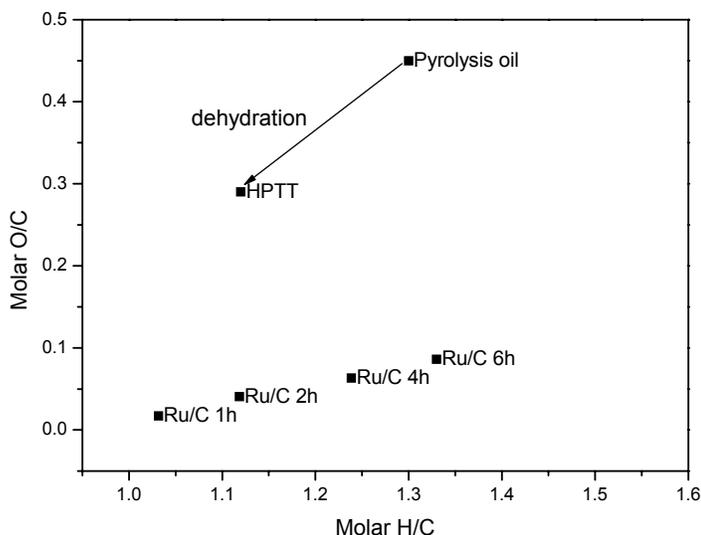


Figure 7. The Van Krevelen plot of the weight average elemental data for the produced oils (dry base) at different reaction times (5 %-wt. Ru/C, 350 °C and 200 bar).

Also shown in the figure is a point indicated with HPTT. This is a process where the pyrolysis oil is heated up to elevated temperatures (250-350 °C) in the absence of hydrogen at a pressure of 200 bar or higher and a residence time of 0.5-2 min. This leads to the formation of two liquid phases *viz* a water phase on top and an oil phase on the bottom which is more viscous than pyrolysis oil. During the HPTT process CO<sub>2</sub> and CH<sub>4</sub> are formed, indicative for the occurrence of thermal decarboxylation and cracking. When comparing the elemental composition of typical HDO oils with that of HPTT oils, it is clear that indeed catalytic hydrotreatment occurs to a significant content when using hydrogen in combination with Ru/C as the catalyst.

The H/C ratio increases from 1.05 to 1.32 as a function of the reaction time indicating hydrogenation activity throughout the time of reaction. The O/C ratio increases from 0.02

to 0.07 when going from 1 h to 6 h reaction time. A possible explanation for the latter observation is transfer of components with a lower O/C ratio from the oil phases to either the gas phase or aqueous phase in the course of the reaction. The formation of significant amounts of higher alkanes (particularly ethane and propane) was indeed observed (Figure 4) showing the validity of this pathway. Another explanation is transfer of components with a higher O/C ratio from the aqueous phase to the oil phase in the course of the reaction. The amount of organics dissolved in the aqueous phase indeed decreases from 7 down to 2 %-wt. with reaction time and the O/C ratio of the organics in the aqueous phase also decreased from 0.89 to 0.13 after 6 h of reaction. Alternatively, cracking of the char molecules could also occur, yielding higher oxygen containing molecules. But considering the limited amount of char reduction in time, this would have a very limited effect on the overall O/C ratio.

It should be noted that composition of the ‘top’ oils and ‘bottom’ oils differs considerably. Figure 8 shows the van Krevelen plot for both phases at different reaction times. The top oils have a higher H/C ratio and O/C ratio than the bottom oils.

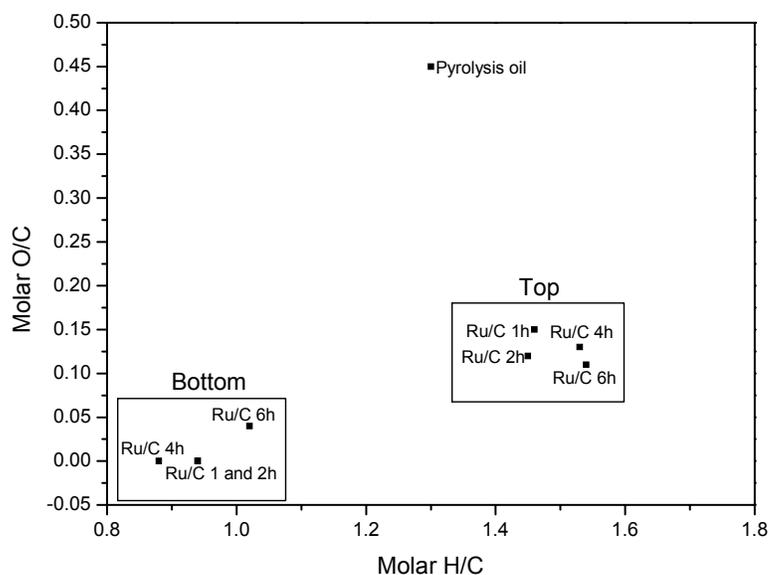


Figure 8. Van Krevelen plot of the elemental data for the produced oils (dry base) at different reaction times (5 %-wt. Ru/C, 350 °C and 200 bar).

<sup>1</sup>H-NMR was used to gain insights in the differences in the molecular composition of the top and bottom oil. The method published by Ingram *et al.* [28] was applied for functional group analyses and quantification, wherein regions in <sup>1</sup>H-NMR spectra are assigned to certain functional groups and the relative amount is calculated from the peak integrals (Table 2).

Table 2. Functional group analyses of the fast pyrolysis oil used in this study and a representative top and bottom hydrotreated product using <sup>1</sup>H-NMR.

Chemical shift region (ppm)	Type of protons [28]	Pyrolysis oil Hydrogen content (% area of total)	Top Product oil (Ru/C) Hydrogen content (% area of total)	Bottom Product oil (Ru/C) Hydrogen content (% area of total)
10-8.0	-CHO, -COOH, downfield ArH	0.9	0	0
8.0-6.8	ArH, HC=C (conjugated)	3.3	1.4	1.6
6.8-6.4	HC=C (nonconjugated)	4.4	3.7	4.2
6.4-4.2	-CH <sub>n</sub> -O-, ArOH, HC=C (nonconjugated)	9.0	1.5	3.1
4.2-3.0	CH <sub>3</sub> O-, -CH <sub>2</sub> O-, -CHO-	26.3	3.2	3.4
3.0-2.2	CH <sub>3</sub> C(=O)-, CH <sub>3</sub> -Ar, -CH <sub>2</sub> Ar	6.4	4.9	13.5
2.2-1.6	-CH <sub>2</sub> -, aliphatic OH	32.7	17.4	32.6
1.6-0.0	-CH <sub>3</sub> -, -CH <sub>2</sub> -	17.0	67.9	32.6
Aliphatic/aromatic <sup>a</sup>	-	6.4	16.4	11.2

a. Ratio of the area % at 2.2-0 ppm and 8-6.4 ppm.

In line with the measured higher H/C ratio, the aliphatics content in the top oil as calculated using this procedure is higher than for the bottom oil. Thus, the top oil is more

apolar in nature as expressed by a higher H/C ratio, contains more aliphatics (NMR), has a lower density than water and possesses a relatively low water content.

### 3.5 Molecular insights by product fractionation using solvent-solvent extraction

A solvent-solvent extraction based on the work of Oasmaa *et al.* [14,15] was used to gain insight in the reactivity of various component classes (fractions) in the fast pyrolysis oil during the catalytic hydrotreatment process. The fractionation scheme (Figure 1) was applied to the original fast pyrolysis oil and oil products obtained at different reaction times (350 °C and 200 bar). The results are given in Figure 9.

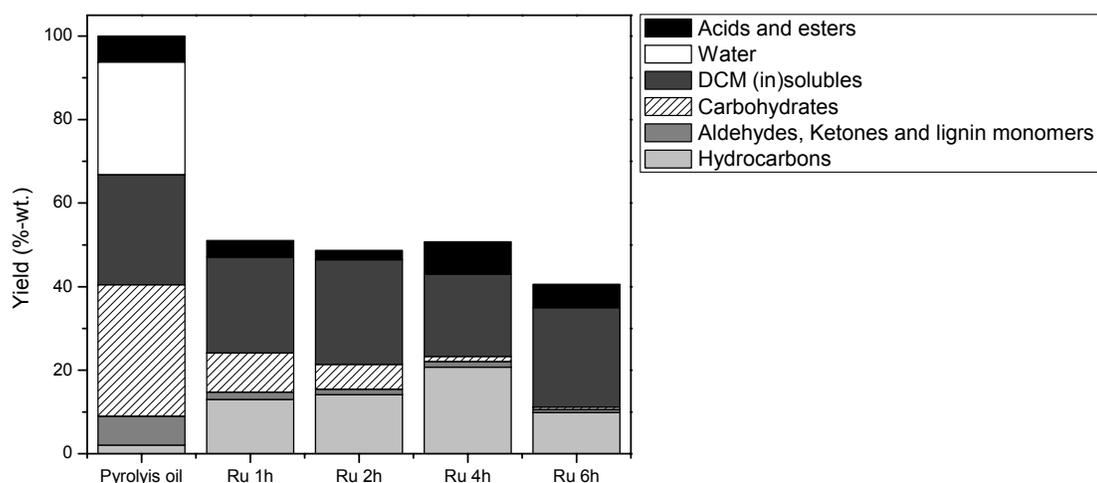


Figure 9. Composition of fast pyrolysis oil and hydrotreated oil products (Ru/C, 350 °C, 200 bar) at various reaction times using solvent-solvent extraction

It shows the amounts of the various fractions (carbohydrates, aldehydes/ketones/lignin monomers, hydrocarbons, acids and esters) as a function of the reaction time.

As expected on the basis of the product composition by elemental analysis and NMR, the amount of hydrocarbons produced during the reaction in the organic products increases from 2.1 to 20.7 %-wt. in the first 4 h. This increase is expected due to hydrodeoxygenation and hydrogenation reactions of oxygenates. However, the amount decreases in the period 4-6 h. A likely explanation is the occurrence of (hydro)cracking reactions of the hydrocarbons to gas phase components. This is confirmed by an increase

in the amounts of ethane and propane in the gas phase in the course of the reaction, see Figure 6 for details.

A large and relatively fast decline in the carbohydrate fraction is visible in the initial part of the reaction and the carbohydrate fraction is almost completely converted to other components within 6 h. The fraction is most likely converted to liquid phase polyols (distributing between the organic and aqueous phase) and subsequently into hydrocarbons as shown by Wildschut *et al.* [13] in a model study using monomeric carbohydrates. Also the aldehyde, ketone and lignin monomer fraction is rapidly decreasing in time, a clear indication for the high reactivity of this compound class. This is in line with catalytic hydrotreatment studies with model components [10,11].

Of interest is the rather constant level of the DCM (in)solubles fraction which is rich in lignin. However, this does not necessary imply that this fraction is inert. The lignin fractions not only contain low and higher molecular weight lignins but a variety of other reactive components. The results imply that conversion to other components not belonging to this fraction occurs with a similar rate as the reactions leading to the formation of components in this fraction.

### 3.6 Reaction network/pathways

In combination with available literature data, this study on the time dependency of the product phases during the catalytic hydrotreatment of fast pyrolysis oil allows construction of an overall reaction scheme (Figure 10). In the course of the hydrotreatment reaction, pyrolysis liquid can react according to various parallel and/or consecutive reactions. At the initial stage of the reaction (order of minutes, not investigated here), it is well known that thermal reactions occur, leading to phase separation (water and organics) [26]. This non-catalytic thermal treatment is referred to as HPTT. The oxygen content of such oils was reduced from 40 %-wt. to ~25 %-wt. in the organic phase of the HPTT product (both on dry basis); the aqueous phase contains 15 to 30 %-wt. organic material. These HPTT reactions appear mainly re-polymerization reactions, which result in a relatively apolar fraction separated from an aqueous phase. Gaseous products are mainly CO<sub>2</sub> and CO. This process is also expected to take place in the presence of hydrogen and catalysts due to its fast nature. The repolymerised, higher

molecular weight products are likely not inert under reaction conditions and further polymerise to solids in the form of char.

Besides these thermal reactions, various catalytic reactions take place when H<sub>2</sub> and catalysts are present. These include catalytic hydrodeoxygenation (water production), catalytic decarboxylation/decarbonylation (CO<sub>2</sub> and CO production) and methanation (Figure 4). Due to a change in the product characteristics upon reaction and particularly the polarity of the various phases a two or three phase liquid system is obtained (an aqueous phase and one or two organic phases), depending on residence time and temperature. At milder conditions (175-250 °C, known as stabilisation, not investigated here), hydrodeoxygenation occurs to a lesser extent and only two liquid phases (watery and one organic phase) are obtained after reaction. At the rather extreme conditions applied in this study (350 °C, 200 bar), the formation of two organic phases with a different composition is observed (Figure 2). The formation of an apolar top phase is likely due to further hydrogenation of various intermediate products leading to components with a more apolar character (higher H/C ratio, see Figure 8). The liquid-liquid extraction study presented here shows that the sugar fraction during deep hydrotreatment is reactive and converted quantitatively. This is associated with the formation of a hydrocarbon rich fraction. The amount of hydrocarbons shows an optimum in time. After 4 h reaction time, the amount decreases, likely due to gasification to (higher) alkanes by hydrocracking reactions. The repolymerised compounds formed by the parallel non-catalytic HPTT reactions are likely not inert under catalytic hydrotreatment conditions and are also hydrotreated to end up in the rather apolar oily product phases. The char formed in the course of the reaction is not necessarily inert (Figure 2) and may participate in various reactions leading to gas phase or liquid phase components. This was also confirmed by model studies on the carbohydrate fraction using Ru/C catalysts [13].

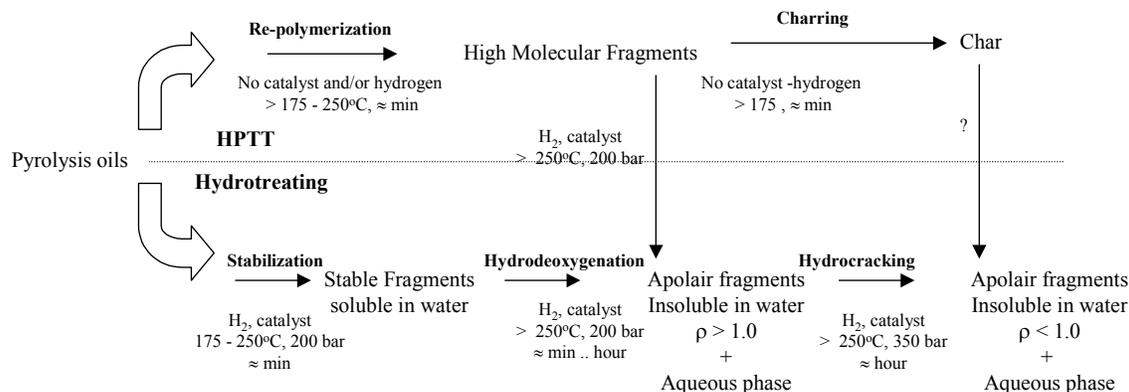


Figure 10. Proposed reaction scheme/pathways for hydrotreatment of fast pyrolysis oil

#### 4. Conclusions

The effect of reaction time (1-6 h) on the product distribution for the catalytic hydrotreatment of fast pyrolysis oil was explored in a batch reactor set-up using a Ru/C catalyst (350 °C, 200 bar). The mass balance and carbon balance for each phase (two oil products, one aqueous phase, gas and solid phase) were determined. The highest oil yield was obtained for 4 h reaction time (65 %-wt.). An increase of the reaction time leads to a decrease of the oil yield due to the formation of gas phase components, the majority being methane, higher alkanes and CO/CO<sub>2</sub>. The amount of solids varies between 6.3 and 4.6 %-wt. and shows an optimum with respect to reaction time, indicating that the solids are not inert but participate in the reactions. Elemental data indicate that the H/C ratio of the oil is a function of the reaction time and increases from 1.05 to 1.35 after 6 h of reaction time. Solvent-solvent extraction shows that the amount of the hydrocarbon fraction is time dependent and actually shows an optimum (20.7 %-wt.) after 4 h reaction time. Of particular interest is the rapid decrease of the carbohydrate fraction in the fast pyrolysis oil, an indication for the high reactivity of this fraction under catalytic hydrotreatment conditions. Together with existing literature data, the findings may be rationalized by a reaction scheme involving repolymerisation, hydrogenation, charring and hydrocracking reactions

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