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Pyrolysis Oil Stabilisation by Catalytic Hydrotreatment

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1. Introduction

Being the only sustainable product containing carbon, biomass is the only alternative for fossil derived crude oil derivatives. Research on the use of biomass for first generation biofuels is rapidly expanding (e.g. bio-ethanol from sugar sources and starches and bio-diesel from pure plant oils). Biomass, and in a particular ligno-cellulosic material, is difficult to convert easily into transportation fuels. Research is focused on indirect routes like: i) the fractionation of biomass and fermentation of the cellulosic and hemi-cellulosic fraction to ethanol, and ii) the destructive gasification of the complete biomass to produce syngas for further upgrading to e.g. methanol or Fischer-Tropsch diesel. Conventional refinery scales (up to 100 t/hr crude oil equivalence) are preferred for economic reason, but problematic for biomass resources, as biomass is scattered and collection is costly. In addition, various types of biomass are very different in structure and composition, have a low energy density compared to many fossil resources, and often contain significant amounts of water and ash. Such disadvantages can be overcome if the biomass is first de-centrally restructured, densified at a scale of 2 to 10 t/hr, and (preferably simultaneously) 'decontaminated'. The intermediate product is then transported to a large central processing unit where it is transformed to the final product (at a scale of say 50 to 200 t/hr). A potentially attractive technology for this purpose is fast pyrolysis (see recent review of Venderbosch&Prins, 2010). Pyrolysis liquids contain negligible amounts of ash, and have a volumetric energetic density 5 to 20 times higher than the original biomass. However, the oil is acidic in nature, polar and not miscible with conventional crude oil. In addition, it is unstable, as some (re)polymerisation of organic matter in the oil causes an increase in viscosity in time. Pyrolysis oil should thus not be regarded as an oil in a historic perspective, but merely as a carbohydrate rich syrup. Proof for this statement is given by a solvent fractionation method, where the largest part of the oil, up to 70%, can be easily extracted by water. A typical example is presented in Figure 1 (and analysis in Table 1), where pyrolysis oil is divided into several groups of compounds, differing in oxygen functionality and molecular size (Oasmaa et al. 2003; Oasmaa, 2003). Interestingly, the large ether insoluble fraction contains significant amounts of sugar-like components, and has the appearance of a syrup-like liquid. The high levels of oxygen in the pyrolysis oil are reported to be the main cause for the unstable character. However, it may be apparent that not the oxygen itself renders the pyrolysis oil unstable, but the nature/reactivity of the oxygen containing functional chemical groups. Especially the carbonyl compounds (aldehydes, ketones) seem to be

responsible for the thermal instability and transformation into less reactive organic groups (f.i. to the corresponding alcohols) seems a viable option.

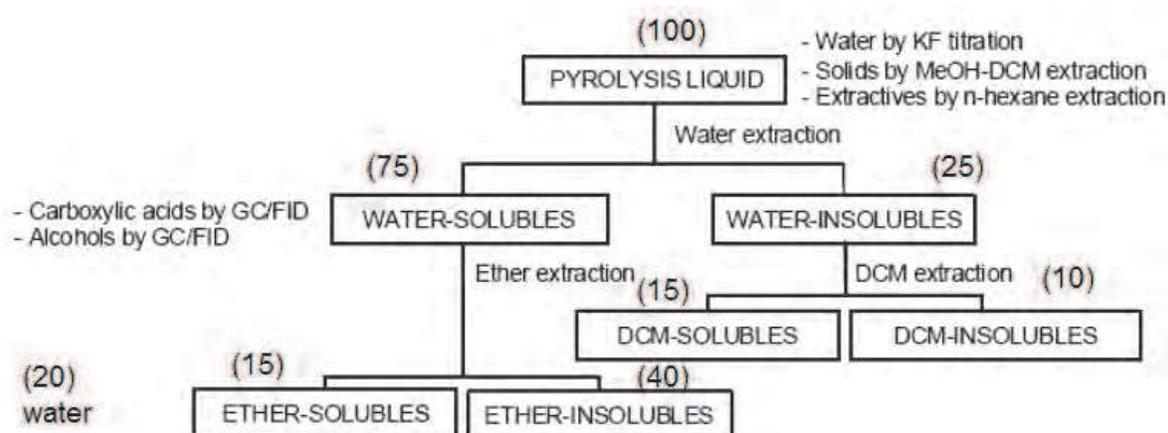


Fig. 1. Fractionation scheme (Oasmaa, 2003)

	wt % (wet basis)	COMPOUND TYPES	C	H	N	O
WATER-SOLUBLES	75-85		wt % (dry basis)			
Acids, alcohols	5-10	$\text{O}=\text{C}-\text{CH}_3$ $\text{HO}-\text{C}-\text{H}$ $\text{H}_3\text{C}-\text{OH}$	36.0	6.0	0	58.0
Ether-solubles	5-15		60.0	6.0	0.1	33.9
Ether-insolubles	30-40		46.0	6.3	0.3	47.4
Water	20-30		0	11.1	0	88.9
WATER-INSOLUBLES	15-25		66.2	6.6	0.3	26.9
n-Hexane-solubles	2-6	$\text{CH}_3-(\text{CH}_2)_n-\text{CO}_2\text{H}$ n = 10-30 $\text{HOCH}_2-(\text{CH}_2)_n-\text{CO}_2\text{H}$ n = 10-28 	77.4	10.4	0	12.2
DCM-solubles	5-10		68.1	6.7	0.4	24.7
DCM-insolubles	2-10	degraded lignin	64.1	5.9	1.5	28.4

Table 1. Chemical composition of reference pine oil and its fractions (Oasmaa, 2003)

A number of catalytic approaches have been proposed to upgrade and improve the product properties of fast pyrolysis oil. A well known example is catalytic cracking of pure biomass and/or pyrolysis oil to oxygen-free products. However, this approach is accompanied by a

significant amount of coke production (up to 40 wt.% of the biomass) (Horne & Williams, 1996; Vispute et al., 2010) and this issue needs to be resolved.

A number of studies have been performed with the objective to remove the bound oxygen in the form of CO and/or CO₂ by decarbonylation and decarboxylation reactions, either thermally or catalytically. The thermal process is known as the HPTT process, a high pressure temperature treatment (De Miguel Mercader et al., 2010). However, oxygen removal beyond a level of 10% appears very difficult with this approach, even when using catalysts, and the product is highly viscous, limiting its application potential.

Catalytic hydroprocessing or hydrotreating of fast pyrolysis oil is a more promising option (Conti, 1997; Elliott, 2007; Elliott et al.; 2009; Kaiser 1997; Rep et al., 2006). In this process, the fast-pyrolysis oil is treated with hydrogen in the presence of a heterogeneous catalyst with the aim to hydro(deoxy)genate the pyrolysis oil to a product with improved product properties.

A potentially attractive outlet for the upgraded oils is its use as co-feed in existing oil refinery units. This enables partial substitution of the fossil carbon in liquid transportation fuels by renewable carbon from biomass in existing infrastructure as proposed in the European Biocoup project. As such, it is expected to lower the investment costs and to facilitate other barriers for introduction of the fast pyrolysis technology. Crude pyrolysis oil, however, cannot be used for co-feeding purposes. It is immiscible with typical petroleum feeds (such as vacuum gas oil) due to the presence of polar components, but moreover, it is highly acidic due to the presence of organic acids (up to 10 wt%) (Oasmaa, 2003) leading to corrosion issues and possibly detrimental effects on typical catalysts in the refinery units (e.g. zeolites in the FCC process) (Dimitrijevic et al., 2006). Furthermore, it has a strong tendency for coking at elevated temperatures.

An alternative product outlet for upgraded pyrolysis oils is the direct use as a green transportation fuel in internal combustion engines. This will require deep hydrotreatment of the pyrolysis oil to an upgraded oil with very low oxygen levels (preferably below 1%) in order to mimic the product properties of conventional hydrocarbon fuels. Hydrogen consumption is expected to be high for this case, and will have a negative impact on the process economics.

This chapter on catalytic hydrotreatment of fast pyrolysis oil is divided in a number of subtopics. A short overview of typical catalysts for the hydrotreatment of pyrolysis oils will be given in part 2, followed by an overview of typical process requirements. Subsequently, in depth process studies using Ru/C as catalyst for the upgrading of fast pyrolysis oil will be provided (part 3). The effect of process conditions on yields, hydrogen uptake and relevant product properties will be discussed and rationalized by a reaction network. On the basis of these findings, improved catalyst formulations have been designed and their performance will be discussed and evaluated (part 5).

2. Catalyst studies on the hydrotreatment of fast pyrolysis oil

Well known catalysts for the hydrotreatment of pyrolysis oil are conventional hydrodesulfurisation catalysts such as sulfided NiMo/Al₂O₃, CoMo/Al₂O₃, and NiMo/Al₂O₃-SiO₂ (Ferrari et al., 2002; Maity et al., 2000) to cope with the harsh reaction conditions (T > 200 C, aqueous environment with organic acids). Carbon-supported CoMo, or Mo supported on TiO₂, ZrO₂ and TiO₂-ZrO₂ mixed oxides (Satterfield&Yang, 1983; Lee&Ollis, 1984) have been tested as well. The latter catalysts all require sulphur in the feed to maintain activity. Pyrolysis

oils contain only limited amounts of sulphur (Furimsky, 2000) and sulphur addition would be required during processing to maintain catalytic activity. This will lead to sulfur emissions e.g. in the flue gas, which is not preferred for an environmental point of view.

Non-sulfided, non noble metal catalysts have also been tested for the catalytic hydrotreatment of pyrolysis oil, but to a far lesser extent. The hydrodeoxygenation of phenol over a Ni/SiO₂ catalyst has been reported and showed low HDO activity. Horne&Williams (1996) tested ZSM-5 zeolites as the catalyst for the deoxygenation of model compounds such as anisole. Their results, though, showed that anisole is mainly converted into phenol and methyl substituted phenols, and not to the oxygen-depleted compounds. Xu, et al. (2010) tested MoNi/ γ -Al₂O₃ (reduced prior to reaction) for the mild hydrotreatment of pyrolysis oil (3 MPa and 200 °C).

Noble metal based catalysts have also been evaluated as substitutes for sulfided catalysts. Examples are Pd on zeolite carriers (Horne&Williams, 1996), Pd on mesoporous CeO₂ and ZrO₂ (Senol et al., 2005), and Rh on zirconia (Gutierrez et al., 2008). Carbon supports have also been explored (Wildschut et al., 2009b; Wildschut et al., 2010a; Wildschut et al., 2010b; Venderbosch et al., 2010). We have recently reported exploratory catalyst studies on the upgrading of fast pyrolysis oil by catalytic hydrotreatment using a variety of heterogeneous noble metal catalysts (Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pt/C and Pd/C) and the results were compared to typical hydrotreatment catalysts (sulfided NiMo/Al₂O₃ and CoMoAl₂O₃). The reactions were carried out at temperatures in the range of 250 and 350 °C and pressures between 100 and 200 bar. The Ru/C catalyst appears superior to the classical hydrotreating catalysts with respect to oil yield (up to 60 %-wt.) and deoxygenation level (up to 90 %-wt.) (Figure 2) (Wildschut et al, 2009).

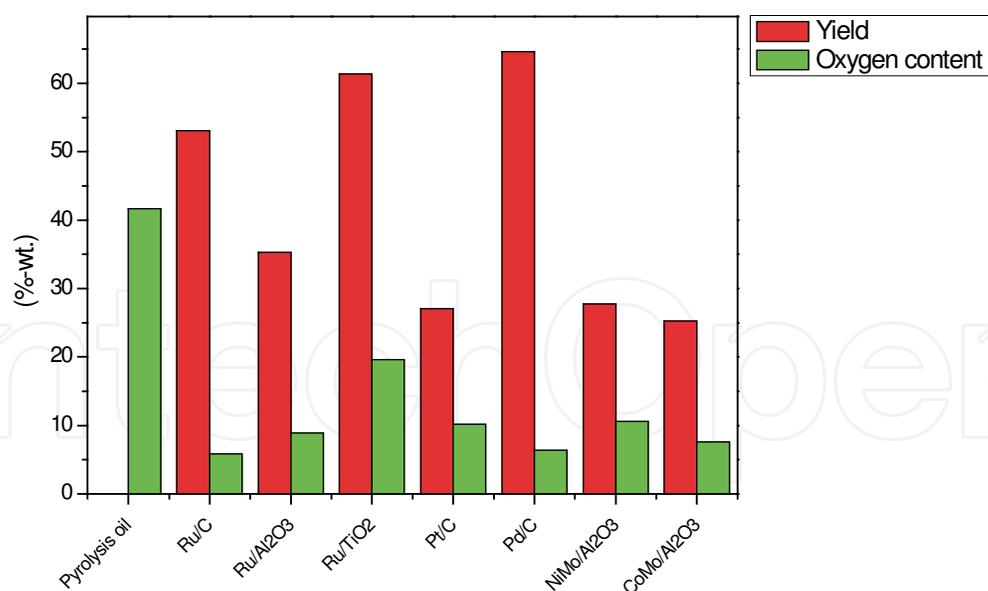


Fig. 2. Catalyst screening studies for noble metal catalysts on various supports

Unfortunately, noble metal catalysts are very expensive and this limits their application potential. The catalytic hydrotreatment of fast pyrolysis oil using much cheaper bimetallic NiCu/ δ -Al₂O₃ catalysts with various Ni/Cu ratios (0.32 - 8.1 w/w) at a fixed total metal intake of about 20 wt% was reported recently (Ardiyanti et al., 2009). Hydrotreatment

reactions of fast pyrolysis oil (batch autoclave, 1 h at 150 °C followed by 3 h at 350 °C, at 200 bar total pressure) were performed and highest catalyst activity (in terms of H₂ uptake per g of Ni) was observed for the catalyst with the lowest Ni loading (5.92Ni18.2Cu). Product oils with oxygen contents between 10 and 17 wt% were obtained and shown to have improved product properties when compared to the feed.

Recently, we have also shown the potential of homogeneous Ru catalysts for the catalytic upgrading of fast pyrolysis oil fractions (Mahfud et al., 2007a). Fractions were obtained by treatment of the pyrolysis oil with dichloromethane or water. The former approach leads to a dichloromethane layer enriched with the lignin fraction of pyrolysis oil. The dichloromethane fraction was hydrogenated in a biphasic system (dichloromethane/water) using a homogeneous water soluble Ru/tri-phenylphosphine-tris-sulphonate (Ru-TPPTS) catalyst. Analysis revealed that the oxygen content of was lowered considerably and that particularly the amounts of reactive aldehydes were reduced substantially.

The water-soluble fraction of pyrolysis oil, obtained by treatment of fast pyrolysis oil with an excess of water was hydrogenated in a biphasic system with a homogeneous Ru-catalyst (Ru/tri-phenylphosphine, Ru-TPP) dissolved in an apolar solvent (Mahfud et al., 2007b). Initial experiments were conducted with representative, water soluble model compounds like hydroxyacetaldehyde and acetol. The effects of process parameters (e.g. temperature, initial H₂ pressure, and initial substrate concentration) were investigated and quantified for acetol using a kinetic model. The hydrogenation of the pyrolysis oil water-soluble fraction using the biphasic system at optimized conditions was performed and significant reductions in the amounts of reactive aldehydes such as hydroxyacetaldehyde and acetol were observed, demonstrating the potential of homogeneous Ru-catalysts to upgrade pyrolysis oils.

3. Process studies on the catalytic hydrotreatment of fast pyrolysis oils

3.1 Introduction

In the past, it was assumed that the catalytic hydrotreatment of pyrolysis oils shows strong resemblances with conventional hydrotreatment processes of fossil feeds (hydrodesulphurisation, hydrodenitrogenation) and typical catalysts, process conditions and reactor configuration were taken from these conventional processes (Elliott, 2007). For all, the objective is a reduction of certain elements (oxygen, sulphur, nitrogen) in the feed by the action of hydrogen and a catalyst. However, common reaction conditions for the hydroprocessing of crude oil derivatives cannot be adopted directly for pyrolysis oils. For instance, pyrolysis oil cannot be treated as such at temperatures exceeding 300 °C because of its high charring tendency.

Numerous papers on hydrotreating pyrolysis oil in packed beds and autoclaves were published in the eighties and nineties, and now very recently as well (Elliott, 2007). Specifically the older literature seems rather phenomenological in nature, and merely focuses on 'fact-finding'. Large differences in operating conditions like in pressure, temperature, residence times and hydrogen consumption are reported. In any case, without active catalyst or (high pressure) hydrogen, significant charring of pyrolysis oil occurs. Reduction of charring is possible by applying a (relatively) low temperature catalytic hydrotreatment at 175 to 250 °C, in which reactive components in the oil are 'stabilized'. Subsequently, the stable product is further processed at higher temperatures (> 300 °C) and pressures (> 150 bar). High pressures are believed to be essential to keep the water in the pyrolysis oil feed in a liquid state (and as such probably reduce the charring reactions), to

promote the solubility of hydrogen in the initially polar bio-oil, and to increase the rate of the actual hydrogenation reactions.

3.2 Process studies using Ru/C

3.2.1 Batch studies

We have recently performed an in depth study in a batch set-up to determine the effects of process conditions on the catalytic hydrotreatment of fast pyrolysis oil using a Ru/C catalyst 350 °C and 200 bar pressure (Wildschut et al., 2010a). 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 one with a density lower than water. Furthermore, substantial amounts of solids (coke/char, about 5 wt% on pyrolysis oil intake) and gas phase organics (CO, CO₂, CH₄) were formed as well. The oil yield and elemental compositions of the product phases were shown to be a strong function of the reaction time. Highest oil yields (65 %-wt.) were obtained after 4 h using a 5 %-wt. intake of catalyst on fast pyrolysis oil (Figure 3). Longer reaction times lead to a reduction of the oil yield due to the formation of gas phase components (methane, ethane, propane, CO/CO₂). Hydrogen uptake after 4 h reaction time was about 400 Nm³/t of pyrolysis oil (dry basis).

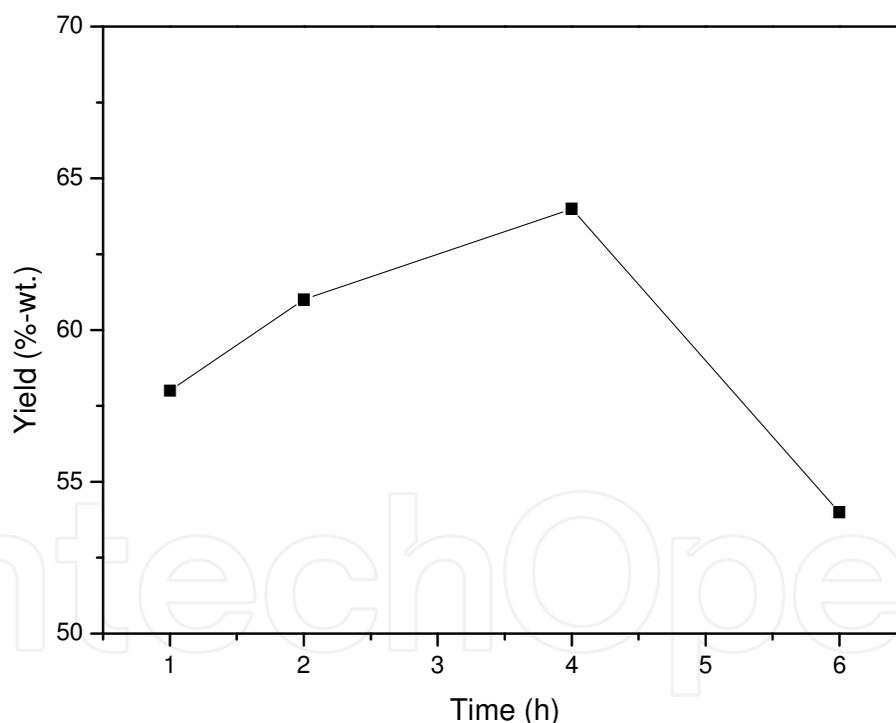


Fig. 3. Total oil yield (dry basis) versus reaction time for the hydrotreatment of pyrolysis oil (350 °C and 200 bar, Ru/C).

A solvent-solvent extraction scheme based on the work of Oasmaa et al. (2003) 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 product oils obtained at different reaction times (350 °C and 200 bar). The results are given in Figure 4.

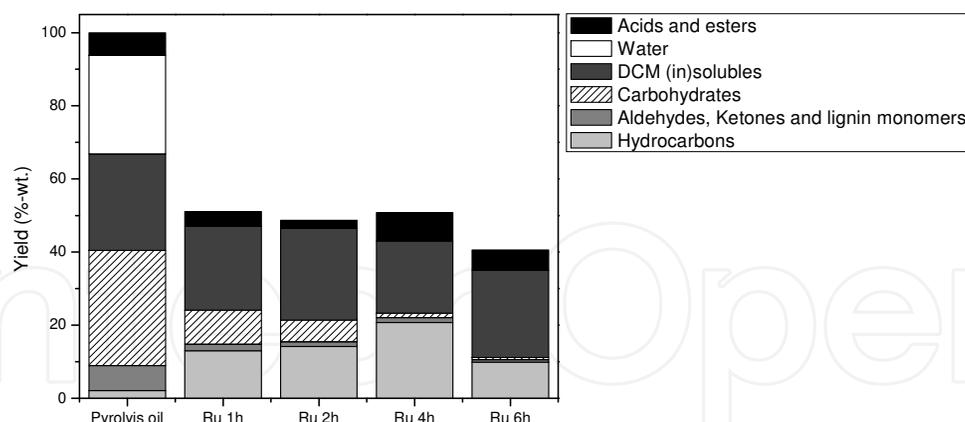


Fig. 4. Composition of fast pyrolysis oil and hydrotreated product oils (Ru/C, 350 °C, 200 bar) at various reaction times using solvent-solvent extraction

It shows the amounts of the various fractions (carbohydrates, aldehydes/ketones/lignin monomers, hydrocarbons, acids and esters) as a function of the reaction time. A fast decline in the carbohydrate fraction versus time is visible. Almost complete conversion to other components within 6 h reaction time is observed, an indication of the high reactivity of this fraction.

3.2.2 Experimental studies with Ru/C in continuous set-ups

Recently, in depth catalytic hydrotreatment experiments with the Ru/C catalyst in a continuous packed bed set-up were reported (Venderbosch et al., 2010). The results of this study will be provided in detail in the following as it provides detailed insights in the effect of process conditions on product yields, product properties and the various reactions taking place on a molecular level. Some experiments were carried out in the absence of catalysts to probe thermal reactions.

The catalytic hydrotreatment reactions were carried out in a set-up consisting of 4 packed bed reactors in series. The temperature in each reactor may be varied independently, allowing experiments at different temperature profiles over the length of the reactor. Typical pressures were between 150 and 300 bar, temperatures between 150 and 400 °C and WHSV's between 2-10 kg/kg.cat.h. In the following, the thermal reactions will be discussed, followed by catalytic hydrotreatment reactions at different temperature levels.

3.2.2.1 Thermal reactions

To study the thermal, non-catalytic reaction in detail, pyrolysis oil was pumped through the reactor (without catalyst) at pressures of up to 300 bar and temperatures of maximum 350 °C for residence times in the order of tenths of second – minutes. Typically under these conditions, a single-phase pyrolysis oil is converted into a viscous organic liquid, an aqueous phase and a gas phase. The carbon content of the viscous phase is about 60 wt.% (starting with 40 wt.% in the original oil), and the oxygen content about 32 wt.%. Additional water is produced, up to 30 % compared to the water initially present in the pyrolysis oil. The water is distributed over the two layers, but most of it ends up in the aqueous phase. Energetically, 80% of the thermal energy in the pyrolysis oil is transferred to the viscous product, less than 20% and 1 % is retained by the water phase and gas phase, respectively. The gas phase in such experiments consists of CO and CO₂ in a ratios varying from 1:10 to

1:3 (depending on temperature, pressure, residence time), and in yields of almost 4 wt.% of the pyrolysis feed.

Although it is unknown at a molecular level which reactions actually take place, at least two parallel pathways can be distinguished, viz. a reaction causing the formation of gas (here referred to as decarboxylation / decarbonylation, yielding CO and/or CO₂), and the other causing dehydration (likely by condensation (polymerisation) reactions). Possible sources of these gases are the organic acids in the oil. For all aqueous (and organic) samples produced the pH, however, is almost similar to the pyrolysis oil feed. This indicates that either the acids are not converted or the acids are converted and simultaneously produced as well. A detailed acid analysis of the products is not available, and the precise events taking place and mechanism however remain unclear. It seems that dilution of the pyrolysis oils with 'inert' solvents suppresses the re-polymerisation. Additionally, the gas yield becomes independent of the temperature and the residence time after a certain threshold in the residence time, while the amount of water produced is increasing. This indicates that the reaction mechanism for the formation of gas is different than the polymerisation reactions.

Phase separation of the oil at these conditions may have a number of causes, e.g. an overall increase in the water content due to the formation of water by condensation reactions. It is known (but not fully explained yet) that above a certain water content pyrolysis oils phase separate into an aqueous phase and a rather nonpolar phase. Repolymerisation of some molecules / fractions in the oil is also a plausible reason, as it renders the products less soluble in water, for example caused by transformation of the polar sugar constituents behaving as bridging agents in the dissolution of hydrophilic lignin material (Diebold 2002).

3.2.2.2 Catalytic hydrotreatment reactions

The catalytic hydrotreatment reactions were carried out at three process severity levels, a mild hydrogenation at either 175 or 225 °C, a mild hydrodeoxygenation (HDO) at 225 - 275 °C and a deep hydrodeoxygenation. For the latter, samples from the mild HDO were first allowed to phase separate completely, after which the organic fraction (containing about 3 wt.% water) was treated at temperatures ranging from 350 °C in the first two reactor segments, to 400 °C in the last two.

3.2.2.3 Visual appearances of liquid phase after reaction

The catalytic hydrotreatment reaction at 175 °C resulted in a single phase oil with a visual appearance close to that of the original feed. Thus, at this temperature, phase separation does not occur. This may be related to the limited production of water at this temperature. The product has a considerable sweeter smell/odor than the original pyrolysis oil. The mild hydrogenation at 225 °C gives two liquid phases, an organic and a water rich phase. The water phase has a higher density than the aqueous phase. A similar situation was observed for experiments at higher process severities (mild HDO), see Figure 5 for details. The second stage HDO product oil has even a lower density than the aqueous phase.

The organic product yields for the various process severities are given in Figure 6. Here, the severity is expressed in terms of hydrogen consumption, and high severity is associated with high hydrogen consumption. The yield is a clear function of the temperature. A drop in the yield to about 40% is observed at about 200 °C due to the occurrence of phase separation and transfer of part of the carbon and oxygen to the aqueous phase. A further slight reduction in yield is observed at higher severities, presumably due to gasification reactions and further net transfer of components from the organic to aqueous phase.



Fig. 5. Pictures of pyrolysis oil (left), mild HDO (middle) and 2nd stage HDO (right) products

Oxygen contents of the product oils are a function of the process severity, see Figure 6 for details. Phase separation between 175 and 225 °C results in a dramatic drop in the oxygen content. This is due to the loss of water and the transfer of very polar highly oxygenated components to the aqueous phase. At the highest severity, the oxygen content is about 15%, compared to about 40% for the original pyrolysis oil.

The hydrogen consumption ranges between 65 and 250 Nm³/t pyrolysis oil. Higher process severities lead to higher hydrogen uptakes (Figure 6).

A useful representation to assess the changes in the elemental composition of the product oils at various process severities is a van Krevelen diagram. Here, the ratio between O/C and H/C of the products are plotted together in a single diagram. In Figure 7, a typical plot is provided for selected literature data on pyrolysis oil hydroprocessing (Elliott, 2007; Venderbosch et al., 2010) and our results with Ru/C at different severities. Presented here are data points from e.g.:

- wood and pyrolysis oil, and for the four cases referred to in this paper (HPTT, hydroprocessing at 175 and 225 °C, Mild HDO and 2nd stage HDO);
- A selection of data points derived from literature studies (Baldauf et al. 2007; Churin et al., 1988; Conti, 1997; Diebold, 2002; Kaiser 1997; Samolada et al., 1998). Some of these data are derived from various oils from a variety of resources and processed in different reactors, different catalysts and at different conditions.

The plot also contains curves to represent the changes taking place in elemental composition during hydroprocessing, a theoretical curve for the dehydration of pyrolysis oil, and trend lines for the thermal (HPTT) route and hydroprocessing routes based upon the experimental data points.

Based on our work on the Ru/C catalysts and supported by the literature points in Figure 7, several reaction pathways can be distinguished:

- a. Essentially repolymerisation of the pyrolysis oil (no catalyst, no hydrogen, 'HPTT');
- b. Merely hydrogenation of the pyrolysis oil at mild conditions (up to 250°C, with catalyst and hydrogen, referred to as mild hydrogenation),
- c. Dehydration of the oil at temperatures near 250-275 °C, and
- d. Hydroprocessing of pyrolysis oil at temperatures up to 400 °C

Upon thermal treatment, the principal reactions are rejection of oxygen as water. Some CO_2 and CO is released as well, which shifts the trend line to slightly higher H/C ratios (but decarboxylation / decarbonylation is limited to approx. 10 wt.% of the feed). A high conversion (i.e. at high temperatures and residence times) eventually leads to a hydrogen-depleted solid material (and probably similar to conventional carbonisation processes, charcoal).

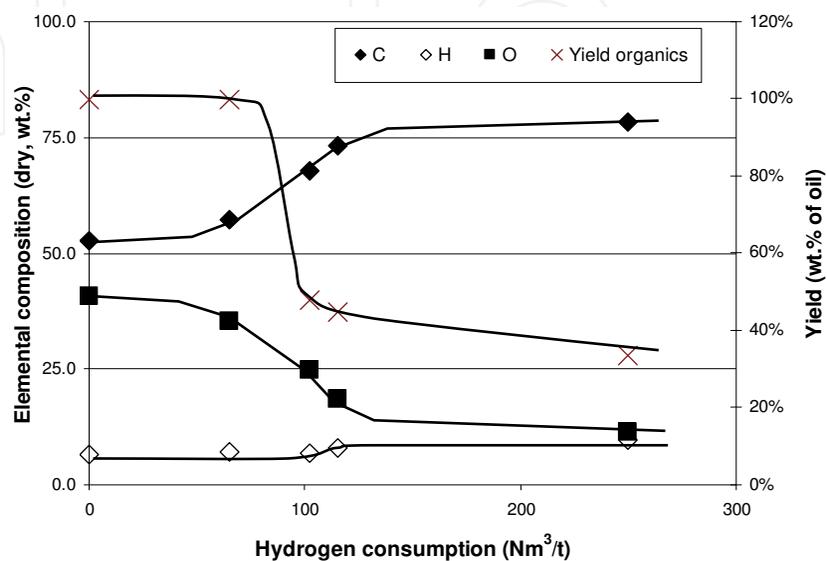


Fig. 6. The elemental composition of the organic oil product (dry basis) versus the hydrogen consumption for pyrolysis oil, mild hydrogenation, mild HDO and 2nd stages HDO

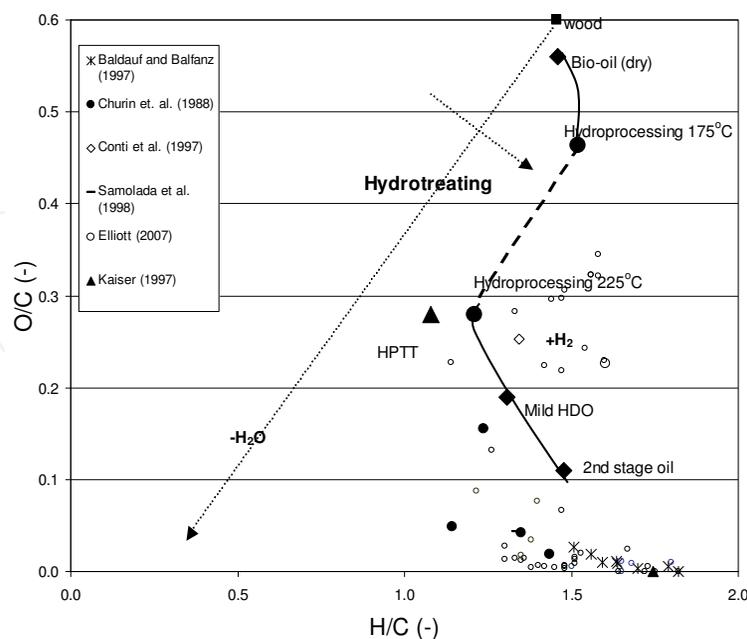


Fig. 7. The Van Krevelen plot for oils derived from the thermal pathway (HPTT), mild hydrogenation, mild HDO and 2nd stages HDO, including relevant literature data points

To obtain a liquid product with a higher H/C ratio, additional hydrogen is thus required. This path is shown in Figure 7 and includes the mild hydroprocessing step, at around 175 °C (no phase separation) and 225 °C (phase separation), followed by further hydrodeoxygenation (and hydrocracking).

3.2.3 Product oil fractionation; insights in molecular changes

The various organic products were subjected to a standardized liquid-liquid fractionation protocol (Oasmaa, 2003, Figure 1) to gain insights on the severity of the hydrotreatment process on product composition. The results are compiled in Figure 8 and show major changes in composition upon reaction. The pyrolysis oil feed mainly consist of ether solubles, ether insolubles and water. The components in these fractions originate from the cellulose and hemi-cellulose fraction in the biomass feed and particularly the ether insoluble fraction is rich in carbohydrates. The amounts of DCM solubles and insolubles, from the lignin fraction of the biomass feed, are by far lower and are about 20% in total.

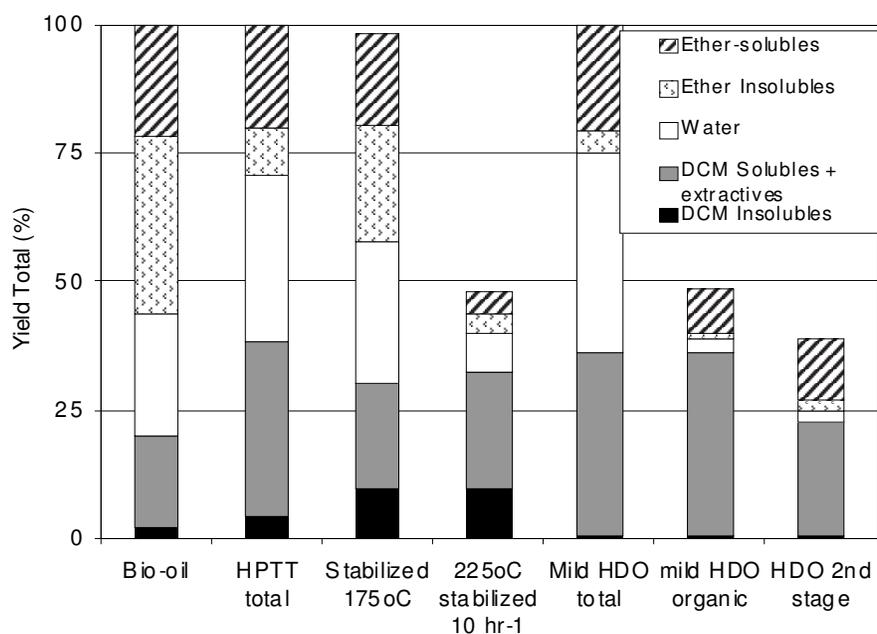


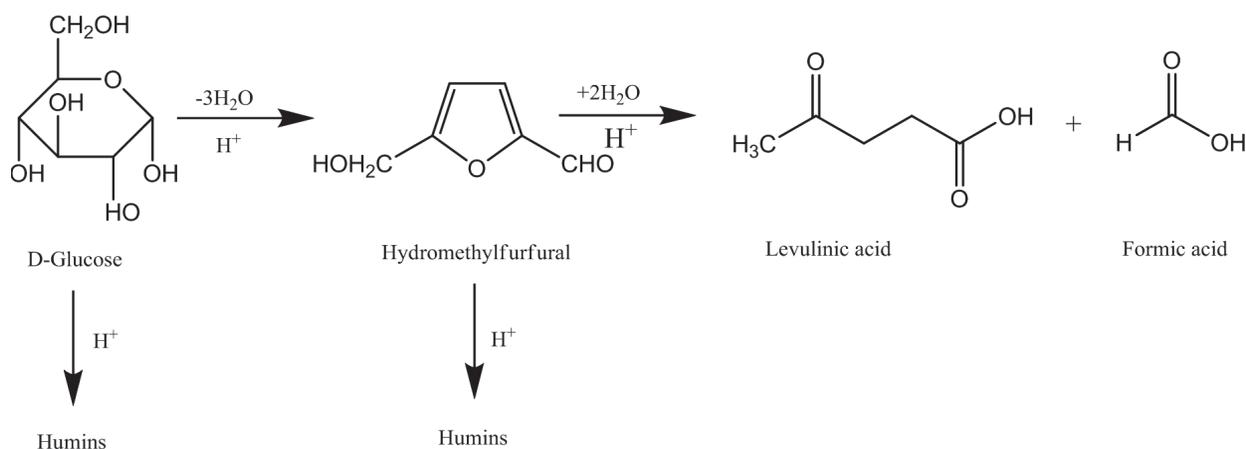
Fig. 8. Comparison of the fractionation results for various process severities

3.2.3.1 Thermal reactions

When comparing the composition of the pyrolysis oil feed with the product from the thermal route, it is clear that the ether insolubles are converted to DCM-solubles and -insolubles, and additional water. A similar change occurs in wood oils, stored for several months or years, where water insoluble products are produced at the expense of the sugar fraction (Oasmaa&Kuoppala, 2003). At higher temperatures and residence times, especially this sugar fraction is responsible for charring, likely through the formation of first DCM solubles and subsequently DCM insolubles ('char'). Solids production upon heating aqueous solution of C-6 sugars (e.g. D-glucose, D-mannose) to temperatures up to 400 °C is well known. Thermal decomposition, either catalytic (mostly by acids) or non-catalytic, leads to solid products referred to as humins (Girisuta et al., 2006; Watanabe et al., 2005a; Watanabe et al., 2005b). The proposed reaction pathway consists of C-6 sugar conversion to

5-hydroxymethyl furfural (HMF) and subsequently levulinic acid (LA) and formic acid (FA). Both reactions also accompanied by solids (humin) formation (Scheme 1).

Solids formation is highly undesirable and limits the yields of the two promising biobased chemicals LA and HMF. Despite large research efforts, it has so far not been possible to avoid solids/humin formation when performing the reactions in aqueous media.



Scheme 1. Decomposition reactions of D-glucose at elevated temperatures.

Higher temperatures and the presence of acid catalysts (homogeneous and heterogeneous) increase the rate of D-glucose decomposition (Girisuta et al., 2006). Such reactions may also occur in the fast pyrolysis oil matrix. The oil is acidic in nature due to the presence of organic acids and these will catalyse the depolymerisation of oligomeric sugars to D-glucose and other C-6 sugars followed by the reaction to solids and hydroxymethylfurfural and levulinic acid/formic acid.

Knezevic et al. (2009) studied the thermal decomposition of D-glucose in hot compressed water under conditions of relevance for the catalytic hydrotreatment of pyrolysis oil (240–374 °C). It was shown that D-glucose decomposes mainly to char and some gaseous components (primarily CO₂), while only a limited number of components remained in the water phase (for example formaldehyde). At these conditions, the reactions are very fast and decomposition to char takes place on the time scale of seconds to minutes.

3.2.3.2 Catalytic hydrotreatment reactions

The composition of the product from a mild hydrogenation at 175 °C (see Figure 8) differs considerably from that of the original pyrolysis oil. The amount of water increased slightly (from 25 up to about 30 wt.%), which appears insufficient for phase separation. In addition, the ether solubles (aldehydes, ketones, acids, etc) are converted, but in smaller amounts compared to HPTT. The ether insoluble (sugar fraction) is reduced considerably from 35 down to 24 wt.%, while the water insoluble fraction is increased accordingly. Simultaneously, the increase of the DCM insoluble fraction is about 8%, while the DCM soluble fraction increases with only 3 wt.%.

Similar to HPTT, we assume that the sugar fraction in the oils is (partially) converted to more water insolubles and some additional water. However, the actual components formed during mild hydrotreatment are different in nature than the HPTT oils and particularly the amount of DCM insolubles is higher.

The results of the fractionation of the product oil derived from an experiment 225 °C (mild hydrogenation) are provided in Figure 8. Phase separation occurs and as such the amount of product oil is reduced considerably. As a result, the amounts of water, ether solubles and ether insolubles in the organic phases are lowered and imply that components have been transferred to the water phase. Figure 8 also shows the result for the mild HDO reaction. Compared with the oil samples obtained at lower temperatures, the DCM insoluble fraction is now almost completely converted to DCM soluble components, evidence that some hydrocracking reaction have taken place here as well. In the 2nd stage hydroprocessing the amount of ether solubles increases, at the expense of DCM solubles and the extractives.

3.3 Product characteristics

In all hydrogenation experiments except those at temperatures below 200°C, the product obtained consisted of two liquid phases, viz. an aqueous phase and brown-red organic phase. For all of them, relevant (basic) characteristics were determined, viz. elemental composition (vide supra, Figure 7), water content and average molecular weight. Additionally, to get some insights in the coking tendency, the samples were analyzed using thermogravimetric analysis (TGA). Here, the residual weight of the sample, heated under N₂ up to about 900°C, was taken as a measure of coking. A high residue indicates a high tendency for coking and thus a low thermal stability at elevated temperature. The residue after a TGA measurement is a strong function of the process severity, see Figure 9 for details.

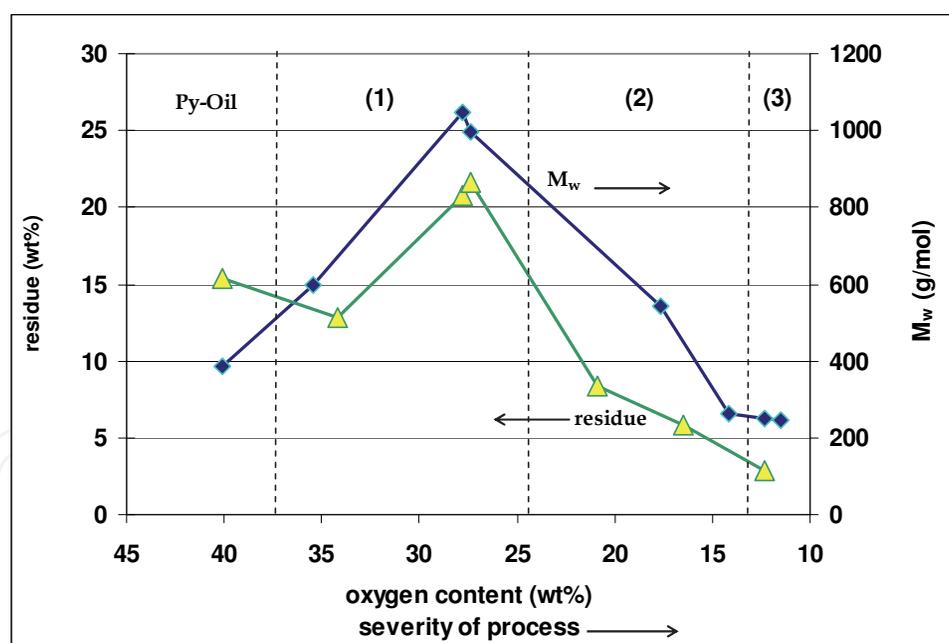


Fig. 9. Mass average molecular weight and TGA residue of products from (1) stabilisation, (2) mild hydrotreating, and (3) 2-stage hydrotreating.

At low process severities, the TGA residue increases and the highest value (22%) is observed at intermediate severities. A further increase in severity leads to a strong reduction in the TGA residue. Thus, it may be concluded that intermediate severities lead to product oils with a high TGA residue and consequently have a higher tendency for coking and may be less suitable as a refinery feedstock.

The organic products were analyzed using gel permeation chromatography (GPC) to determine the average molecular weights and the results are given in Figure 9. The molecular weight of the product oils increases compared to the pyrolysis oil feed at low severity hydrotreatment reactions. Apparently, polymerisation occurs and this has also been observed when heating up pyrolysis oil to 275°C in the absence of catalysts (HPTT process) (Rep et al., 2006). A further increase in the severity (higher temperatures, shorter WHSV's) leads to a reduction of the molecular weight and a value of less than 300 is observed at the highest severities.

Of particular interest is the relation between the molecular weight of the products and the TGA residue. Products with a higher Mw also lead to higher TGA residues and this may be rationalized by assuming that the higher molecular weight fragments in the products are precursors for coke formation.

4. Proposed reaction pathways and implications

4.1 Reaction pathways

A schematic and simplified representation of relevant reactions assumed on basis of this work is presented in Figure 10. In the initial phase of the hydrotreatment process, catalytic hydrogenation and thermal, non-catalytic repolymerisation occur in a parallel mode.

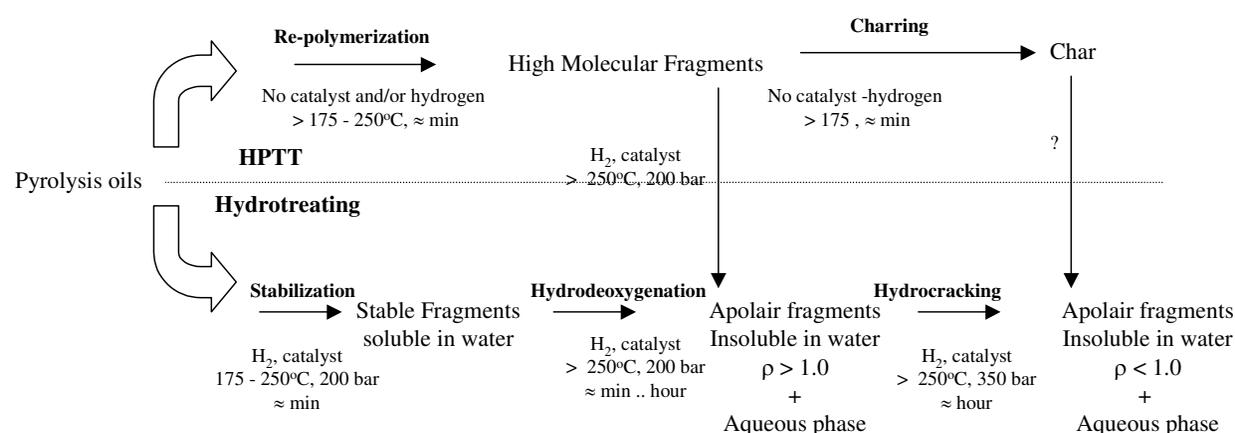


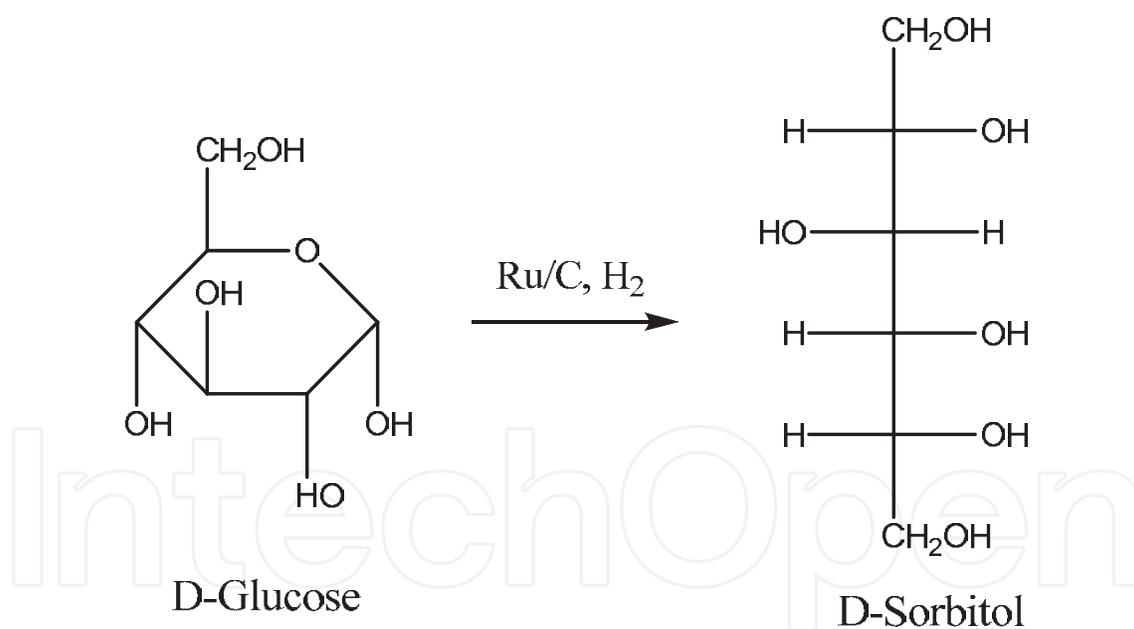
Fig. 10. Proposed pathways for the catalytic hydrotreatment of pyrolysis oils

Repolymerisation leads to the formation of soluble higher molecular weight fragments which upon further condensation reactions give char. This route is as such not preferred and the rate of the polymerisation reactions should be reduced as much as possible. The preferred pathway involves hydrogenation of the thermally labile components in the pyrolysis oil feed to stable molecules that are not prone to polymerisation. Subsequent reactions (hydrogenations and hydrocracking) on a time scale of hours lead to products with reduced oxygen contents and ultimately to higher H/C ratio's (Figure 7). The observed molecular weight of the organic phase as a function of the process severity (Figure 9) implies that upon the use of Ru/C as the catalyst, the repolymerisation step cannot be avoided, and a slight increase in molecular weight is observed at low process severities. However, higher severities lead to a reduction in the average molecular weight, an indication that soluble higher molecular weight fragments may also be (partly) depolymerised by the action of hydrogen and a catalyst.

As stated earlier, pyrolysis oil contains large amounts of oligo- and monomeric sugars, arising from the cellulose and hemi-cellulose fraction of the lignocellulosic biomass feed. As such, it is of interest to compare the reaction pathways provided in Figure 10 for pyrolysis oil with that of typical hydrogenation and thermal reactions occurring for carbohydrates at various process severities.

Thermal decomposition of various monomeric sugars in aqueous media has been studied in detail and is known to lead to oligomerisation to soluble and subsequently to insoluble humins (Girisuta et al., 2006). As an example, Knezevic et al. (2009) studied the thermal decomposition of D-glucose in hot compressed water at elevated temperatures (240-374 °C), giving solids (char, humins) and some gaseous components (primarily CO₂). At these conditions, the reactions are very fast and decomposition to char takes place on the time scale of seconds to minutes.

Catalytic hydrotreatment of carbohydrates using heterogeneous catalysts has been reported extensively in the literature. The main focus is on the hydrogenation of D-glucose to D-sorbitol, a well-known chemical with use in the pharmaceutical and the food industry (Kusserow et al., 2003). Catalytic hydrotreatment of D-glucose over Ni, Ru based and Pd based heterogeneous catalysts at 80 °C, 80 bar yields D-sorbitol in high yields (Crezee et al., 2003; Makkee et al., 1985) (Scheme 2). The hydrogenation reactions at these low temperature levels may be considered as the stabilisation step in fast pyrolysis oil upgrading.

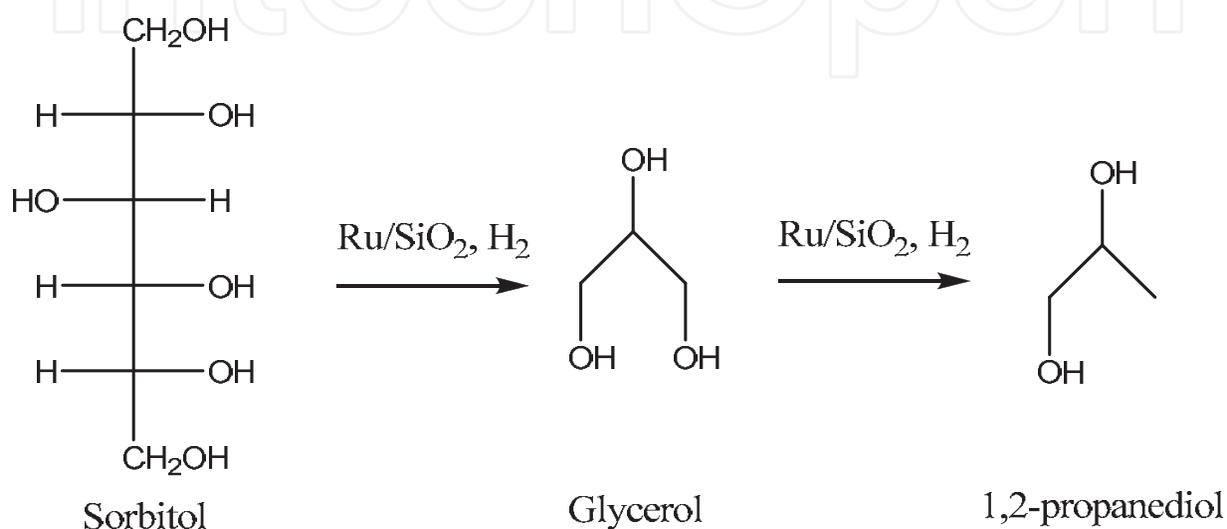


Scheme 2. Catalytic hydrogenation of D-glucose to D-sorbitol

In the presence of hydrogen and a catalyst, D-sorbitol is not inert at elevated temperatures (above 180 °C) and may be converted to a variety of products. For instance, Huber et al. (2004) showed that D-sorbitol can be converted to n-hexane in high yield using Pd and Pt catalyst on SiO₂ or Al₂O₃ (225-265 °C and 26-58 bar). Over Ru/SiO₂, hydrogenolysis of D-sorbitol at 180-240 °C and 80-125 bar hydrogen pressure yields mainly glycerol and 1,2-propanediol (Sohounloue et al., 1982) (Scheme 3). This implies that C-C bond cleavage occurs readily, leading to the formation of lower molecular weight products.

These reactions are likely also occurring upon the catalytic hydrotreatment of fast pyrolysis and may explain the formation of more apolar lower molecular weight products at higher process severities.

Thus, it may be concluded that the typical reaction pathways for pyrolysis oils at typical low severity hydrotreatment conditions mimic those of low molecular weight sugars viz. repolymerisation reactions to solids (humins) and hydrogenation/C-C bond cleavage reactions to for instance polyols and finally to hydrocarbons. This strengthens our initial hypothesis that pyrolysis oil should be regarded as a carbohydrate rich "syrup" and not a conventional fossil derived hydrocarbon liquid.



Scheme 3. Hydrogenolysis of D-sorbitol to glycerol and 1,2-propanediol.

4.2 Process implications

The proposed reaction pathway for catalytic hydrotreatment of pyrolysis oil (Figure 10) implies that the rate of the hydrogenation route should be much higher than the rate of the repolymerisation route to obtain good quality upgraded pyrolysis oil (low molecular weight, low viscosity, low coking tendency). An obvious solution is the development of highly active hydrogenation catalysts. These studies will be reported in the next paragraph of this paper. However, a smart selection of process conditions and reactor configurations may also be considered, particularly to enhance the rate of the hydrogenation/hydrodeoxygenation pathway compared to the repolymerisation pathway. In this respect, it is highly relevant to gain some qualitative insights in the factors that determine the rate of the individual pathways (hydrogenation versus repolymerisation).

A schematic plot is presented in Figure 11, where an envisaged reaction rate (arbitrary values, in mole reactant/min) is presented versus the actual reaction temperature. The lines drawn are taken in case (i) gas-to-liquid mass transfer determines the overall reaction rate (ii) the catalytic hydrotreatment reactions dominate, and (iii) polymerisation reactions prevail. Figure 11 is derived on basis of simplified kinetics for the glucose hydrogenation – polymerisation reactions, but a detailed outline of all assumptions made is beyond the scope of the presentation here. For this reason the exact values on the x- and y-axes are omitted. The following relations are taken into account to derive Figure 11:

- The conversion rate due to the hydroprocessing reactions R_H (mol/m³.s) can be simplified as a product of the intrinsic kinetic rate expression k_R and the surface area

available per reactor volume. Being a catalytic reaction, the influence of temperature can be rather high.

- The overall gas-to-solid mass transfer rate of hydrogen depends on reactor geometry and operating variables. In case of stirred tank reactors (including batch-wise operated autoclaves), the actual stirring rate is important, while in packed bed the catalyst particle wetness is relevant. In both, the concentration of hydrogen (thus hydrogen pressure) is important, together with catalyst particle size, and, to a limited extent, temperature.
- The rate of polymerisation, R_p , will depend largely on the temperature, and, being a reaction with order in reactant(s) > 1 (and probably up to 2 or 3), on the concentration of the reactant.

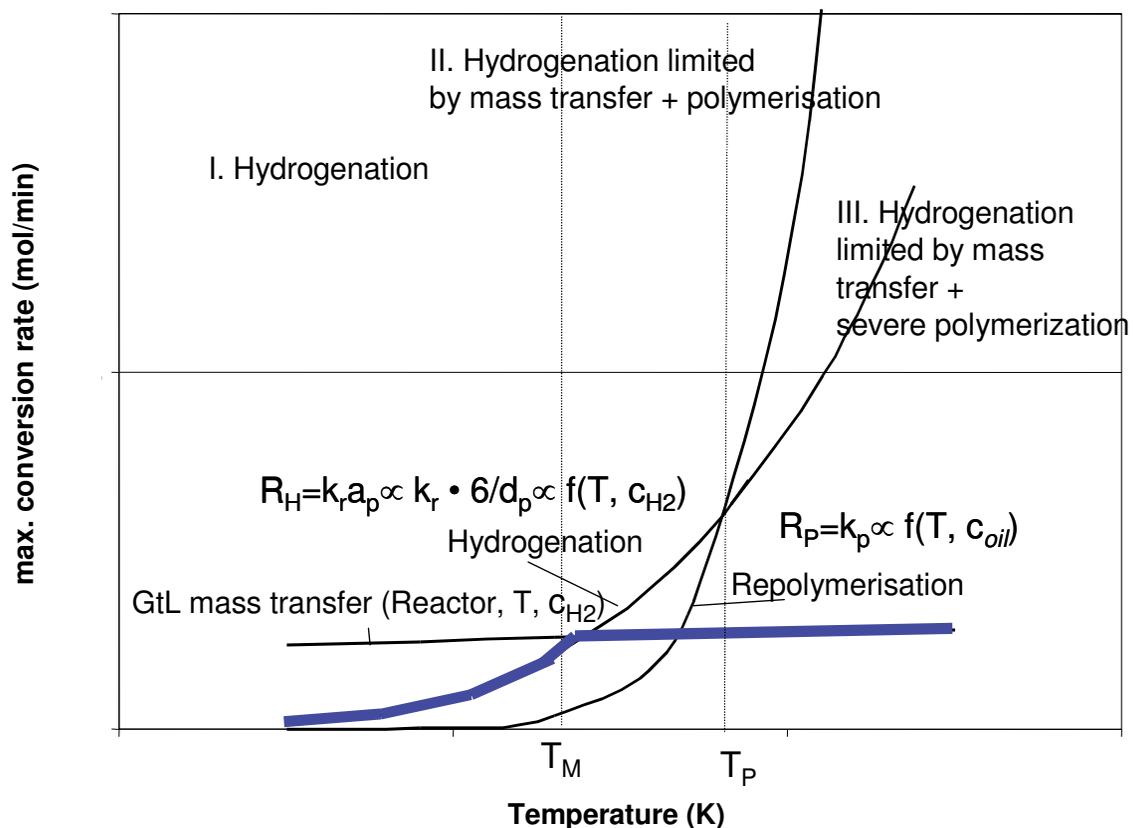


Fig. 11. Schematic indication of the conversion rates in case of mass transfer, hydrogenation and polymerisation reactions as a function of temperature. The blue solid line would be the net effective conversion rate.

A number of options may be envisaged to promote the hydrogenation pathway:

- Increase the hydroprocessing reaction rate, for instance by a higher catalyst intake or by an increase in the effective hydrogen concentration in the liquid (pressure, application of a solvent with a high hydrogen solubility).
- Reducing the polymerisation reaction, a.o. by performing the initial stabilisation step at a low temperature ($< 100^\circ\text{C}$) and reduction of the concentration of the reactants (a.o. by dilution).

- Increase the overall gas-to-liquid mass transfer rate in case the reaction is performed in the gas-liquid mass transfer limited regime. This may be possible by increasing the mass transfer surface area in the reactor, higher mass transfer coefficient and / or increasing the concentration difference between the gas and the liquid.

5. Improved catalyst formulations for the catalytic hydrotreatment of fast pyrolysis oil

The development of highly active metal catalysts is of prime importance to reduce the tendency for repolymerisation during catalytic hydrotreatment. All data presented in this chapter so far are based on a Ru/C catalyst. Ru, however, is an expensive noble metal and there is an incentive to identify not only more active but also cheaper catalysts for the hydrotreatment reaction. A possibility is the use of cheaper bimetallic metal catalysts based on Ni. Ni is known to have high hydrogenation activity for a variety of organic functional groups and particularly for reactive ketones and aldehydes, and as such is a potential active metal for hydrotreatment reactions. However, monometallic Ni catalysts (on silicon oxide, γ - or δ -alumina, or other supports) at the typical temperature and pressures applied here are not suitable to be used as a hydrogenation catalyst. There are basically two reasons: 1) Ni requires high reduction temperature (typically 700 °C) for complete reduction, and 2) Ni catalysts are known to deactivate rapidly at elevated conditions by char deposition ("coking"). The carbon deposition can block the nickel surface, or the pore mouths, and, eventually leading to a strong reduction in the reaction rates. These two drawbacks regarding the use of Ni were solved a.o. by using another element (metal or non-metal), also designated as a promoter. One of these proprietary catalysts was studied in detail and will be referred to in the following as catalyst D.

Figure 12 shows the liquid phase after a hydrotreatment over Cat D versus the severity of the process, showing the original oil (left) and an oil derived at the most severe conditions tested here on the right. Interestingly, the product oils obtained over cat D are much more transparent than those derived from the Ru/C catalyst.

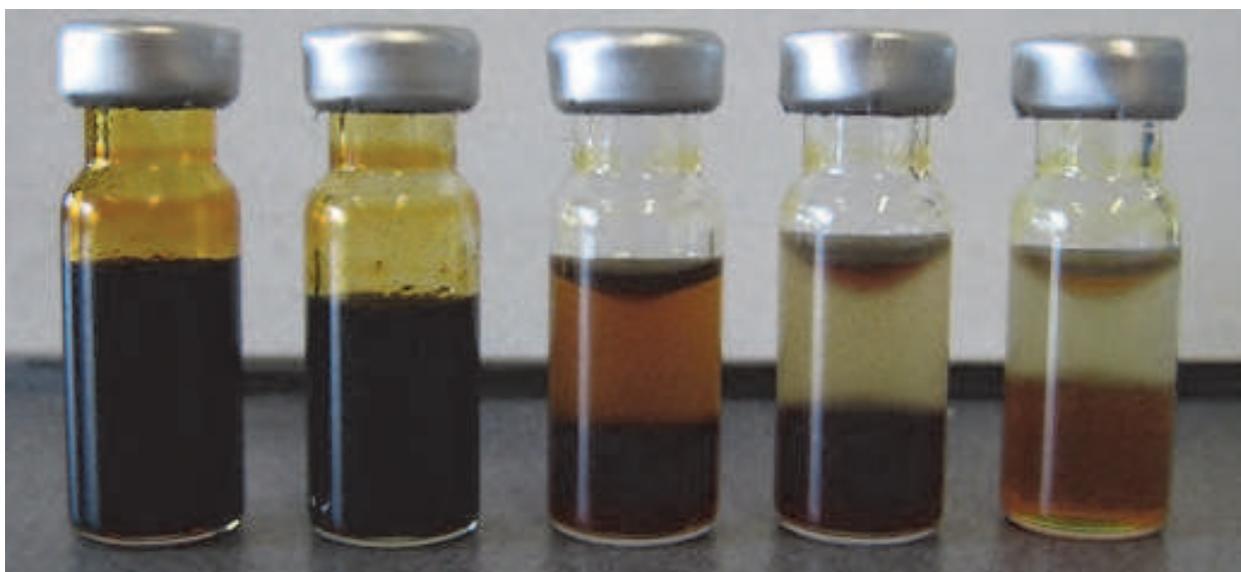


Fig. 12. Visual appearance of the liquid phase after hydrotreatment over catalyst D

A van Krevelen plot gives valuable insights in the difference in performance between catalyst D and Ru/C (Figure 13). A similar pattern for both is observed as a function of severity but the curve for Cat D is shifted to higher H/C values. Thus, at a similar oxygen content, the H/C ratio is higher for catalyst D. This is indicative for a higher hydrogenation rate for cat D and is known to be favorable regarding product properties.

Repolymerisation reactions appear to occur to a limited extent when using cat D instead of Ru/C. This is evident when comparing the average molecular weight of the final products (Figure 14a), as determined by GPC, for both Cat D and Ru/C. For Ru/C the average molecular weight shows a significant increase from 400 up to 1000 Da at low severities, but a constant value over the oxygen content interval of 400-450 Da for catalyst D is observed.

TGA residues of the product oils using cat D (Figure 14b) show carbon residues of around 5%. Surprisingly, and not expected on basis of test carried out using other catalysts, already at less severe operating conditions, a significant reduction in the TGA residues is achieved. Thus, products with a higher H/C ratio and a lower carbon residue were obtained with cat D indicating that the rate of the hydrogenation/hydrodeoxygenation reactions over catalysts D are higher than for Ru/C.

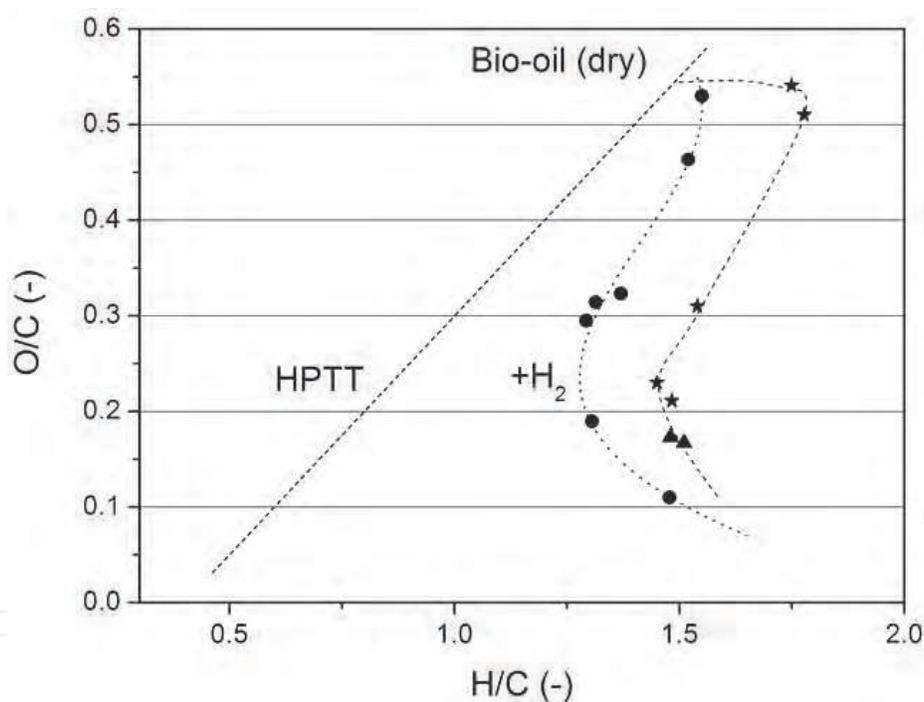


Fig. 13. Van Krevelen plot for oils derived over catalyst Ru/C (circles) and over catalyst D (stripes). Lines are trendlines.

An important product property for the upgraded oils is the viscosity. In Figure 15, the viscosity profile of the product oils versus the oxygen content is compared for conventional catalysts (Ru/C and NiMo, CoMo) and catalyst D. Clearly, the viscosity in the mid range of oxygen contents is much lower for cat D. Further testing at the extreme of low oxygen content will be required to grab the full picture but it is clear that cat D gives upgraded products with a lower viscosity than for conventional catalysts. The lower viscosity is likely the result of a lower average molecular weight of the products, as shown earlier and the result of higher hydrogenation/hydrodeoxygenation rates for Cat D compared to Ru/C.

On the basis of the product properties of the upgraded oils obtained with cat D, we can conclude that repolymerisation is not occurring to a considerable extent. As a result, product oils with a lower molecular weight and a concomitant lower viscosity, lower TGA residue is obtained. Thus, the reaction pathway for catalyst D may be simplified considerably, see Figure 16 for details.

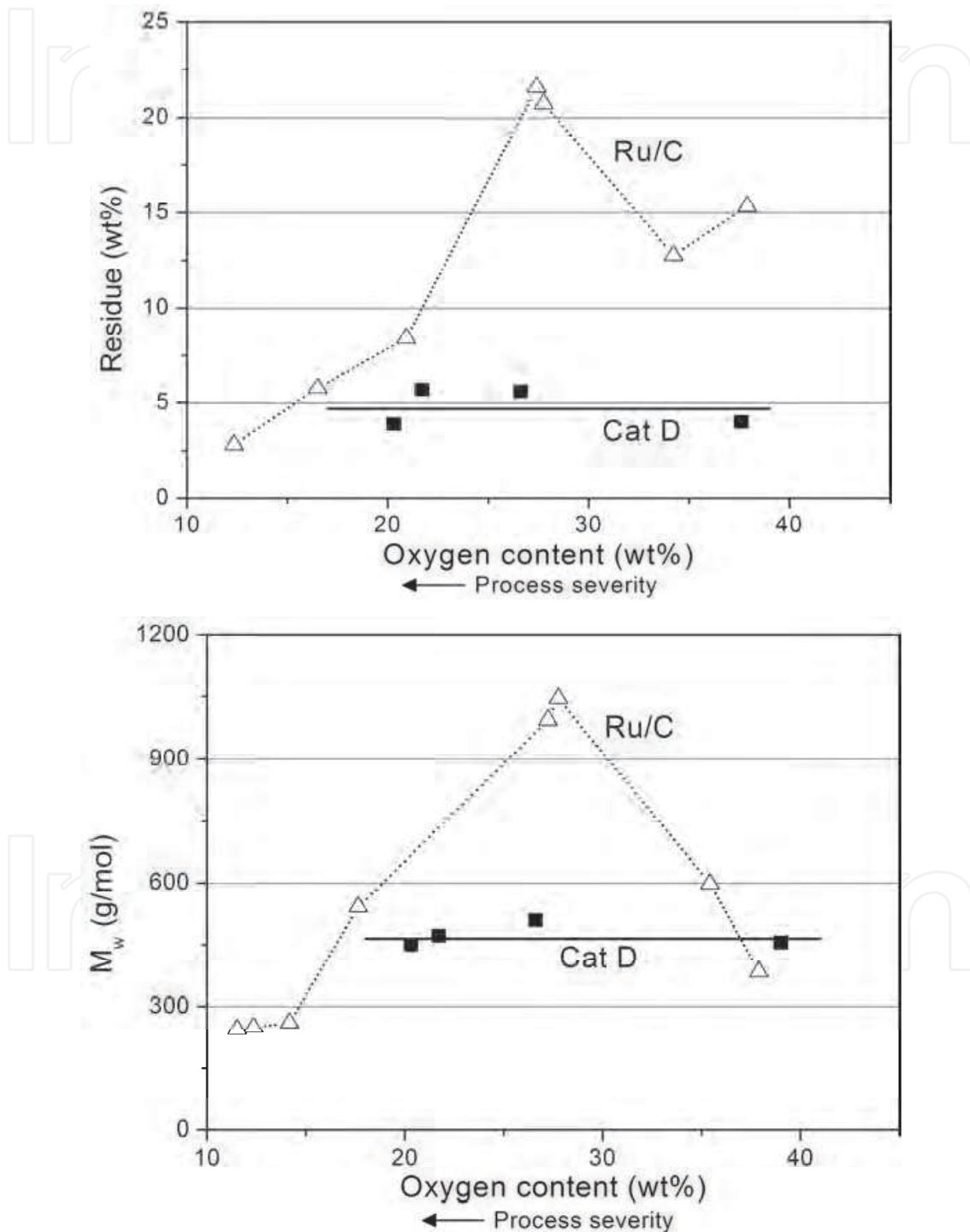


Fig. 14. TGA residue (wt%) for catalyst Ru/C and the catalyst D (top); average molecular weight of final product (bottom)

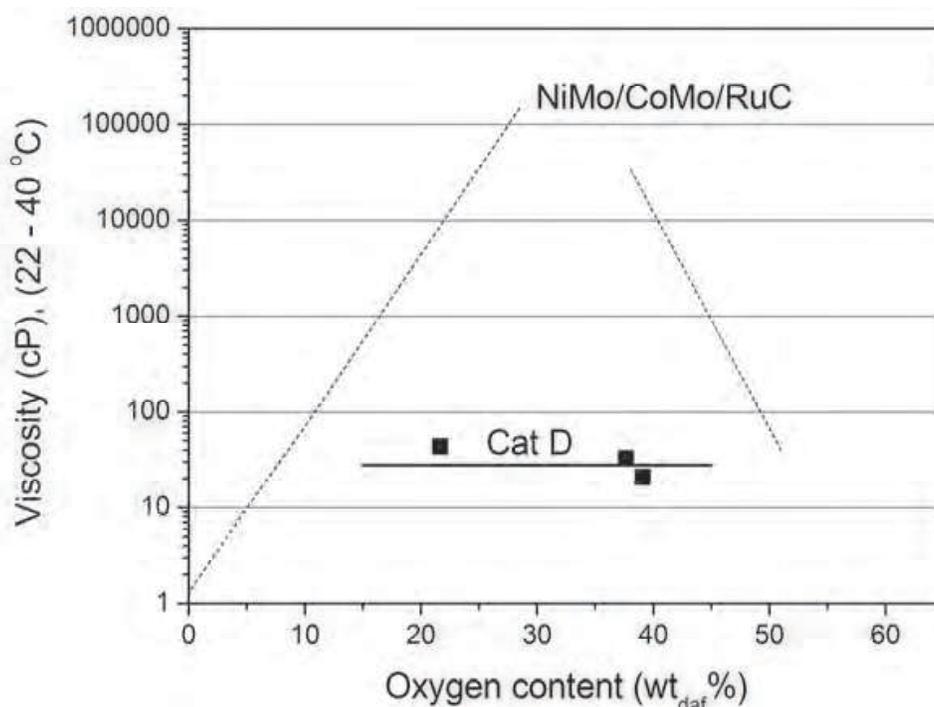


Fig. 15. Viscosity of the oil versus the oxygen content for conventional catalysts and for Cat D.

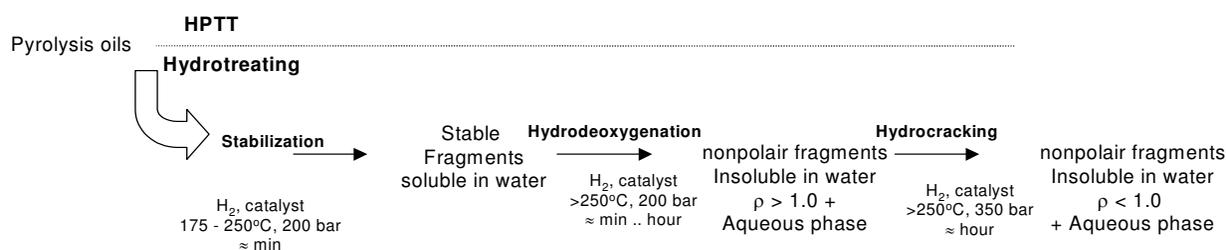


Fig. 16. Proposed pathways for the mild hydrotreating of pyrolysis oils over catalyst D.

6. Application potential of upgraded oils and critical product properties

The research described here is principally meant to produce pyrolysis oil derived products with the potential to be co-fed in crude oil refineries. It is of interest to discuss some of the relevant product properties that likely are crucial for this application. An important product property of the product oil is its tendency to produce coke upon heating, for example determined by the ‘Conradson Carbon Residue’ (CCR) or residue upon an thermogravimetric analysis (‘TGA residue’, *vide supra*) (Furimsky, 2000). In general, pyrolysis-oils show CCR values around 20 to 30% (Samolada, 1998) and this limits its direct use as a co-feed. The TGA residues for upgraded oils obtained with Ru/C and cat D as presented in this paper, show values between 3 and 22 wt% (see Figure 14) and are tunable by process severity (temperature, residence/batch time). It should be realized that low TG residue values are accessible for hydrotreated products which still contain considerable amounts of bound oxygen (> 10 wt%). Thus, stable oils may be prepared despite relatively high bound oxygen contents. From a processing point of view this is also advantageous as it

limits the hydrogen usage for the catalytic hydrotreatment process, a major variable cost contributor.

Recently investigations have been reported on the co-processing of hydrotreated pyrolysis oils obtained with a Ru/C catalyst (oxygen contents > 5 wt%) in a lab scale simulated FCC unit (MAT) (de Miguel Mercader et al., 2010). The hydrotreated products were successfully dissolved and processed in Long Residue (20 wt% upgraded oil). The yields of FCC gasoline (44–46 wt.%) and Light Cycle Oil (23–25 wt.%) were close to the base feed and an excessive increase of undesired coke and dry gas was not observed. Experiments with undiluted upgraded oils were less successful and dry gas and coke yield were significantly higher than in case of co-feeding. This clearly demonstrates that co-processing is necessary to obtain good product yields. This study also shows that, in contrast to initial thoughts, it is likely not necessary to aim for an upgraded oil with an oxygen content lower than 1 wt%.

Further MAT testing with product oils derived from catalyst D is in progress and will allow the establishment of detailed process-product relations for co-feeding purposes. The upgraded oils prepared with cat D have a much higher thermal stability than the original pyrolysis oil, as evident from the TGA residues (Figure 14). Preliminary investigations have shown that this allows distillation of the oil in various fractions without the formation of excessive amounts of char. Further detailed studies are in progress and will be reported in due course.

7. Conclusions

The upgrading of pyrolysis oil by catalytic hydrotreatment reactions using heterogeneous catalysts was studied in detail using a Ru/C catalyst. The investigations provided valuable insights in the chemical transformations occurring during catalytic hydrotreatment and include both thermal and hydrogenation/hydrodeoxygenation pathways. The repolymerisation pathway in which the oils are further condensed to soluble oligomers and eventually to char components competes with a catalytic hydrogenation reaction. In case H₂ is present with a proper catalyst, these soluble oligomers may be depolymerised to stabilized components that can be further upgraded. In this respect, the pyrolysis oils show reactivity typically observed for carbohydrates, which is rationalised by considering the high amounts of oligo- and monomeric sugars in the oil. New, highly active Ni-based catalysts have been developed, which show much better performance than conventional ones and provide products with improved properties.

Experimental work is foreseen to elucidate the reaction pathways occurring during catalytic hydrotreatment in more detail and to develop efficient processes to obtain a stabilized oil with the desired product properties at the lowest manufacturing costs. These include:

- Determination of the effects of reactor configuration on the reaction rates (including mass transfer issues) and subsequent reactor selection;
- Determination of relevant physical properties (e.g hydrogen solubility);
- Optimisation of the hydroprocessing conditions and particularly the required hydrogen levels
- Determination of product-process relations. The effective hydroprocessing severity required for further co-refining must be defined;
- The source and availability for hydrogen: perhaps even syngas is applicable;
- Effects of reaction exothermicity need to be determined.

8. Acknowledgement

The authors would like to acknowledge the EU for partial funding of the work through the 6th Framework Program (Contract Number: 518312). We also would like to thank the partners of BIOCUP project, and especially D. Assink (BTG), A. Ardiyanti and J. Wildschut (RuG, The Netherlands) for performing (part of) the experiments and mutual interpretation of results, VTT (Finland) and particularly A. Oasmaa for the fractionation analysis and V. Yakovlev and S.A. Khromova of the Boreskov Institute for Catalysis (Russia) for catalyst preparation and stimulating discussions. Furthermore, financial support from SenterNovem (in CORAF, project no. EOSLT04018, and NEO-project, no. 0268-02-03-03-0001) is gratefully acknowledged.

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Biofuel's Engineering Process Technology

Edited by Dr. Marco Aurelio Dos Santos Bernardes

ISBN 978-953-307-480-1

Hard cover, 742 pages

Publisher InTech

Published online 01, August, 2011

Published in print edition August, 2011

This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Venderbosch R.H. and Heeres H.J. (2011). Pyrolysis Oil Stabilisation by Catalytic Hydrotreatment, Biofuel's Engineering Process Technology, Dr. Marco Aurelio Dos Santos Bernardes (Ed.), ISBN: 978-953-307-480-1, InTech, Available from: <http://www.intechopen.com/books/biofuel-s-engineering-process-technology/pyrolysis-oil-stabilisation-by-catalytic-hydrotreatment>

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