

University of Groningen

Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts

Wang, Yuehu

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Wang, Y. (2017). *Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

Copyright

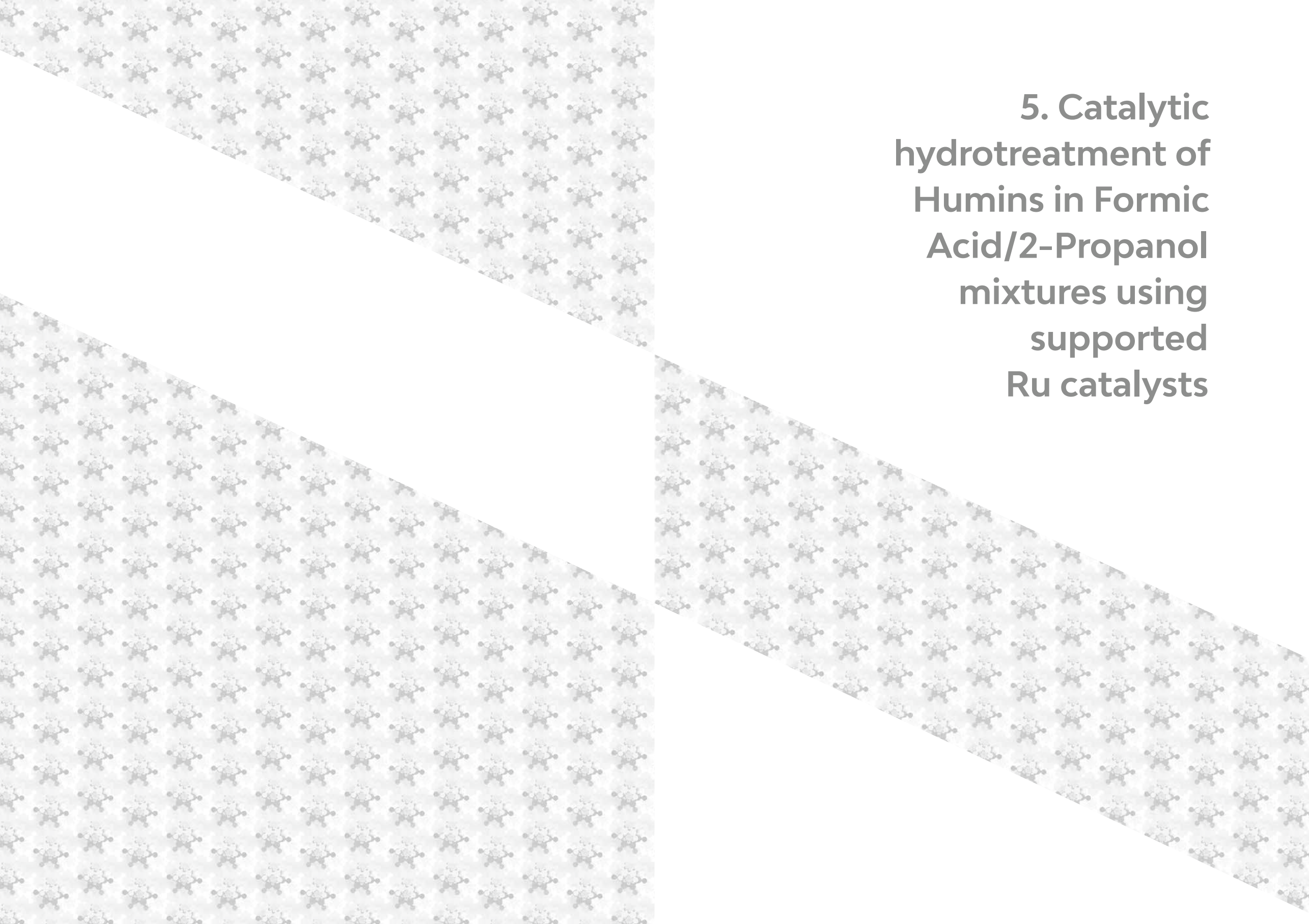
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

The background of the slide features a repeating pattern of a chemical structure, likely a benzene ring with a central atom, arranged in a grid. The pattern is light gray and covers the entire background, with a white diagonal band running from the top-left to the bottom-right.

5. Catalytic hydrotreatment of Humins in Formic Acid/2-Propanol mixtures using supported Ru catalysts

ABSTRACT

The catalytic hydrotreatment of humins, the solid byproducts from the conversion of C₆ sugars (glucose, fructose) to 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), using supported Ru catalysts has been investigated. Reactions were carried out in a batch set-up at elevated temperatures (400 °C) using a hydrogen donor (formic acid (FA) in isopropanol (IPA) or hydrogen gas), with humins obtained from D-glucose. Humin conversions of up to 69% were achieved using Ru/C and FA, whereas the performance for the Ru on alumina was slightly worse (59 % humin conversion). The humin oils were characterised using a range of analytical techniques (GC, GC-MS, GC×GC, GPC) and were shown to consist of monomers, mainly alkyl phenolics (> 45% based on GC detectables) and higher oligomers. A reaction network for the reaction is proposed based on structural proposals for humins and the main reaction products.

Keywords: biomass, heterogeneous catalysis, ruthenium, supported catalysts, synthesis design

Y. Wang, S. Agarwal, A. Kloekhorst, H. J. Heeres, Catalytic hydrotreatment of Humins in Formic Acid/2-Propanol mixtures using supported Ru catalysts, *ChemSusChem*, 2016, 9(9), 951-961.

5.1. INTRODUCTION

Lignocellulosic biomass has been identified as a potentially attractive source for chemical products and is considered a promising raw material to (partly) substitute fossil carbon resources.^[1-5] It is available in large quantities from agricultural resources, forestry, aquatic plants, and industrial waste streams (e.g. paper manufacture). Substantial research efforts are currently undertaken to develop and commercialise processes to convert biomass to bulk chemicals and derivatives (e.g. novel biobased polymers).

A potentially very powerful approach is the conversion of the cellulose and hemicellulose fraction into platform chemicals using either biochemical (fermentation or enzymatic) or metal/Brønsted acid catalysed transformations.^[1-6] Attractive platform chemicals are levulinic acid (LA) and 5-hydroxymethylfurfural (HMF).^[7-11] LA is conventionally obtained from the C₆sugars of lignocellulosic biomass in water and may be converted to a number of derivatives with high application potential (e.g. gamma-valerolactone). HMF is best prepared from D-fructose containing feeds and may, for instance, be oxidised to 2,5-furandicarboxylic acid (FDCA). The latter is used to produce polyethylenefuranoate (PEF), a high-potential biobased polyethyleneterephthalate (PET) replacement, in which the terephthalic acid moiety is replaced by FDCA.^[12]

However, the conventional synthetic methodology to prepare LA and HMF in water using a mineral acid as the catalyst suffers from the formation of solid byproducts, known as humins. These not only cause operational issue (fouling) but also lower the carbon efficiencies considerably.^[13-15]

The negative effects associated with humin formation can be partly reduced by the development of value-added products from the humins. For the rational design of catalytic methodology, insight in the molecular structure of humins is essential.

However, relatively little is known about the molecular structure of humins. Most information is based on structural characterisation studies on hydrothermal carbons (HTCs). These materials are typically obtained by

heating various lignocellulosic biomass sources in water at elevated temperatures and pressures. Though the synthetic procedures for humin and HTC formation differ considerably (thermal reactions for HTC, in combination with the use of lignocellulosic biomass sources including lignins versus Brønsted acid catalysts and the use of simple monomeric sugars for humins), some similarities may be present at the molecular level. Bacile *et al.* have reported that HTC has a furanic structure with methylene linkages, mainly based on 2D solid state NMR measurements.^[16] However, Sevilla *et al.* proposed that humins consist of condensed polyaromatic structures (XPS, IR, Raman).^[17-19]

A limited number of characterisation studies have been reported for humins from monomeric sugars. Zarubin *et al.* proposed a furan-rich structure with ether and (hemi) acetal linkages (elemental analyses, IR, NMR of acetone extracts).^[20] Lund *et al.* reported that humins from HMF are formed by aldol condensation reactions of the intermediate 2,5-dioxo-6-hydroxyhexanal (including reactions with HMF) giving a furan rich structure, with the exact amounts of furanic fragments depending on the level of HMF involved in the aldol condensation reactions.^[21] We have recently proposed a structural model for humins based on extensive characterisation studies (elemental analysis, IR, solid state NMR and pyrolysis GC-MS).^[22-23] In this proposal, the structure is assumed to consist of an HMF derived, furan rich polymeric network in which the furan units are linked by short aliphatic chains with several oxygen functionalities (Figure 5-1).

A number of valorisation routes can be envisaged for humins (Figure 5-2). The overall objectives are the depolymerisation of the humin structure to low molecular weight components and the subsequent conversion to biobased chemicals. In this respect, there are similarities between humins and lignins.^[24-28] Lignins are also poorly soluble, highly cross linked thermosets. However, it should be noted that the molecular structure of humins is markedly different from that of lignins. Lignins are known to consist of aromatic building blocks with various types of linkages between the aromatic nuclei (*vide supra*).^[29]

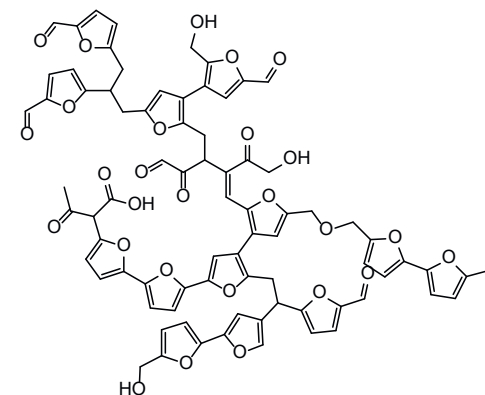


Figure 5-1. Proposed structure for humins from D-glucose (reproduced with permission).^[23]

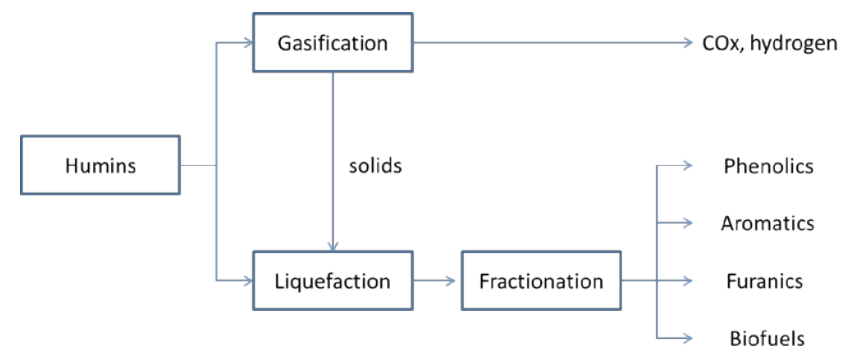


Figure 5-2. Possible valorisation routes for humins.

Gasification and particularly steam reforming of humins (900-1200 °C) with the objective to obtain syngas (mixture of CO_x and hydrogen) was studied by Hoang *et al.*^[30] It was shown that the presence of sodium carbonate is essential, acting as a catalyst and enhancing the rate of gasification reactions. The H₂ to CO ratio of the produced syngas was about 2. However, substantial loss of carbon was observed during the heating stage (up to 45 wt% on intake). To improve carbon yields, a second catalytic reactor is proposed to gasify the volatiles formed during the heating and to increase the solid to gas carbon efficiency.

Liquefaction of humins using pyrolysis technology was investigated by Rasrendra *et al.*^[31] Pyrolysis GC-MS showed the presence of furanics and organic acids in the vapour phase, though the individual components were present in only minor amounts (< 1 wt%). Micro-pyrolysis yielded 30 wt% gaseous and liquid products, the remainder being a solid char. Gas-liquid yields were lower than obtained for a typical lignin sample (Kraft lignin) under similar conditions. As such, pyrolysis seems to be cumbersome leading to relatively low liquid yields.

Our interest regarding the catalytic conversion of humins involves liquefaction using a catalytic hydrotreatment catalysed by a supported metal catalyst in combination with a hydrogen donor. The hydrogen donor can be either molecular hydrogen or a donor solvent like formic acid (FA). This synthetic methodology has been explored in detail for the depolymerisation of lignin to low molecular weight chemicals.^[24] Examples are the catalytic hydrotreatment of lignin using metal supported catalysts like NiMo and CoMo on various supports.^[32, 33] Relatively harsh conditions (temperatures up to 450 °C, pressures up to 200 bar) are required for substantial depolymerisation activity. The use of hydrogen donor solvents in both the presence or absence of metal catalysts has been reported. A well known hydrogen donor is FA, which is *in situ*, either thermally or catalytically, converted to hydrogen and CO/CO₂. Other solvents, either for dilution or to act as a hydrogen donor, are alcohols (ethanol, methanol, IPA), and water. Temperatures between 573 and 653 K have been explored, with reaction times ranging from 2-17 h. Kleinert *et al.* were able to convert alkaline extracted lignin from spruce, pine, birch, and aspen wood to a liquid products in 93% mass on lignin intake yield at 653 K with a reaction times of 17 h using FA in iso-propanol.^[24, 34] Recent research by Liguori *et al.* showed that the reaction times and temperature can be reduced drastically when using a catalytic version (Pd/C) in water.^[35] Major products were guaiacols (4.6% mass on lignin intake) and catechols (4.7% mass on lignin intake). It was hypothesised that the heterogeneous catalyst enhances the FA decomposition rate at lower temperature and as such has a positive effect on lignin depolymerisation rates and the

rate of the subsequent deoxygenation of the lower molecular weight fragments. Recent work from Xu *et al.* reported the use of Pt/C with ethanol and formic acid for the conversion of switchgrass lignin, and they reported that the combination of both formic acid and Pt/C promotes higher amounts of lower molecular weight compounds in the liquid phase.^[36]

Recently, Trautment *et al.* have reported studies on the catalytic treatment of HTC materials to biofuels.^[37, 38] Various HTC materials were tested using Ni on titania as the catalyst at temperatures between 473 and 523 K, and reaction times between 3 and 20 h. Here, hydrogen is formed *in situ* which then serves as the reactant for hydrocracking reactions and the formation of liquid products. Although HTC materials are likely more complex in nature than humins and for instance also contain lignins and minerals, which may be catalytically active, these findings suggest that catalytic hydrotreatment reactions for humins to liquid products may also be feasible.

In this work we report experimental studies on the catalytic conversion of humins using Ru based catalysts (carbon and alumina support) with a mixture of FA/IPA as the hydrogen donor solvent. The results will be compared with experiments using IPA in the presence of molecular hydrogen. This system was selected based on recent results in our group showing that it is suitable for lignin depolymerisation and further hydrodeoxygenation reactions.^[39] For instance, when using Alcell lignin in IPA/FA mixtures (1 to 1 wt. ratio) using Ru/C as the catalyst (400 °C, 4 h, 28 wt% lignin intake on IPA/FA), lignin oils were obtained in good yields (up to 71 wt% intake on lignin) and shown to consist of a mixture of mainly monomeric aromatics (10.5 wt%), alkylphenolics (6 wt%), catechols (8.7 wt%), guaiacols (1.3 wt%), and alkanes (5.2 wt%). The remainder being soluble higher molecular weight compounds (GC×GC-FID and GPC). In this system, Ru has a dual function and catalyses the formation of hydrogen from IPA and FA as well as subsequent hydrocracking and hydrodeoxygenation of the low molecular weight fragments.

The objective of the current study was to develop an efficient way to depolymerise the humins and to convert the fragments to valuable bulk chemicals (furanics, aromatics, phenolics). Product characterisation was

carried out using a range of analytical techniques (including GC×GC) and the effect of process parameters like humin-to-solvent ratio, catalyst loading and reaction time were investigated. To the best of our knowledge, this is the first report on the catalytic hydrotreatment of humins.

5.2. MATERIALS AND METHODS

Chemicals. D-glucose, H₂SO₄, FA, dichloromethane (DCM), di-n-butylether (DBE), Ru/C and Ru/Al₂O₃ (5 wt% on supports) were obtained from Sigma Aldrich. IPA was from Fluka. Hydrogen (> 99.99%) and nitrogen gas (> 99.8%) were obtained from Hoekloos. All chemicals were used without further purification.

Humins synthesis. The humins used in this study were synthesised by the conversion of D-glucose in water at elevated temperature (180 °C) using sulphuric acid as the catalyst, as reported in the literature.^[22] The elemental composition of the humins was 64.64 wt% carbon, 4.38 w% hydrogen and 30.9 wt% oxygen by difference (H/C: 0.81 and O/C: 0.36 mol/mol), which agrees well with reported values.^[22]

Catalytic hydrotreatment experiments. The catalytic hydrotreatment experiments were performed in a batch Parr reactor system consisting of a batch autoclave (100 mL, model number 4590 with a maximum operating pressure of 350 bar and temperature of 500 °C) with electric heating, equipped with an overhead stirrer and temperature control. The stirring speed was set at 1400 rpm for all experiments. In a typical experiment, the reactor was charged with a humin sample (7.0 g), IPA (9.0 g), FA (9.0 g) and Ru/C (0.35 g, 5 wt% on humin intake). The reactor was closed and tested for leakage by pressurising with 80 bar of nitrogen. The pressure was released and the reactor was subsequently flushed twice with nitrogen gas. The reactor was heated to 400 °C at a rate of about 9 °C/min and the reaction was allowed to proceed for 6 h. After reaction, the reactor was cooled to room temperature and the pressure was recorded for calculation of the amount of gases

formed during the reaction. The pressure was released and the gas phase was collected in a 3 L plastic gas bag and was analysed with gas chromatography. The suspension was removed from the reactor, weighed and placed in a centrifuge tube (50 mL). After 45 min of centrifugation at 4500 rpm, two liquid phases and a solid phase were obtained. The organic (upper liquid phase, designated oil 1) was separated and weighed. The remaining aqueous phase and the solid residue were extracted with DCM (50 mL). The DCM was evaporated (70 °C, 0.03 bar for 2 h) leaving a dark brown residue (oil 2). The oil samples (1 and 2) were combined and weighed. For some of the analyses, residual amounts of IPA/FA and other low molecular weight reaction products arising from the solvents (e.g. acetone, *vide infra*) in the humin oils were removed by evaporation (70 °C, 0.03 bar for 12 h). It was shown that also considerable amounts of low molecular weight low boiling compounds and particularly cycloalkanes were removed from oil 1 by this procedure and as such the amount of these components is underestimated when considering the composition of the humin oils after this evaporation step. The solid residue (unreacted humins, catalyst) was dried overnight in a vacuum oven at 70 °C, 0.03 bar and weighted for mass balance calculations. An overview of the hydrogenation protocol is shown in Figure 5-3.

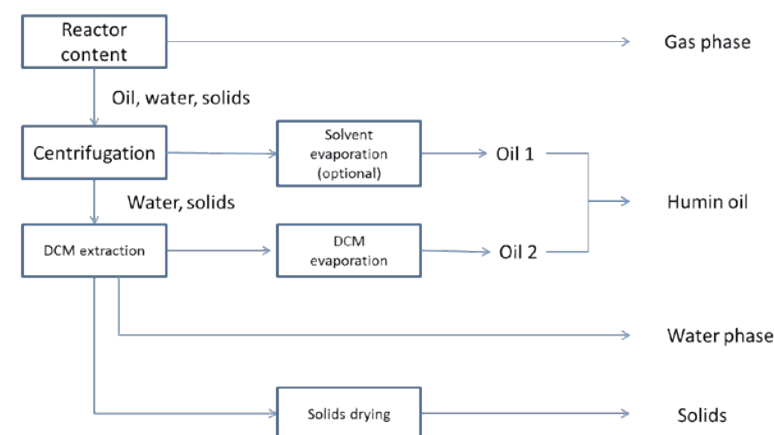


Figure 5-3: Experimental protocol for catalytic humin hydrotreatment in a mixture of FA and IPA (Solids include the char, unconverted humins and catalyst).

The humin oil yield on humin intake (Equation 5-1), humin oil on total feed intake (Equation 5-2) and the humin conversion (Equation 5-3) are mass based and are calculated as follows:

$$\text{Humin oil yield on humin intake} = \frac{\text{weight of humin oil}}{\text{humin intake}} \times 100\% \quad (5-1)$$

$$\text{Humin oil yield on reactor intake} = \frac{\text{weight of humin oil}}{\text{total feed intake}} \times 100\% \quad (5-2)$$

$$\text{Humin conversion} = \frac{\text{humin, in} - (\text{solids, out} - \text{catalyst})}{\text{humin, in}} \times 100\% \quad (5-3)$$

In Equation 5-1, the weight of humin oil is the sum of oil 1 and oil 2. Oil 1 is the organic phase after reaction including some of the organic solvents and reaction products derived thereof (*vide infra*). As such, the humin oil yield can be higher than 100%. The total feed intake is defined as the sum of the amounts of humin and solvents (IPA/FA). Humin conversion was calculated based on humin intake and the solid products obtained after reaction. It assumes that the solid residue consists of unconverted humins and as such solids formation due to repolymerisation reactions of reactive intermediates is not taken into account.

Elemental Analysis. Elemental analysis of humins and humin oils were performed using a EuroVector EA3400 Series CHN-O with acetanilide as the reference. The composition of oxygen was determined by the difference. All samples were analysed at least twice and the average value is reported.

GC-MS-FID. GC-MS-FID analyses were performed on organic product samples using a Hewlett Packard 5890 series II plus equipped with a Quadrupole Hewlett Packard 5972 MSD and an FID. A Restek RTX-1701 capillary column (60 × 0.25 mm i.d. and 0.25 μm film thickness) was used, which was split in a 1:1 ratio to the MSD and FID. The injector temperature was set at 250 °C. The oven temperature was kept at 40 °C for 5 minutes then heated up to 250 °C at a rate of 3 °C min⁻¹.

Residual amounts of FA and IPA were quantified with GC-MS-FID. For this purpose, the FID signal was used, which is better for quantification

than the MS signal. Calibration was done with pure components, giving calibration lines with R² values above 0.9998 for 5 different concentrations.

Two-Dimensional Gas Chromatography (GC×GC-FID). GC×GC-FID analyses were performed on a Trace GC×GC system from Interscience equipped with a cryogenic trap and two columns (30 m × 0.25 mm-i.d. and 0.25 μm-film RTX-1701 capillary column connected to a 120 cm × 0.15 mm-i.d. and 0.15 μm-film Rxi-5Sil MS column). A flame ionization detector (FID) was used. A dual-jet modulator was applied using carbon dioxide to trap the samples. Helium was used as the carrier gas (flow rate of 0.6 mL/min). The injector temperature and FID temperature were set at 280 °C. The oven temperature was kept at 60 °C for 5 min and then heated to 250 °C with a rate of 3 °C min⁻¹. The pressure was set at 0.7 bar. The modulation time was 6 s.

From the GC×GC-FID chromatograms, the yields of aromatics, phenolics, ketones, alkanes, naphthenes and acids were calculated based on the humin intake. The identification of main GC×GC component groups (e.g. alkanes, aromatics, alkylphenolics) in the lignin oils was done by spiking with representative model compounds for the component groups, GC-MS-FID analysis, and GC×GC-TOFMS analysis for a representative sample (Figure S5-1 and Table S5-2, supplementary information). Quantification was performed by using an average relative response factor (RRF) per component group with di-n-butyl ether (DBE) as the internal standard (see supplementary information).

All the samples were diluted in THF before analysis. In case of the blank experiments (Table 5-1, experiment 3) the samples were not diluted to allow identification of minor components.

GC×GC with Time-of-flight Mass Spectrometer. A representative sample (from Run 1 in Table 5-1) was analysed on a GC×GC-HR TOFMS from JEOL equipped with a cryogenic trap system and two columns: a RTX-1701 capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness) connected by a Melfit to a Rxi-5Sil MS column (120 cm × 0.15 mm i.d. and 0.15 μm film thickness). A TOFMS JMS-T100GCV 4G detector was used with a scanning speed of 50 Hz with a mass range of 35-600 m/z.

Helium was used as the carrier gas (0.8 mL min^{-1}). The injector temperature and TOFMS temperature were set at $250 \text{ }^\circ\text{C}$. The oven temperature was kept at $40 \text{ }^\circ\text{C}$ for 5 minutes then heated up to $250 \text{ }^\circ\text{C}$ at a rate of $3 \text{ }^\circ\text{C min}^{-1}$. The pressure was set at 77.5 kPa at $40 \text{ }^\circ\text{C}$. The modulation time was 6 s. The MS-spectra were analysed with GC Image[®] software and a homemade Matlab routine.

Gas phase analysis. The gas phase samples were collected in a gasbag (SKC Tedlar 3 L sample bag $9.5'' \times 10''$ with a polypropylene septum fitting) after the hydrotreatment reaction. The gaseous products were analysed using a GC (Hewlett Packard 5890 Series II equipped with a Poraplot Q $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ column and a molecular sieve (5 \AA) column) and a thermal conductivity detector (TCD). Both columns were maintained at the same temperature. The injector and detector temperature were set at $150 \text{ }^\circ\text{C}$ and $90 \text{ }^\circ\text{C}$ respectively. The oven temperature was kept at $40 \text{ }^\circ\text{C}$ for 2 minutes then heated to $90 \text{ }^\circ\text{C}$ at the rate of $20 \text{ }^\circ\text{C min}^{-1}$ and kept at this temperature for another 2 min. For identification and quantification, a reference gas mixture (55.19% H_2 , 19.70% CH_4 , 3.00% CO , 18.10% CO_2 , 0.51% ethylene, 1.49% ethane, 0.51% propylene and 1.50% propane) was used.

Gel Permeation Chromatography (GPC). Gel permeation chromatography was performed on an Agilent HPLC 1100 system. Three columns (PLgel $3 \mu\text{m MIXED-E}$, length 300 mm, inside diameter of 7.5 mm) were used. Polystyrene samples with different molecular weights were used to obtain a standard calibration curve. In a typical analysis, the product (20 mg) was dissolved in THF (2 mL), then filtered using a PTFE filter (0.2 mm pores size) with glass injector to avoid contamination from plastic injector and then injected with a 2 mL autosample vial.

TOC determinations. The total organic carbon (TOC) in the water phase was measured using a Shimadzu TOC-VCSH TOC machine with an OCT-1 sampler port.

5.3. RESULTS AND DISCUSSION

5.3.1. SCREENING EXPERIMENTS.

A standard catalytic hydrotreatment reaction was performed using a humin sample (28 wt% intake) obtained from D-glucose in a mixture of IPA and FA (1:1 wt ratio) with Ru/C (5 wt% on humin) as the catalyst. The reaction was carried out in a batch autoclave at $400 \text{ }^\circ\text{C}$ for a reaction time of 6 h. During heating, the pressure in the reactor increased typically to 200 bar when the temperature approached $400 \text{ }^\circ\text{C}$, likely due to the catalytic decomposition of FA to hydrogen and CO_x and the formation of other gas phase components (*vide infra*). After reaction, two immiscible liquid phases were obtained: an organic phase (humin oil 1) at the top and an aqueous phase at the bottom. After work-up (Figure 5-3), the organic phase, designated as humin oil was isolated and analysed in detail.

For the hydrotreatment in FA/IPA using Ru/C as the catalyst (Table 5-1, experiment 1), the amounts of solids after reaction (excluding catalyst) was 8.8 wt% on total feed, corresponding with a humin conversion of 69 wt%. Apparently, under these conditions, a considerable amount of the humins is converted to a liquid product. The humin oil yield on humin intake was 55.4 wt%. The occurrence of hydrodeoxygenation reactions is confirmed by the formation of a separate water phase (12 wt% on feed). The major product phase, however, is a gas phase, with yields up to 51% on total feed intake, due to the (desired) catalytic composition reaction of FA to hydrogen and CO_x . Quantitative FA conversion was observed (GC) after 6 h reaction time. In addition, IPA was also shown to be reactive and a considerable amount of the IPA was converted (up to 95%, GC) to liquid and gas phase components (*vide infra*).

The formation of gas phase components from IPA/FA was confirmed by performing a reaction in the absence of humins, i.e. a catalytic experiment with IPA/FA and Ru/C only (Table 5-1, experiment 3). After reaction, a liquid phase was obtained in a yield of about 20 wt% on IPA/FA intake. The majority of the solvents were converted to gas phase components (63 wt%),

Table 5-1. Product yields and compositions for the catalytic hydrotreatment using supported Ru catalysts.^a

Experiment	1	2	3	4
Solvent/reagents ^b	IPA/FA	IPA	IPA/FA	IPA/
Catalyst	Ru/C	Ru/C	Ru/C	Ru/Al ₂ O ₃
Hydrogen addition (bar)	-	20	-	-
Humin intake (wt% on feed)	28	28	-	28
Oil yield, wt% on total feed	15.5	35.0	19.4	8.7
Oil yield, wt% on humin intake	55.4	125.7	-	31.0
Aqueous phase, wt% on total feed	12.1	28.0	- ^c	6.9
C content water phase, wt%	5.5 ^e	n.d.	-	n.d.
Solids, wt% on total feed	8.8	11.7	-	14.1
Humin conversion, wt%	69	58	-	59
Gas phase, wt% on total feed	51	20.2	63	58.3
Carbon dioxide, mol%	29.6	39.0	54.5	24.5
Carbon monoxide, mol%	-	< 1	< 1	< 1
Ethylene, mol%	< 1	-	-	< 1
Ethane, mol%	< 1	4.0	2.4	< 1
Propylene, mol%	< 1	< 1	< 1	1.1
Propane, mol%	1.2	16.9	4.3	1
Methane, mol%	8.2	-	24.6	8.5
Hydrogen, mol%	58.9	38.9	13.0	63.5
Mass balance closure (wt%)	88	95	82	85
Elemental composition humin oil (wt%) ^d				
Carbon	83.59	82.6	-	82.16
Hydrogen	8.11	8.3	-	7.92
Oxygen	8.30	9.1	-	9.92

a) All reactions were carried out with 28% humin intake (from D-glucose) on solvent, 5 wt% Ru/C on humin intake and 400°C for 6 h b) IPA and FA ratio of 1 on wt. basis. c) no phase separation, one liquid phase after reaction d) after solvent evaporation e) before extraction of the water phase with DCM

indicating that not only FA but also IPA is reactive under the prevailing reaction conditions. The molecular composition of the product phases is given in the following paragraphs.

It must be noted that IPA not only acts as a solvent during the hydrotreatment reaction, but also contributes as a hydrogen donor. This can be

clearly seen in Table S5-3 (supplementary information) where in the presence of IPA (without H₂ gas or FA), 37% conversion of humins and 50 wt% oil yield (on total feed) was observed.

Mass balance closures were satisfactorily (> 82 wt%), the main issue being the large amounts of gas phase components formed which are cumbersome to quantify accurately. The reproducibility of the standard reaction (Table 5-1, experiment 1, humins, IPA/FA) was determined and the results are given in the supplementary information (Table S5-1). The product distribution as well as the mass balance closure are within 3%, showing that the reproducibility of the reaction is good.

For comparison, a reaction was carried out in IPA with molecular hydrogen (20 bar) as the hydrogen donor instead of FA (Table 5-1, experiment 2). In this case, the amount of gas phase after reaction is, as expected, less than for FA (20.2. wt% on total intake, versus 51% for FA). However, the humin conversion is lower than for FA (69% versus 58%). These differences in performance could be due to either a different reaction pathway for both reagents or differences in the hydrogen pressure in the reactor. A quick estimation (assuming the ideal gas law in case of hydrogen), indicates that the amount of hydrogen at the start of the reaction is lower for the experiment with hydrogen gas (0.06 mol) than for an experiment with FA (0.2 mol of hydrogen, assuming that 1 mol of formic acid gives one mole of hydrogen). As such, a lower hydrogen pressure is likely the cause for the lower humin conversion observed for the experiment with molecular hydrogen and not an intrinsic feature of the reaction.

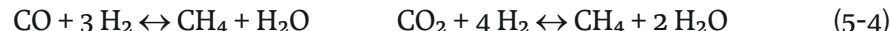
Thus, we can conclude that humins can indeed be solubilised by a catalytic hydrotreatment reaction using FA in IPA as the hydrogen donor. However, IPA is also not inert under these conditions and contributes to the formation of gas phase components and other products in the liquid phase (*vide infra*). Besides FA, molecular hydrogen can also be applied, though the humin conversion seems to be lower than when using FA as the hydrogen donor.

5.3.2. COMPOSITION OF THE GAS AND LIQUID PHASE FOR CATALYTIC HYDROTREATMENTS WITH RU/C

5.3.2.1. GAS PHASE COMPOSITION

The composition of the gas phase for the standard reaction with FA/IPA, hydrogen as well as the blank reaction without the humin sources were determined (Table 5-1). The main gas phase component for the standard experiment is hydrogen (59 mol%) followed by CO₂ (29 mol%) and some methane (8 mol%). Part of the gas phase components are formed from FA, which is known to decompose in the presence of Ru/C to give CO, CO₂ and hydrogen.^[40]

Methane may either be formed by reactions of the humins, e.g. cleavage of alkyl substituents and/or by subsequent gas phase hydrogenation reactions of CO_x with hydrogen (Equation 5-4). The latter methanation reaction is known to be catalysed by supported Ru catalysts.^[39, 41]



5.3.2.2. LIQUID PHASE COMPOSITION FOR EXPERIMENTS WITH RU/C

5.3.2.2.1. ELEMENTAL COMPOSITION OF THE HUMIN OILS

The elemental composition of the humin oils after solvent evaporation for the standard catalytic solvolysis experiment with IPA/FA (Table 5-1, experiment 1) and the reaction with IPA/H₂ (Table 5-1, experiment 2) together with some relevant other products are given in the form of a Van Krevelen plot (Figure 5-4). The H/C content of both humin oils is higher than for the humin starting material. Thus, hydrogenation reactions and the formation of compounds with a higher H/C ratio have occurred to a significant extent. The O/C ratio of the oil is considerably lower than for the parent

humins. As such, hydrodeoxygenation reactions take place as well, in line with the formation of water and the molecular composition of the humin oils (*vide infra*). In the Van Krevelen plot, also relevant ratios of some HTC materials and the product oil after a liquefaction reaction have been added. It is evident that the HTC materials differ substantially from humins when considering the elemental composition. Moreover, liquefaction of these materials mainly result in a reduction in the O/C and not in an increase in the H/C ratio. As such, hydrogenation is occurring to a far lesser extent with the liquefaction of the HTC materials than with our procedure involving a hydrogen donor (H₂ and/or IPA).^[37, 38]

The HHV of the two product oils, calculated from the elemental composition using the Milne equation^[42] were about 38.5 MJ/kg, which is more than 1.5 times the value of the starting humin sample derived from D-glucose (22.6 MJ/kg). As such, considerable energy densification has occurred. However, humin liquefaction to a biofuel with a higher heating value than the original humins was not the major objective of this study. The main interest concerns the conversion of the humins to higher added value biobased chemicals like BTX and alkylphenolics. Therefore, a detailed characterisation study on the liquid organic products was performed.

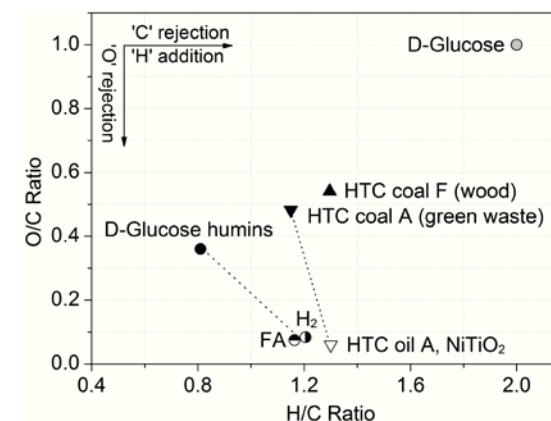


Figure 5-4. Van Krevelen plot showing the composition of the humin sample, two humin oils and data for HTC materials and liquefaction products.^[37, 38]

5.3.2.2. MOLECULAR COMPOSITION OF THE HUMIN OILS

The molecular composition of the humin oils from a standard experiment using FA/IPA as the solvent (Table 5-1, experiment 1) was determined using GC-MS-FID and GC×GC-FID. A typical GC-MS-FID spectrum of this humin oil is shown in Figure 5-5. Clearly, a wide range of products is formed, including phenolics, aromatics, as well as ketones and alcohols.

The humin oil from the standard experiment was also analysed with GC×GC for quantification of products (Figure 5-6). This technique allows rapid assessment of major organic compound classes (e.g. aromatics, alkylphenolics, aliphatic hydrocarbons) in an organic biomass derived liquid.^[43, 44] Clearly, good separation between the various organic compound classes is possible and discrete, well separated regions are visible.

A summary of the various component classes and some representative components of each component class is provided in Table 5-2. Apart from aromatics and phenolics, multiphenylic oxygenated aromatics (MPOA), polycyclic aromatic hydrocarbons (PAHs) and cycloalkanes were observed (Figure 5-6). Since humins contain significant amounts of furanic units, one would expect the presence of furanics in the final product oil. However, these were not identified by GC-MS/-ID and GC×GC analysis. A possible explanation is the high reactivity of (substituted) furanics under the prevailing reaction conditions in the presence of heterogeneous metal catalysts, which may lead to a wide range of products.^[45-48] It is well possible that aromatisation of furanics is occurring to a significant extent during the hydrotreatment reaction. Such reactivity has been reported in the literature and was recently also observed when heating up humins in water in the presence of a base.^[23]

Based on mass balance considerations (Table 5-1), the blank reaction (Table 5-1) and literature precedents,^[49-53] it is highly likely that IPA is not inert under the prevailing reaction conditions and that the product oils contain product derived from IPA. To gain insights in this possibility, the liquid reaction product of the blank reaction (Table 5-1, experiment 3) was

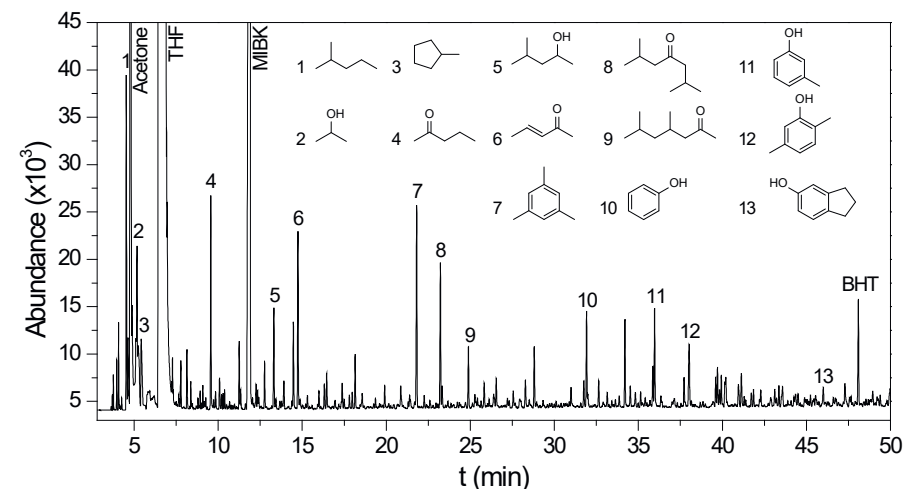


Figure 5-5. GC-MS/FID spectrum of a humin oil before evaporation of solvents (Table 5-1, experiment 1; Ru/C, 400 °C, 6 h).

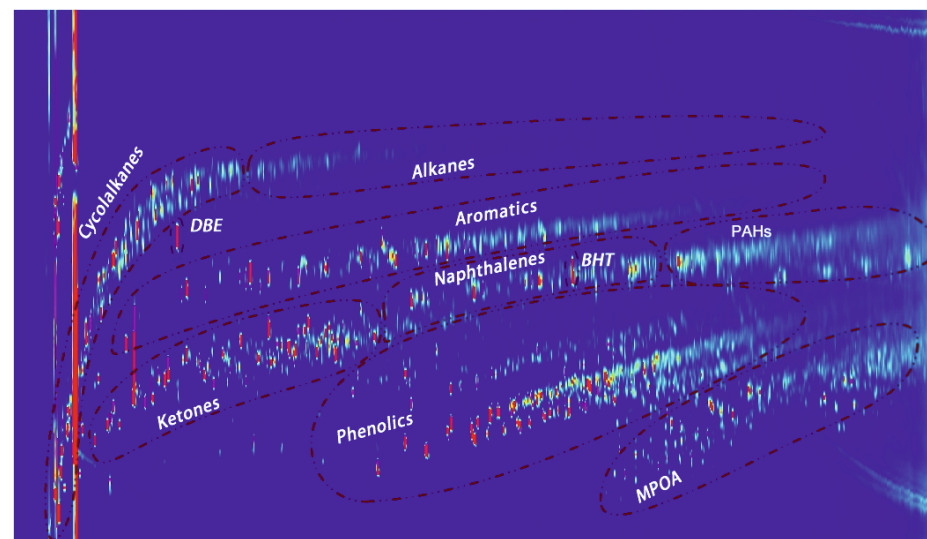









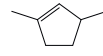
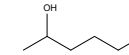





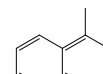
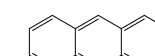
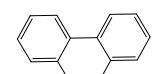
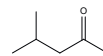
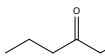
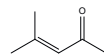
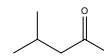
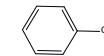
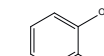
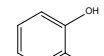
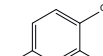
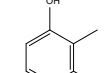
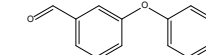


Figure 5-6. GC×GC plot of a representative humin oil (standard experiment: Ru/C, 400 °C, 6 h, crude reaction mixture before solvent evaporation, BHT is the stabiliser in THF).

Table 5-2. Major component classes and representative individual components in the humin oil obtained at standard conditions (GC×GC).

Alkanes	 Isobutane	 Butane, 2-methyl-	 Pentane	 Pentane, 2-methyl-	 Heptane, 2-methyl-
Cycloalkanes	 Cyclopentane	 Cyclopentane, methyl-	 Cyclohexane, methyl-	 Cyclopentane, 1-ethyl-3-methyl-	
Alkenes	 Cyclopentene, 1,2,3-trimethyl-				
Alcohols	 2-Hexanol				
Aromatics	 Toluene	 Ethylbenzene	 p-Xylene	 Benzene, 1,2-dimethyl-	 Benzene, 1,2,3-trimethyl-
Naphthalenes	 Naphthalene, 1-methyl-				
Poly aromatic hydrocarbons (PAHs)	 anthracene		 phenanthrene		
Ketones	 Methyl Isobutyl Ketone	 3-Hexanone	 3-Penten-2-one, 4-methyl-	 3-Hexanone, 5-methyl-	
Phenolics	 Phenol	 Phenol, 2-methyl-	 Phenol, 2-ethyl-	 Phenol, 2,4-dimethyl-	 Phenol, 2,3-dimethyl-
Multiphenylic oxygenated aromatics (MPOA)	 3-phenoxybenzaldehyde				

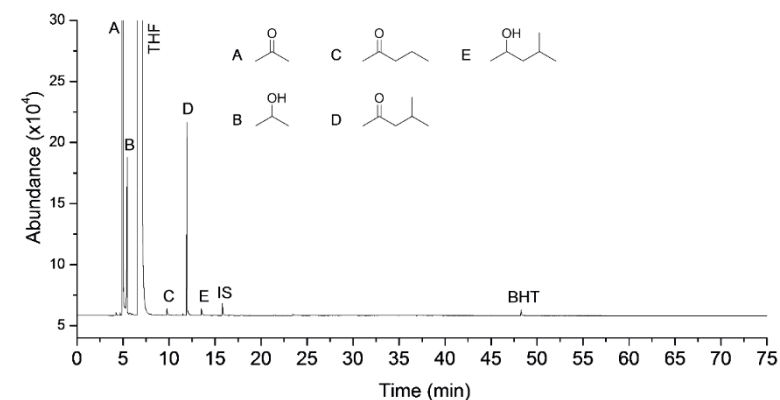
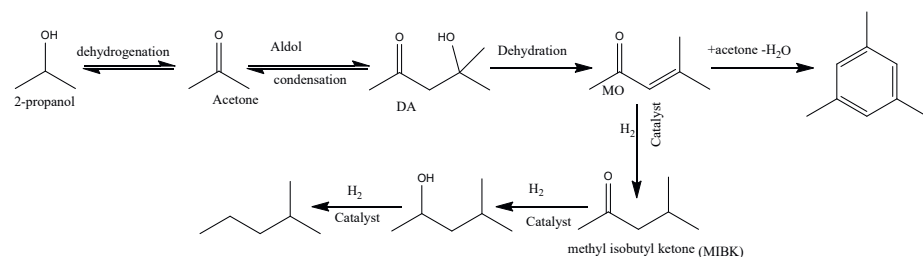


Figure 5-7. GC-MS/FID spectrum for the blank experiment (Table 5-1, experiment 3, FA/IPA, Ru/C, 6 h, 400 °C, BHT is the stabilizer in the solvent, IS is the internal standard).

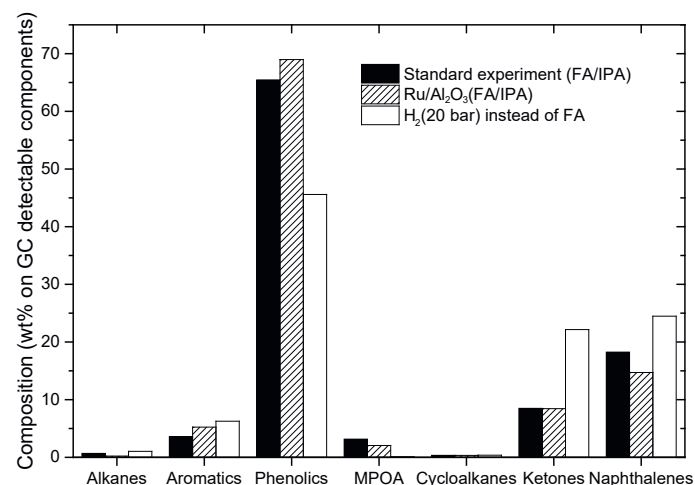
also analysed in detail. GC-MS analyses reveals that mainly alcohols and ketones were present (Figure 5-7), examples are acetone, and methyl isobutyl ketone (MIBK).

These products likely all originate from IPA by a reaction pathway provided in Scheme 5-1.^[53] It involves the initial dehydrogenation of IPA to acetone, followed by an aldol condensation to diacetylacetone (DA). DA may subsequently dehydrate to mestityloxyde (MO), which is then catalytically hydrogenated to MIBK. The latter is also expected to be reactive under the reaction conditions (hydrogen, Ru catalyst) to give the corresponding alcohol. Similar reactivity of IPA has been observed by Kleinert *et al.*^[24] for the non-catalytic solvolysis of lignin in FA/IPA mixtures as well as by Kloekhorst *et al.* for the catalytic solvolysis of lignin in FA/IPA mixtures using Ru/C.^[39]

It has been reported that IPA can be transformed to aromatics (e.g. mesitylene) during these condensation reactions.^[53] However, clear peaks associated with aromatics formation were not observed in the blank experiment. Hence, it appears that the aromatics, naphthalenes and alkylphenolics formed in the catalytic hydrotreatment reactions of humins arise from humins only and not from either IPA or FA. Further evidence that IPA does not form higher molecular weight compounds, was obtained by solvent



Scheme 5-1. Reaction pathways for 2-propanol under hydrotreatment conditions

Figure 5-8. Composition of the humin oils (after solvent evaporation) for experiments with FA/IPA (Ru/C and Ru/Al₂O₃) and an experiment with IPA/H₂ (Ru/C).

evaporation. For the blank experiment with IPA, the major products were evaporated under the conditions applied, whereas in the case of the catalytic hydrotreatment of the humin samples significant amounts of organic products were retained.

Quantification of the amounts of the major component classes in the humin oils after solvent evaporation was done based on the GC×GC measurements (Figure 5-8).

Phenolics are by far the most abundant compound class in the humin oils, followed by naphthalenes whereas only minor amounts of aromatics,

alkanes, cycloalkanes and MPOA's are present. Moreover, furanics were absent. The phenolics and naphthalenes are primarily formed from the humins and not from IPA (blank experiments, *vide supra*). As such, we can conclude that the catalytic hydrotreatment reactions of humins does not lead to furanics (as could be envisaged from the proposed molecular structure for humins) but mainly forms phenolics.

The amount of alkylphenolics on humin intake (and not on total GC detectables) for the standard experiment has been tentatively determined using GC×GC-MS. Quantification was performed with an internal standard method and the use of an average response factor per product class (see supplementary information). This resulted in a total alkylphenolics yield of about 9 wt% on humin intake. This number is likely to be slightly overestimated as it is based on the amount of alkylphenolics in evaporated oil samples. During evaporation of solvent, some of the lower molecular weight products such as low boiling alkanes are removed.

The total amount of detectable species using GC techniques (about 12-15% on humin intake according to a semi-quantitative GC×GC method) is by far less than the total amount of organic product oils present after reaction. This is due to the presence of a higher molecular weight, non-volatile fraction in the oils (typically > 250 Da) that are not detectable by GC techniques. To gain insights in the relative amounts of higher molecular weight products, the organic product phases were subjected to GPC analyses (Figure 5-9).

On the basis of the GPC data, we can conclude that the humin oils comprise of a mixture of components with a range of molecular weights. As such, the oils contain both low molecular weight, GC detectable compounds and higher molecular weight species, for instance oligomers.

The GPC profiles for both experiments do not differ considerably, though it appears that the degree of depolymerisation is slightly higher for the reaction with FA as the hydrogen donor. A possible explanation is the on average higher hydrogen content in the reaction mixture for this system (see Table 5-1, hydrogen content after reaction).

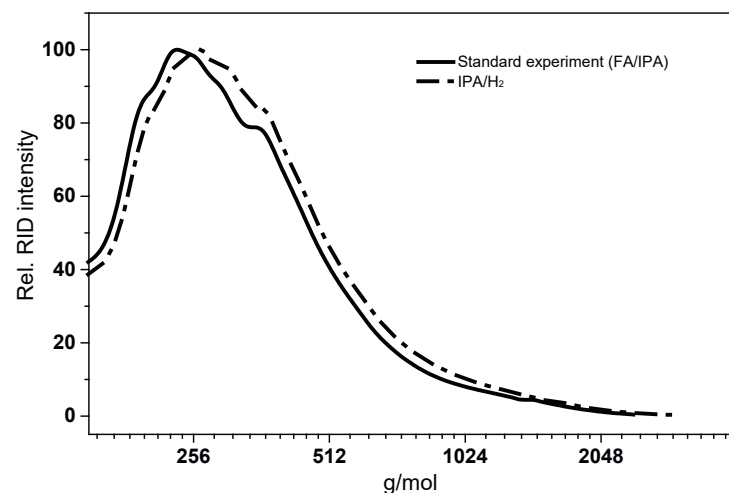


Figure 5-9. Molecular weight distributions for humin oils at standard conditions (IPA/FA) and IPA/H₂ using Ru/C (after solvent evaporation)

5.3.2.2.3. CATALYST SUPPORT EFFECTS

To gain some insight in catalyst support effects, we have carried out an experiment with Ru on alumina (5 wt% Ru) instead of Ru/C at standard conditions using FA as the hydrogen donor (Table 5-1, experiment 4). The results were worse than for Ru/C: a lower oil yield on total feed (8.7 versus 15.1 wt%), more solid residue (14.1 versus 8.8 wt% on total feed) and a higher amount of gas phase components (58.3 versus 51.2 wt% on total feed). Moreover, the resulting humin oil showed a higher O content than for the oil prepared with Ru/C (9.93 versus 8.30 wt%). As such, the extent of hydrodeoxygenation reactions with the concomitant formation of water is less than for Ru/C. In line with the latter is the formation of less water after reaction when using alumina as the support (6.9 versus 12.1 wt% on total feed intake). The molecular weight distributions for both oils is essentially similar, *viz.* 340 for Ru on alumina versus 330 for Ru/C.

The product distribution in the humin oil from the reaction with Ru/Al₂O₃ was also determined by GC×GC-FID and the results are given in

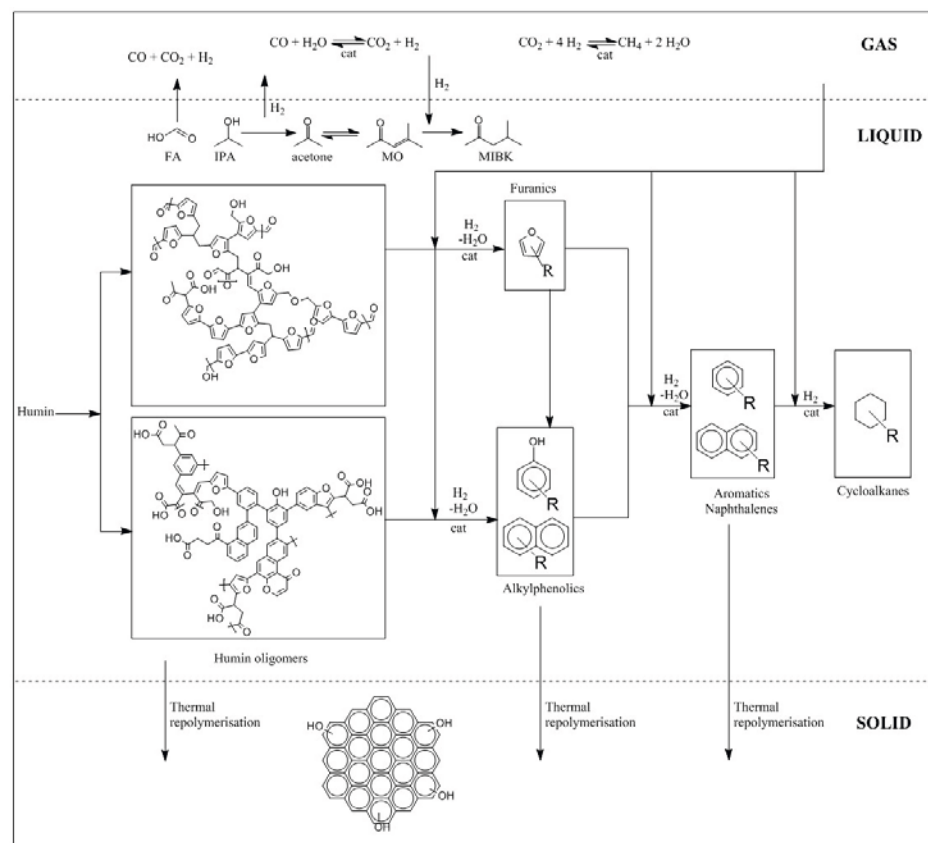
Figure 5-8. The main component classes are alkylphenolics and naphthalenes and the amounts are very close to the values found for Ru on carbon.

Hence, we conclude that supports have a major effect on the humin oil yield for Ru based catalysts, though the chemical composition of the humin oils are rather similar. A neutral support like carbon seems to provide better results than an acidic support like alumina. A possible explanation is the presence of acid sites in alumina, which may lead to repolymerisation of reactive intermediates, like has been shown in lignin depolymerisation studies.^[54, 55] In addition, the textural properties for alumina differ considerably from that of carbon (BET surface area and porosity) and it is well possible that the active metal sites are more accessible for the anticipated rather large molecules for subsequent reactions.

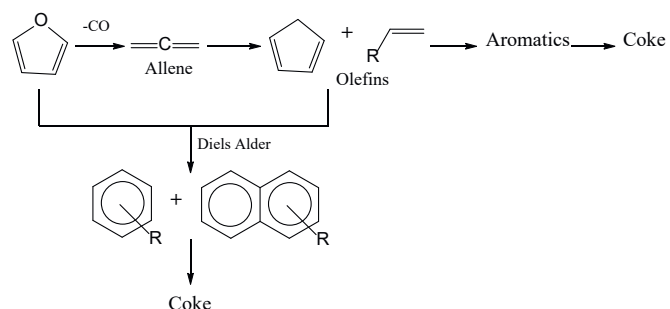
5.3.3. REACTION PATHWAYS

Based on the detailed product analysis for the gas and liquid phase, we propose a possible reaction pathway for the catalytic hydrotreatment of humins (Scheme 5-2).

In the liquid phase, reactions involving the humins as well as those for the solvents (IPA and FA) have to be considered. As pointed out earlier, IPA is converted to a number of dimerisation products amongst others MIBK (aldol condensation) whereas FA decomposes to CO_x and H₂. All these reactions (except the aldol condensation reactions) are expected to be catalyzed by Ru. For the humins, we propose a reaction scheme involving a number of parallel/series pathways with multiple intermediates. The main products to be considered are (substituted) alkylphenolics and naphthalenes, see the product distribution in Figure 5-8. Though the molecular weight of the humins has not yet been established unequivocally, it is evident that depolymerisation reactions occur to a significant extent as the product oils contain, besides oligomers (GPC, Figure 5-9), considerable amounts of monomeric, GC detectable products. The main linkages between the furanic



Scheme 5-2. Proposed reaction pathways for the catalytic hydrotreatment of humins



Scheme 5-3: Possible routes from furanics to aromatics and naphthalenes.

fragments in the humin structure are C-C bonds and, in analogy with lignin, these are expected to be relatively strong (in contrast to ether bonds). However, Ru catalysts have shown to be able to substantially depolymerise lignin (including C-C linkages) and as such this reaction seems feasible.^[32, 33] As such, low molecular weight furanics are expected to be formed. However, these are not identified in the reaction mixtures. It is well possible that the furanics are converted to substituted aromatics and naphthalenes by a number of established reaction pathways (Scheme 5-3).^[46-49, 56]

Though not very common, it also appears that furanics may be converted to multi-substituted phenolics. For instance, van Luijk *et al.* demonstrated that HMF may be converted to 1,2,4 benzenetriol in reasonable yields at temperatures in the range of 300-400 °C.^[57, 58]

An alternative pathway to consider is the conversion of the furanic fragments into aromatic structure in the humins prior to depolymerisation reactions. For instance, Van Zandvoort *et al.* have shown that heating up the humins to 240 °C in the presence of a base leads to structural changes and the formation of aromatic structures (Scheme 5-3, bottom humine structure).^[23] These reactions also seem to be possible by thermal action only. For instance, Chao *et al.* investigated the residue after heating up humins between 400 and 700 °C and found that the structure is strongly aromatised (lower H/C ratios, lower O/C ratios).^[30] For the time being, the actual pathway (aromatisation of the humin structure or cleavage of furanic building blocks to low molecular weight furanics) remains unclear and it is well possible that both pathways occur simultaneously.

Depolymerisation of the aromatised humins is expected to lead to substituted aromatics and naphthalenes and possibly also alkylphenolics. Our product mixtures also showed the presence of cycloalkanes. These are likely formed by overhydrogenation reactions of the naphthalenes and aromatics. Such reactions are also taking place to a significant extent for Ru based depolymerisation reactions of lignins.

5.4. CONCLUSIONS

We have shown that liquefaction of humins is possible using a catalytic hydrotreatment approach using Ru based catalysts with either FA or molecular hydrogen as the hydrogen donor in IPA as the solvent. Even though, IPA is not inert under these reaction conditions but act as an additional hydrogen source. Best results were obtained using Ru/C and humin conversions up to 69% were obtained using FA/IPA as the hydrogen donor. Elemental analysis showed that the oils have a considerably reduced oxygen content compared to the humin feed, with HHV's up to 38 MJ/kg. The product oils were shown to consist of both monomeric and oligomeric compounds (GPC). Main GC detectable species arising from the humins were substituted alkylphenolics, naphthalenes and cyclic alkanes (GC-MS-FID, GC×GC). A reaction network is proposed based on structural proposals for humins and the main reaction products. These findings reveal that the recalcitrant structure of humins may be (partly) depolymerised to a liquid biofuel with the potential to be a source for interesting bulk chemicals after fractionation. This opens new venues for the development of value-added outlets for humins beyond the use as a solid fuel. As such, these will have a positive effect on the technological viability of biorefinery schemes involving the conversion of C₆ sugars to biobased chemicals like levulinic acid and HMF.

5.5. REFERENCES

- Lichtenthaler FW, Peters S. Carbohydrates as Green Raw Materials for the Chemical Industry. *Comptes Rendus Chimie*. 2004; 7(2): 65-90.
- Bozell JJ, Petersen GR. Technology Development for the Production of Biobased Products From Biorefinery Carbohydrates - the US Department of Energy's "Top 10" Revisited. *Green Chemistry*. 2010; 12(4): 539-554.
- Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick Jr. WJ, Hallett JP, Leak DJ, Liotta CL, Mielenz JR, Murphy R, Templer R, Tschaplinski T. The Path Forward for Biofuels and Biomaterials. *Science*. 2006; 311(5760): 484-489.
- Zhou CH, Xia X, Lin CX, Tong DS, Beltrami J. Catalytic Conversion of Lignocellulosic Biomass to Fine Chemicals and Fuels. *Chemical Society Reviews*. 2011; 40(11): 5588-5617.
- Delidovich I, Leonhard K, Palkovits R. Cellulose and Hemicellulose Valorisation: An Integrated Challenge of Catalysis and Reaction Engineering. *Energy and*

- Environmental Science*. 2014; 7(9): 2803-2830.
- Sheldon RA. Green and Sustainable Manufacture of Chemicals From Biomass: State of the Art. *Green Chemistry*. 2014; 16(3): 950-963.
- Girisuta B, Janssen LPBM, Heeres HJ. Kinetic Study On the Acid-Catalyzed Hydrolysis of Cellulose to Levulinic Acid. *Industrial and Engineering Chemistry Research*. 2007; 46(6): 1696-1708.
- Wang T, Nolte MW, Shanks BH. Catalytic Dehydration of C₆ Carbohydrates for the Production of Hydroxymethylfurfural (HMF) as a Versatile Platform Chemical. *Green Chemistry*. 2014; 16(2): 548-572.
- Girisuta B, Janssen LPBM, Heeres HJ. A Kinetic Study On the Decomposition of 5-Hydroxymethylfurfural Into Levulinic Acid. *Green Chemistry*. 2006; 8(8): 701-709.
- Van Putten RJ, Van Der Waal JC, De Jong E, Rasrendra CB, Heeres HJ, De Vries JG. Hydroxymethylfurfural, a Versatile Platform Chemical Made From Renewable Resources. *Chemical Reviews*. 2013; 113(3): 1499-1597.
- Lange JP, Van Der Heide E, Van Buijtenen J, Price R. Furfural-A Promising Platform for Lignocellulosic Biofuels. *ChemSusChem*. 2012; 5(1): 150-166.
- Pin JM, Guigo N, Mija A, Vincent L, Sbirrazuoli N, Van Der Waal JC, De Jong E. Valorization of Biorefinery Side-Stream Products: Combination of Humins with Polyfurfuryl Alcohol for Composite Elaboration. *ACS Sustainable Chemistry and Engineering*. 2014; 2(9): 2182-2190.
- Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenschwander GG, Fitzpatrick SW, Bilski RJ, Jarnefeld JL. Production of Levulinic Acid and Use as a Platform Chemical for Derived Products. *Resources, Conservation and Recycling*. 2000; 28(3-4): 227-239.
- Girisuta B, Janssen LPBM, Heeres HJ. Green Chemicals: A Kinetic Study On the Conversion of Glucose to Levulinic Acid. *Chemical Engineering Research and Design*. 2006; 84(5 A): 339-349.
- Hayes DJ, Fitzpatrick S, Hayes MHB, Ross JRH. *The Biofine Process - Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks*. 2008: 139.
- Baccile N, Laurent G, Babonneau F, Fayon F, Titirici MM, Antonietti M. Structural Characterization of Hydrothermal Carbon Spheres by Advanced Solid-State MAS ¹³C NMR Investigations. *Journal of Physical Chemistry C*. 2009; 113(22): 9644-9654.
- Sevilla M, Fuertes AB. Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides. *Chemistry - a European Journal*. 2009; 15(16): 4195-4203.
- Sevilla M, Maciá-Agulló JA, Fuertes AB. Hydrothermal Carbonization of Biomass as a Route for the Sequestration of CO₂: Chemical and Structural Properties of the Carbonized Products. *Biomass and Bioenergy*. 2011; 35(7): 3152-3159.
- Sevilla M, Fuertes AB. The Production of Carbon Materials by Hydrothermal Carbonization of Cellulose. *Carbon*. 2009; 47(9): 2281-2289.
- Sumerskii IV, Krutov SM, Zarubin MY. Humin-Like Substances Formed Under the Conditions of Industrial Hydrolysis of Wood. *Russian Journal of Applied Chemistry*. 2010; 83(2): 320-327.
- Patil SKR, Heltzel J, Lund CRF. Comparison of Structural Features of Humins Formed Catalytically From Glucose, Fructose, and 5-Hydroxymethylfurfural-dehyde. *Energy and Fuels*. 2012; 26(8): 5281-5293.
- Van Zandvoort I, Wang Y, Rasrendra CB, Van Eck ERH, Bruijninx PCA, Weckhuysen BM. Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem*. 2013; 6(9): 1745-1758.
- Van Zandvoort I, Van Eck ERH, De Peinder P, Heeres HJ, Bruijninx PCA, Weckhuysen BM. Full, Reactive Solubilization of Humin Byproducts by Alkaline Treatment and Characterization of the Alkali-Treated Humins Formed. *ACS Sustainable Chemistry and Engineering*. 2015; 3(3): 533-543.
- Kleinert M, Barth T. Towards a Lignocellulosic Biorefinery: Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel. *Energy and Fuels*. 2008; 22(2): 1371-1379.
- Dorrestijn E, Kranenburg M, Poinot D, Mulder P. Lignin Depolymerization

- in Hydrogen-Donor Solvents. *Holzfor-schung*. 1999; 53(6): 611-616.
- 26 Carrier M, Loppinet-Serani A, Absalon C, Aymonier C, Mench M. Degradation Pathways of Holocellulose, Lignin and A-Cellulose From *Pteris Vittata* Fronds in Sub- and Super Critical Conditions. *Bio-mass and Bioenergy*. 2012; 43: 65-71.
- 27 Tang Z, Zhang Y, Guo Q. Catalytic Hydro-cracking of Pyrolytic Lignin to Liquid Fuel in Supercritical Ethanol. *Industrial and Engineering Chemistry Research*. 2010; 49(5): 2040-2046.
- 28 Piskorz J, Majerski P, Radlein D, Scott DS. Conversion of Lignins to Hydrocarbon Fuels. *Energy & Fuels*. 1989; 3(6): 723-726.
- 29 Zakzeski J, Bruijninx PCA, Jongerius AL, Weckhuysen BM. The Catalytic Valoriza-tion of Lignin for the Production of Re-newable Chemicals. *Chemical Reviews*. 2010; 110(6): 3552-3599.
- 30 Hoang TMC, Lefferts L, Seshan K. Valori-zation of Humin-Based Byproducts From Biomass Processing - a Route to Sustain-able Hydrogen. *ChemSusChem*. 2013; 6(9): 1651-1658.
- 31 Rasrendra CB, Windt M, Wang Y, Adisas-mito S, Makertihartha IGBN, Van Eck ERH, Meier D, Heeres HJ. Experimental Stud-ies On the Pyrolysis of Humins From the Acid-Catalysed Dehydration of C6-sug-ars. *Journal of Analytical and Applied Py-rolysis*. 2013; 104: 299-307.
- 32 Kloekhorst A, Heeres HJ. Catalytic Hy-drotreatment of Alcell Lignin Using Sup-ported Ru, Pd, and Cu Catalysts. *ACS Sustainable Chemistry and Engineering*. 2015; 3(9): 1905-1914.
- 33 Jongerius AL, Jastrzebski R, Bruijninx PCA, Weckhuysen BM. CoMo Sul-fide-Catalyzed Hydrodeoxygenation of Lignin Model Compounds: An Extended Reaction Network for the Conversion of Monomeric and Dimeric Substrates. *Jour-nal of Catalysis*. 2012; 285(1): 315-323.
- 34 Kleinert M, Gasson JR, Eide I, Hilmen AM, Barth T. Developing Solvolytic Con-VERSION of Lignin-To-Liquid (LTL) Fuel Com-ponents: Optimization of Quality and Process Factors. *Cellulose Chemistry and Technology*. 2011; 45(1-2): 3-12.
- 35 Liguori L, Barth T. Palladium-Nafion SAC-13 Catalysed Depolymerisation of Lignin
- to Phenols in Formic Acid and Water. *Journal of Analytical and Applied Pyroly-sis*. 2011; 92(2): 477-484.
- 36 Xu W, Miller SJ, Agrawal PK, Jones CW. Depolymerization and Hydrodeoxygen-ation of Switchgrass Lignin with Formic Acid. *ChemSusChem*. 2012; 5(4): 667-675.
- 37 Trautmann M, Löwe A, Traa Y. An Alter-native Method for the Production of Sec-ond-Generation Biofuels. *Green Chemis-try*. 2014; 16(8): 3710-3714.
- 38 Trautmann M, Lang S, Traa Y. Direct Liquefaction of Lower-Rank Coals and Biocoals with Magnetically Separable Catalysts as a Sustainable Route to Fuels. *Fuel*. 2015; 151: 102-109.
- 39 Kloekhorst A, Shen Y, Yie Y, Fang M, Heeres HJ. Catalytic Hydrodeoxygen-ation and Hydrocracking of Alcell[®] Lignin in Alcohol/Formic Acid Mixtures Using a Ru/C Catalyst. *Biomass and Bioenergy*. 2015; 80: 147-161.
- 40 Loges B, Boddien A, Gärtner F, Junge H, Beller M. Catalytic Generation of Hydro-gen From Formic Acid and its Derivatives: Useful Hydrogen Storage Materials. *Top-ics in Catalysis*. 2010; 53(13-14): 902-914.
- 41 Kloekhorst A, Wildschut J, Heeres HJ. Catalytic Hydrotreatment of Pyrolytic Lignins to Give Alkylphenolics and Aromatics Using a Supported Ru Catalyst. *Catalysis Science and Technology*. 2014; 4(8): 2367-2377.
- 42 Milne TA, Brennan AH, Glenn BH. *Source-book of Methods of Analysis for Biomass and Biomass Conversion Processes*. 1990.
- 43 Marsman JH, Wildschut J, Evers P, de Koning S, Heeres HJ. Identification and Classification of Components in Flash Pyrolysis Oil and Hydrodeoxygenated Oils by Two-Dimensional Gas Chroma-tography and Time-Of-Flight Mass Spec-trometry. *Journal of Chromatography a*. 2008; 1188(1): 17-25.
- 44 Marsman JH, Wildschut J, Mahfud F, Heeres HJ. Identification of Components in Fast Pyrolysis Oil and Upgraded Prod-ucts by Comprehensive Two-Dimen-sional Gas Chromatography and Flame Ionisation Detection. *Journal of Chroma-tography a*. 2007; 1150(1-2): 21-27.
- 45 Bottari G, Kumalaputri AJ, Krawczyk KK, Feringa BL, Heeres HJ, Barta K. Copper-

- Zinc Alloy Nanopowder: A Robust Pre-cious-Metal-Free Catalyst for the Con-VERSION of 5-Hydroxymethylfurfural. *Chem-SusChem*. 2015; 8(8): 1323-1327.
- 46 Cheng YT, Huber GW. Production of Tar-geted Aromatics by Using Diels-Alder Classes of Reactions with Furans and Olefins Over ZSM-5. *Green Chemistry*. 2012; 14(11): 3114-3125.
- 47 Cheng YT, Huber GW. Chemistry of Furan Conversion Into Aromatics and Olefins Over HZSM-5: A Model Biomass Con-VERSION Reaction. *ACS Catalysis*. 2011; 1(6): 611-628.
- 48 Grandmaison JL, Chantal PD, Kaliaguine SC. Conversion of Furanic Compounds Over H-ZSM-5 Zeolite. *Fuel*. 1990; 69(8): 1058-1061.
- 49 Karakuş Y, Aynaci F, Kipçak E, Akgün M. Hy-drogen Production From 2-Propanol Over Pt/Al₂O₃ and Ru/Al₂O₃ Catalysts in Super-critical Water. *International Journal of Hy-drogen Energy*. 2013; 38(18): 7298-7306.
- 50 Torres G, Apesteguía CR, Di Cosimo JI. One-Step Methyl Isobutyl Ketone (MIBK) Synthesis From 2-Propanol: Catalyst and Reaction Condition Optimization. *Ap-plied Catalysis a: General*. 2007; 317(2): 161-170.
- 51 Ando Y, Yamashita M, Saito Y. Reaction Mechanism of 2-Propanol Dehydroge-nation with a Carbon-Supported Ru-Pt Composite Catalyst in the Liquid Phase. *Bulletin of the Chemical Society of Japan*. 2003; 76(10): 2045-2049.
- 52 Sakurai M, Honda H, Kameyama H. Fun-damental Study of a Non-Steady Oper-ation for 2-Propanol De-Hydrogenation. *International Journal of Hydrogen Ener-gy*. 2007; 32(9): 1303-1308.
- 53 Bagabas AA, Mokhtar M, Akhmedov VM, Narasimharao K, Basahel SN, Al-Rabi-ah A. Ru-C-ZnO Composite Catalysts for the Synthesis of Methyl Isobutyl Ke-tone Via Single Step Gas Phase Acetone Self-Condensation. *Catalysis Letters*. 2014; 144(7): 1278-1288.
- 54 Guan Q, Mao T, Zhang Q, Miao R, Ning P, Gu J, Tian S, Chen Q, Chai XS. Catalytic Gasification of Lignin with Ni/Al₂O₃-SiO₂ in Sub/Supercritical Water. *Journal of Supercritical Fluids*. 2014; 95: 413-421.
- 55 Jongerius AL, Copeland JR, Foo GS, Hofmann JP, Bruijninx PCA, Sievers C, Weckhuysen BM. Stability of Pt/ γ -Al₂O₃ Catalysts in Lignin and Lignin Mod-el Compound Solutions Under Liquid Phase Reforming Reaction Conditions. *ACS Catalysis*. 2013; 3(3): 464-473.
- 56 Hurd CD, Goldsby AR. Furan Reactions. I. The Pyrolysis of Furan. *Journal of the American Chemical Society*. 1932; 54(6): 2530-2531.
- 57 Luijckx GCA, van Rantwijk F, van Bekkum H. Hydrothermal Formation of 1,2,4-Ben-zenetriol From 5-Hydroxymethyl-2-Fural-dehyde and D-Fructose. *Carbohydrate Research*. 1993; 242(C): 131-139.
- 58 Luijckx GCA, van der Horst W, Koskinen SOA, van Rantwijk F, van Bekkum H. Hy-drothermal Formation of Hydroxylated Benzenes From Furan Derivatives. *Jour-nal of Analytical and Applied Pyrolysis*. 1994; 28(2): 245-254.

5.6. SUPPLEMENTARY INFORMATION

Table S5-1: Duplicate experiment for the catalytic solvolysis reaction of humins in FA/IPA using Ru/C (400 °C, 6 h, with 28 wt% of humin intake on feed)

Experiment	1	1 duplicate
Solvent/reagents	IPA/FA	IPA/FA
Oil yield, wt% on total feed	15.5	16.3
Oil yield, wt% on humin intake	55.4	57.6
Aqueous phase, wt% on total feed	12.1	12.5
Solids, wt% on total feed	8.8	9.6
Mass balance closure (wt%)	88	91
Humin conversion (wt%)	69	66
Gas phase, wt% on total feed	51	52
Carbon dioxide, mol%	29.6	30.6
Carbon monoxide, mol%	< 1	< 1
Ethylene, mol%	< 1	< 1
Ethane, mol%	< 1	< 1
Propylene, mol%	< 1	< 1
Propane, mol%	1.2	1.0
Methane, mol%	8.2	8.3
Hydrogen, mol%	58.9	57.6
Elemental composition humin oil (wt%) ^a		
Carbon	83.59	83.52
Hydrogen	8.11	8.16
Oxygen	8.31	8.32

^aData for the oil after solvent evaporation.

Table S5-2: GC×GC TOF/MS data

TOFMS Group identification (Part I)	Structure
<i>Aromatics</i>	
1. Toluene	
2. Benzene, 1,2,3-trimethyl-	
<i>Indanes/Tetralines</i>	
3. 1,6-Dimethylindan	
4. 5-Ethyltetralin	
5. 1,2,3,6,7,8-Hexahydro-as-indacene	
<i>Ketones/Alcohols</i>	
6. Methyl Isobutyl Ketone	
7. 4-Heptanone, 2,6-dimethyl-	
8. 2-Nonanone, 9-hydroxy-	
9. 2-Cyclopenten-1-one, 2,3-dimethyl-	
10. à-Isophoron	
<i>Benzofuran</i>	
11. Benzofuran, 2-methyl-	
12. Benzofuran, 4,7-dimethyl-	
<i>Naphthalenes</i>	
13. Naphthalene, 2-methyl-	
14. Naphthalene, 2-(1-methylethenyl)-	
<i>Biphenyl</i>	
15. 2,2'-Dimethylbiphenyl	
16. 1,1'-Biphenyl, 2,3'-dimethyl-	
17. 3,4'-Dimethyldiphenylmethane	

Table S5-2: GC×GC TOF/MS data, continued

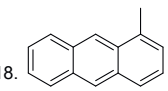
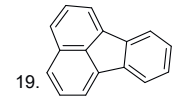


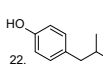
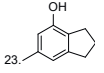
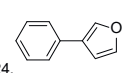
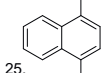
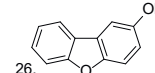
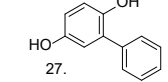
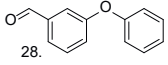


TOFMS Group identification (Part II)	Structure
PAC	
18. Anthracene, 1-methyl-	
19. Fluoranthene	
Phenolics	
20. Phenol, 3,4-dimethyl-	
21. Phenol, 2,3,6-trimethyl-	
22. Phenol, 4-(2-methylpropyl)-	
23. 6-Methyl-4-indanol	
MPOA	
24. Furan, 3-phenyl-	
25. 1-Naphthalenol, 4-methyl-	
26. 2-Dibenzofuranol	
27. [1,1'-Biphenyl]-2,5-diol	
28. Benzaldehyde, 3-phenoxy-	
Furans	
29. 2-Furanol, tetrahydro-	
30. Butyrolactone	

Table S5-3: Experimental results for the catalytic solvolysis reaction of humins with IPA only using Ru/C (400 °C, 6 h, with 28 wt% of humin intake on feed)

Humint (g)	Catalyst (g)	IPA (g)	Temperature (°C)	Reaction time (hr)	Conversion (on humin intake %)	Oil yield (on humin intake %)	Oil Yield (on total feed %)
7	0.35	18	400	6	37	179	50

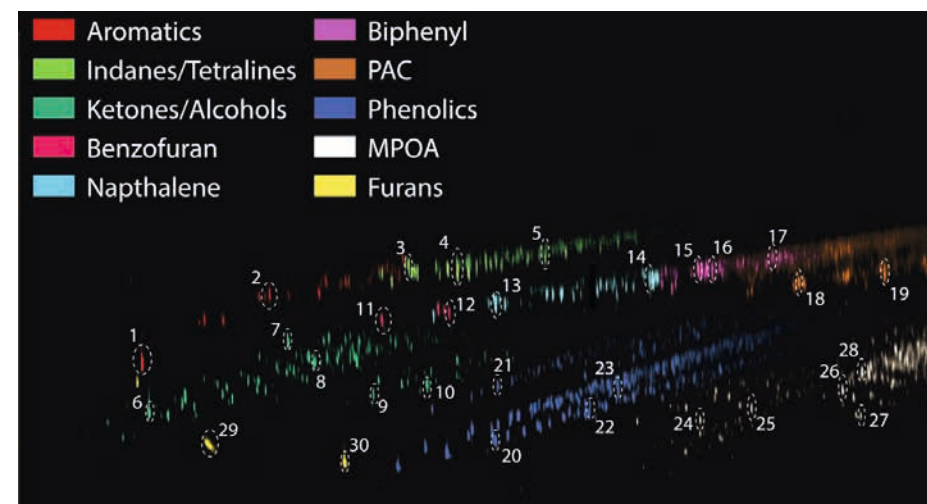


Figure S5-1: GC×GC TOF/MS plot (standard experiment: Ru/C, 400 °C, 6 h, crude reaction mixture after solvent evaporation).

CALIBRATION OF GC×GC-FID CHROMATOGRAMS

The first step in the quantification procedure involved determination of the RRF value for a number of representative model components belonging to the various compound groups (alkylphenolics, aliphatic hydrocarbons, aromatics). The following equation was used to calculate the RRF for an individual model component:

$$RRF = \frac{C_{IS} \cdot A_C}{C_C \cdot A_{IS}}$$

where CIS is the concentration of the internal standard, AIS the area of the internal standard (di-n-butylether, DBE), CC the concentration of the component C, AC is the area of the component, and RRF is the relative response factor for compound C.

The RRF value for an individual model component was determined by plotting the ratio C_C/C_{IS} versus the ratio A_C/A_{IS} . In such a plot, (see below), the slope is the RRF value for the individual model component. For alkylphenolics, the component group of relevance with regards to the manuscript, the RRF factor was 1.45.