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Catalytic Hydrotreatment of Humins in Mixtures of Formic Acid/2-Propanol with Supported Ruthenium Catalysts

Yuehu Wang, Shilpa Agarwal, Arjan Kloekhorst, and Hero Jan Heeres^{*[a]}

The catalytic hydrotreatment of humins, which are the solid byproducts from the conversion of C₆ sugars (glucose, fructose) into 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), by using supported ruthenium catalysts has been investigated. Reactions were carried out in a batch setup at elevated temperatures (400 °C) by 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 with Ru/C and FA, whereas the performance for Ru

on alumina was slightly poorer (59% humin conversion). Humin oils were characterized by using a range of analytical techniques (GC, GC–MS, GCxGC, gel permeation chromatography) and were shown to consist of monomers, mainly alkyl phenolics (> 45% based on compounds detectable by GC) and higher oligomers. A reaction network for the reaction is proposed based on structural proposals for humins and the main reaction products.

Introduction

Lignocellulosic biomass has been identified as a potentially attractive source for chemical products and is considered to be 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 being undertaken to develop and commercialize processes to convert biomass into 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 by using either biochemical (fermentation or enzymatic) or metal/Brønsted acid catalyzed transformations.^[1–6] Attractive platform chemicals are levulinic acid (LA) and 5-hydroxymethylfurfural (HMF).^[7–11] LA is conventionally obtained from the C₆ sugars of lignocellulosic biomass in water and may be converted into a number of derivatives with high application potential (e.g., γ -valerolactone). HMF is best prepared from D-fructose-containing feeds and may, for instance, be oxidized into 2,5-furandicarboxylic acid (FDCA). The latter is used to produce polyethylenefuranoate (PEF), which is 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 with 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 added-value products from the humins. For the rational design of catalytic methodology, insights 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 characterization studies on hydrothermal carbons (HTCs). These materials are typically obtained by heating various lignocellulosic biomass sources in water at elevated temperatures and pressures. Although 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. Baccile et al. reported that HTC has a furanic structure with methylene linkages, mainly based on 2D solid-state NMR spectroscopy measurements.^[16] However, Sevilla et al. proposed that humins consisted of condensed polyaromatic structures (X-ray photoelectron spectroscopy (XPS), IR, Raman).^[17–19]

A limited number of characterization 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 spectroscopy of acetone extracts).^[20] Lund et al. reported that humins from HMF formed through 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 recently proposed a structural model for humins based on extensive characterization studies

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(elemental analysis, IR, solid-state NMR spectroscopy, 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 1).

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

A number of valorization routes can be envisaged for humins (Figure 2). The overall objectives are depolymerization 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 (see above).^[29]

Gasification, and particularly steam reforming of humins (900–1200 °C) with the objective of obtaining syngas (mixture of CO_x and hydrogen), was studied by Hoang et al.^[30] It was shown that the presence of sodium carbonate, which acted as a catalyst and enhanced the rate of gasification reactions, was essential. The H₂ to CO ratio of the produced syngas was about two. 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 volatile compounds formed during the heating up phase and to increase the solids to gas carbon efficiency.

Liquefaction of humins by using pyrolysis technology was investigated by Rasrendra et al.^[31] Pyrolysis GC–MS showed the

presence of furanics and organic acids in the vapor phase, although the individual components were present in only minor amounts (< 1 wt%). Micropyrolysis yielded 30 wt% gaseous and liquid products; the remainder was a solid char. Gas–liquid yields were lower than those 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 in the catalytic conversion of humins involves liquefaction by using a catalytic hydrotreatment catalyzed by a supported metal catalyst in combination with a hydrogen donor. The hydrogen donor can be either molecular hydrogen or a donor solvent such as formic acid (FA). This synthetic methodology has been explored in detail for the depolymerization of lignin into low-molecular-weight chemicals.^[24] Examples include the catalytic hydrotreatment of lignin by using supported metal catalysts, such as NiMo and CoMo, on a variety of supports.^[32,33] Relatively harsh conditions (temperatures up to 450 °C, pressures up to 200 bar; 1 bar = 10⁵ Pa) are required for substantial depolymerization activity. The use of hydrogen donor solvents in both the presence and absence of metal catalysts has been reported. A well-known hydrogen donor is FA, which is in situ, either thermally or catalytically, converted into hydrogen and CO/CO₂. Other solvents, either for dilution or to act as a hydrogen donor, are alcohols (ethanol, methanol, isopropanol (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 liquid products in 93% mass on lignin intake yield at 653 K with reaction times of 17 h by using FA in IPA.^[24,34] Recent research by Liguori and Barth showed that the reaction times and temperature could be reduced dramatically 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 hypothesized that the heterogeneous catalyst enhanced the FA decomposition rate at a lower temperature and, as such, had a positive effect on lignin depolymerization rates and the rate of subsequent deoxygenation of the lower molecular weight fragments. Recent work from Xu et al. reported the use of Pt/C with ethanol and FA for the conversion of switchgrass lignin, and they reported that the combination of both FA and Pt/C promoted higher amounts of lower molecular weight compounds in the liquid phase.^[36]

Recently, Trautment et al. reported studies on the catalytic treatment of HTC materials to generate biofuels.^[37,38] Various HTC materials were tested by using nickel on titania as the catalyst at temperatures between 473 and 523 K, and reaction times between 3 and 20 h. 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 to be 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 form liquid products may also be feasible.

Figure 2. Possible valorization routes for humins.

Herein, we report experimental studies on the catalytic conversion of humins by using ruthenium-based catalysts (carbon and alumina support) with a mixture of FA/IPA as the hydrogen-donor solvent. The results are compared with experiments by using IPA in the presence of molecular hydrogen. This system was selected based on recent results in our group, which showed that it was a suitable catalytic system for lignin depolymerization and further hydro(-deoxy)genation reactions.^[39] For instance, when using Alcell lignin in mixtures of IPA/FA (1:1 w/w) with 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 was soluble higher molecular weight compounds (GCxGC-FID (FID = flame ionization detection) and gel permeation chromatography (GPC)). In this system, ruthenium has a dual function and catalyzes the formation of hydrogen from IPA and FA, as well as subsequent hydrocracking and hydrodeoxygenation of the low-molecular-weight fragments.

The objective of this study was to develop an efficient way to depolymerize the humins and to convert the fragments into valuable bulk chemicals (furanics, aromatics, phenolics). Product characterization was carried out by using a range of analytical techniques (including GCxGC) and the effect of process parameters such as 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.

Experimental Section

Chemicals

D-Glucose, H₂SO₄, FA, CH₂Cl₂, di-*n*-butyl ether (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.

Humin synthesis

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

Catalytic hydrotreatment experiments

The catalytic hydrotreatment experiments were performed in a batch Parr reactor system, which consisted 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 pressurizing 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⁻¹ and the reaction was allowed to proceed for 6 h. After the reaction, the reactor was cooled to room temperature and the pressure was recorded to calculate 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 analyzed by GC. 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 solid residue were extracted with CH₂Cl₂ (DCM, 50 mL). 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 analyzes, residual amounts of IPA/FA and other low-molecular-weight reaction products arising from the solvents (e.g., acetone, see below) in the humin oils were removed by evaporation (70 °C, 0.03 bar for 12 h). It was also shown that 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 was underestimated when considering the composition of the humin oils after this evaporation step. The solid residue (unreacted humins, catalyst) was dried at 70 °C, 0.03 bar, overnight and weighed for mass balance calculations. An overview of the hydrogenation protocol is shown in Figure 3.

The humin oil yield on humin intake [Eq. (1)], humin oil on total feed intake [Eq. (2)], and the humin conversion [Eq. (3)] were mass based and calculated:

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

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

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

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

In Equation (1), the weight of humin oil was the sum of oils 1 and 2. Oil 1 was the organic phase after the reaction, including some of the organic solvents and reaction products derived thereof (see below). As such, the humin oil yield could be higher than 100%. The total feed intake was 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 the reaction. It assumed that the solid residue consisted of unconverted humins and, as such, solid formation due to repolymerization reactions of reactive intermediates was not taken into account.

Elemental analysis

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

GC-MS-FID

GC-MS-FID analyzes were performed on organic product samples by using a Hewlett Packard 5890 series II plus instrument equipped with a Quadrupole Hewlett Packard 5972 mass selective detector (MSD) and an FID. A Restek RTX-1701 capillary column (60 × 0.25 mm inner diameter (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 min then heated to 250 °C at a rate of 3 °C min⁻¹.

Residual amounts of FA and IPA were quantified by GC-MS-FID. For this purpose, the FID signal was used, which was better for quantification than the MS signal. Calibration was performed with pure components, giving calibration lines with *R*² values above 0.9998 for 5 different concentrations.

GCxGC-FID

GCxGC-FID analyzes were performed on a Trace GCxGC 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 FID was used. A dual-jet modulator was applied by using carbon dioxide to trap the samples. Helium was used as the carrier gas (flow rate of 0.6 mL min⁻¹). 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 at a rate of 3 °C min⁻¹. The pressure was set at 0.7 bar. The modulation time was 6 s.

From the GCxGC-FID spectra, the yields of aromatics, phenolics, ketones, alkanes, naphthenes, and acid were calculated based on the humin intake. The identification of the main GCxGC component groups (e.g., alkanes, aromatics, alkylphenolics) in the lignin oils was achieved by spiking with representative model compounds for the component groups, GC-MS-FID analysis, and GCxGC-TOFMS analysis for a representative sample (Figure S1 and Table S2 in the Supporting Information). Quantification was performed by using an average relative response factor (RRF) per component group with DBE as the internal standard (see the Supporting Information).

Table 1. Product yields and compositions for the catalytic hydrotreatment by using supported ruthenium catalysts.^[a]

Condition	Experiment			
	1	2	3	4
solvent/reagents ^[b]	IPA/FA	IPA	IPA/FA	IPA/FA
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 ^[d]	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
CO ₂ [mol%]	29.6	39.0	54.5	24.5
CO [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%] ^[e]				
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 one (w/w). [c] No phase separation; one liquid phase after the reaction. [d] Before extraction of the water phase with CH₂Cl₂. [e] After solvent evaporation.

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

GCxGC with TOF mass spectrometer

A representative sample (from Table 1, expt 1) was analyzed on a GCxGC-HR TOFMS instrument 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 Meltfit 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 and a mass range of *m/z* 35–600. Helium was used as the carrier gas (0.8 mL min⁻¹). The injector temperature and TOFMS temperature were set at 250 °C. The oven temperature was kept at 40 °C for 5 min then heated up to 250 °C at a rate of 3 °C min⁻¹. The pressure was set at 77.5 kPa at 40 °C. The modulation time was 6 s. The mass spectra were analyzed with GC Image[®] software and a homemade Matlab routine.

Gas-phase analysis

The gas-phase samples were collected in a gas bag (SKC Tedlar 3 L sample bag 9.5" × 10" with a polypropylene septum fitting) after the hydrotreatment reaction. The gaseous products were analyzed by using a gas chromatograph (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 Å) column) and a thermal conductivity detector (TCD). Both columns were maintained at the same temperature. The injector and detector temperatures were set at 150 and 90 °C, respectively. The oven temperature was kept at 40 °C for 2 min, heated to 90 °C at a rate of 20 °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.

GPC

GPC was performed on an Agilent HPLC 1100 system. Three columns (PLgel 3 µm MIXED-E, length 300 mm, 7.5 mm i.d.) 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 through a polytetrafluoroethylene (PTFE) filter (0.2 mm pores size) with a glass injector to avoid contamination from plastic parts, added to a 2 mL autosample vial.

TOC determinations

The total organic carbon (TOC) in the water phase was measured by using a Shimadzu TOC-V_{CSH} TOC machine with an OCT-1 sampler port.

Results and Discussion

Screening experiments

A standard catalytic hydrotreatment reaction was performed by using a humin sample (28 wt% intake) obtained from D-glucose in a mixture of IPA and FA (1:1 w/w) with Ru/C (5 wt% on humin) as the catalyst. The reaction was carried out in a batch autoclave at 400 °C for a reaction time of 6 h. During heating, the pressure in the reactor increased to typically 200 bar when the temperature approached 400 °C; this was likely to be due to the catalytic decomposition of FA into hydrogen and CO_x and the formation of other gas-phase components (see below). 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 workup (Figure 3), the organic phase, designated as humin oil, was isolated and analyzed in detail.

For hydrotreatment in FA/IPA with Ru/C as the catalyst (Table 1, expt 1), the amounts of solids after the reaction (excluding catalyst) were 8.8 wt% of the total feed, corresponding to a humin conversion of 69 wt%. Apparently, under these conditions, a considerable amount of humins is converted into a liquid product. The humin oil yield on humin intake was 55.4 wt%. The occurrence of hydrodeoxygenation reactions was confirmed by the formation of a separate water phase (12.1 wt% on feed). The major product phase, however, was a gas phase, with yields of up to 51% on total feed intake, due to the (desired) catalytic decomposition reaction of FA into hydrogen and CO_x . Quantitative FA conversion was observed (GC) after 6 h of reaction. In addition, IPA was also shown to

be reactive and a considerable amount of IPA was converted (up to 95%, GC) into liquid and gas-phase components (see below).

The formation of gas-phase components from IPA/FA was confirmed by performing a reaction in the absence of humins, that is, a catalytic experiment with IPA/FA and Ru/C only (Table 1, expt 3). After the reaction, a liquid phase was obtained in a yield of about 20 wt% on IPA/FA intake. The majority of solvents were converted into gas-phase components (63 wt%), which indicated that not only FA, but also IPA was 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 S3 in the Supporting Information: in the presence of IPA (without H_2 gas or FA), 37% conversion of humins and 50 wt% oil yield (on total feed) was observed.

Mass balance closures were satisfactory (> 82 wt%); the main issue is the large amounts of gas-phase components formed, which are cumbersome to quantify accurately. The reproducibility of the standard reaction (Table 1, expt 1; humins, IPA/FA) was determined and the results are given in Table S1 in the Supporting Information. The product distribution and the mass balance closure are within 3%, which shows 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 1, expt 2). In this case, the amount of gas phase after reaction was, as expected, less than that for FA (20.2 wt% on total intake, versus 51% for FA). However, the humin conversion was lower than that 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 the 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 that for an experiment with FA (0.2 mol of hydrogen, assuming that 1 mol of FA gives 1 mol of hydrogen). As such, a lower hydrogen pressure is likely to be responsible 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 solubilized by a catalytic hydrotreatment reaction with 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 (see below). Apart from FA, molecular hydrogen can also be applied, although the humin conversion seems to be lower than that with FA as the hydrogen donor.

Composition of the gas and liquid phases for catalytic hydrotreatments with Ru/C

Gas-phase composition

The composition of the gas phase for the standard reaction with FA/IPA, hydrogen, and the blank reaction without humin sources were determined (Table 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, for example, cleavage of alkyl substituents, or by subsequent gas-phase hydrogenation reactions of CO_x with hydrogen [Eq. (4)]. The latter methanation reaction is known to be catalyzed by supported ruthenium catalysts.^[39,41]

Liquid-phase composition for experiments with Ru/C

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 1, expt 1) and the reaction with IPA/H₂ (Table 1, expt 2) together with some relevant other products are given in the form of a van Krevelen diagram (Figure 4). The H/C content of both humin oils is higher than that 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 oxygen/carbon ratio of the oil is considerably lower than that for the parent humins. As such, hydrodeoxygenation reactions take place as well, in line with the formation of water and the molecular composition of

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

the humin oils (see below). In the van Krevelen plot (Figure 4), relevant ratios of some HTC materials and the product oil after a liquefaction reaction have also been added. It is evident that the HTC materials differ substantially from humins when considering the elemental composition. Moreover, liquefaction of these materials mainly results in a reduction in the O/C ratio and not in an increase in the H/C ratio. As such, hydrogenation occurs to a far less extent with the liquefaction of the HTC materials than that with our procedure involving a hydrogen donor (H₂ and/or IPA).^[37,38]

The higher heating values (HHVs) of the two product oils, calculated from the elemental composition by using the Milne equation,^[42] were about 38.5 MJ kg⁻¹, which was more than 1.5 times the value of the starting humin sample derived from D-glucose (22.6 MJ kg⁻¹). As such, considerable energy densification has occurred. However, humin liquefaction to form a bio-fuel with a higher HHV than the original humins was not the major objective of this study. Our main interest concerns the conversion of the humins into higher added value biobased chemicals, such as benzene–toluene–xylenes (BTX) and alkyl-phenolics. Therefore, a detailed characterization study on the liquid organic products was performed.

Molecular composition of the humin oils

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

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

The humin oil from the standard experiment was also analyzed by GCxGC to quantify products (Figure 6). This technique allows a 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 are provided

Figure 6. GCxGC plot of a representative humin oil (standard experiment: Ru/C, 400 °C, 6 h, crude reaction mixture before solvent evaporation, butylated hydroxytoluene (BHT) as the stabilizer in THF).

in Table 2. Apart from aromatics and phenolics, MPOA, PAHs, and cycloalkanes were observed (Figure 6). Because 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–FID and GCxGC analyses. A possible explanation is the high reactivity of (substituted) furanics under the prevailing reaction conditions in the pres-

ence of heterogeneous metal catalysts, which may lead to a wide range of products.^[45–48] It is likely that aromatization of furanics occurs to a significant extent during the hydrotreatment reaction. Such reactivity has been reported in the literature and has recently also been observed when heating humins in water in the presence of a base.^[23]

Based on mass balance considerations (Table 1), the blank reaction (Table 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 1, expt 3) was also analyzed in detail. GC–MS analysis reveals that mainly alcohols and ketones were present (Figure 7), including acetone, and methyl isobutyl ketone (MIBK).

These products are all likely to originate from IPA through a reaction pathway provided in Scheme 1.^[53] It involves the initial dehydrogenation of IPA to acetone, followed by aldol condensation to form diacetylacetone (DA). DA may subsequently dehydrate into mestityl oxide (MO), which is then catalytically hydrogenated to give MIBK. MIBK 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 and Barth for the noncatalytic sol-

Table 2. Major component classes and representative individual components in the humin oil obtained under standard conditions (GCxGC).

Component	Structure
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-
polyaromatic 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 (MPOAs)	 3-phenoxybenzaldehyde

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

volysis of lignin in FA/IPA mixtures,^[24] and by Kloekhorst et al. for the catalytic solvolysis of lignin in mixtures of FA/IPA by using Ru/C.^[39]

It has been reported that IPA can be transformed into aromatics (e.g., mesitylene) during these condensation reactions.^[53] However, clear peaks associated with the formation of aromatics 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 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 achieved based on GCxGC measurements (Figure 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 MPOAs are present. Moreover, furanics were absent. The phenolics and naphthalenes are primarily formed from humins and not from IPA (blank experiments, see above). As such, we can conclude that the catalytic hydrotreatment reactions of humins do not

Figure 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).

lead to furanics (as could be envisaged from the proposed molecular structure for humins), but mainly form phenolics.

The amount of alkylphenolics on humin intake (and not on total compounds detectable by GC) for the standard experiment has been tentatively determined by using GCxGC-MS. Quantification was performed with an internal standard method and the use of an average response factor per product class (see the Supporting Information). This resulted in a total alkylphenolics yield of about 9 wt% on humin intake. This number is likely to be slightly overestimated because 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 species detectable by means of GC techniques (about 12–15% on humin intake according to a semiquantitative GCxGC method) is far less than the total amount of organic product oils present after the reaction. This is due to the presence of a higher molecular weight, nonvolatile fraction in the oils (typically >250 Da) 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 analysis (Figure 9).

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

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

On the basis of 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, although it appears that the degree of depolymerization 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 1, hydrogen content after reaction).

Catalyst support effects

To gain some insight into the effects of catalyst supports, we have carried out an experiment with Ru on alumina (5 wt% Ru) instead of Ru/C under standard conditions with FA as the hydrogen donor (Table 1, expt 4.) The results were poorer than those for Ru/C: a lower oil yield on total feed (8.7 versus 15.5 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 wt% on total feed). Moreover, the resulting humin oil showed a higher O content than that 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 that for Ru/C. In agreement with the latter is the formation of less water phase after the reaction when using alumina as the support (6.9 versus 12.1 wt% on total feed intake). The molecular weight distributions for both oils were essentially similar, that is, 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 GCxGC-FID (Figure 8). The main component classes are alkylphenolics and naphthalenes, and the amounts are very close to the values found for ruthenium on carbon.

Hence, we conclude that supports have a major effect on the humin oil yield for ruthenium-based catalysts, although the chemical composition of the humin oils are similar. A neu-

tral support, such as carbon, seems to provide better results than an acidic support, such as alumina. A possible explanation is the presence of acid sites in alumina, which may lead to re-polymerization of reactive intermediates, as shown in lignin depolymerization studies.^[54,55] In addition, the textural properties for alumina differ considerably from than of carbon (BET surface area and porosity) and it is likely that the active metal sites are more accessible for the anticipated rather large molecules for subsequent reactions.

Reaction pathways

Based on detailed product analysis for the gas and liquid phases, we propose a possible reaction pathway for the catalytic hydrotreatment of humins, see Scheme 2 for details.

In the liquid phase, reactions involving the humins and those for the solvents (IPA and FA) have to be considered. As noted earlier, IPA is converted into a number of dimerization products, including MIBK (aldol condensation), whereas FA decomposes into CO_x and H₂. All of these reactions (except the aldol condensation reactions) are expected to be catalyzed by ruthenium. For the humins, we propose a reaction scheme involving a number of parallel/series pathways with multiple intermediates. The main products to consider are (substituted) alkylphenolics and naphthalenes, see the product distribution in Figure 8. Although the molecular weight of the humins has not yet been established unequivocally, it is evident that depolymerization reactions occur to a significant extent because the product oils contain, apart from oligomers (GPC; Figure 9), considerable amounts of monomeric, GC-detectable products. The main linkages between the furanic 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 linkages). However, ruthenium catalysts have shown to be able to substantially depolymerize lignin (including C–C linkages), so this reaction seems feasible.^[32,33] Thus, low-molecular-weight furanics are expected to be formed. However, these are not identified in the reaction mixtures. It is likely that the furanics are converted into substituted aromatics and naphthalenes by a number of established reaction pathways (Scheme 3).^[46–49,56]

Although rare, it also appears that furanics may be converted into multisubstituted phenolics. For instance, Luijck et al. demonstrated that HMF could be converted into 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 structures in the humins prior to depolymerization reactions. For instance, van Zandvoort et al. showed that heating humins to 240 °C in the presence of a base led to structural changes and the formation of aromatic structures (Scheme 3, bottom humin structure).^[23] These reactions also seem to be possible by thermal action only. For instance, Hoang et al. investigated the residue after heating humins between 400 and 700 °C and found that the structure was strongly aromatized (lower H/C ratios, lower O/C ratios).^[30] To date, the actual pathway (aromatization of the humin struc-

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

Scheme 3. Possible routes from furanics to aromatics and naphthalenes.

ture or cleavage of furanic building blocks to low-molecular-weight furanics) remains unclear and it is possible that both occur simultaneously.

Depolymerization of the aromatized humins is expected to lead to substituted aromatics and naphthalenes, and possibly also alkylphenolics. Our product mixtures also showed the presence of cycloalkanes. These were likely to have formed through overhydrogenation reactions of the naphthalenes and

aromatics. Such reactions also take place to a significant extent for ruthenium-based depolymerization reactions of lignins.

Conclusions

We showed that liquefaction of humins was possible by using a catalytic hydrotreatment approach with Ru-based catalysts and either FA or molecular hydrogen as the hydrogen donor in IPA as the solvent. IPA was not inert under these reaction conditions, but acted as an additional hydrogen source. The best results were obtained with Ru/C and humin conversions of up to 69% were obtained with FA/IPA as the hydrogen donor. Elemental analysis shows that the oils had a considerably reduced oxygen content compared with the humin feed, with HHVs up to 38 MJ kg^{-1} . The product oils consisted of both mono- and oligomeric compounds (GPC). The main species that could be detected by GC arising from the humins were substituted alkylphenolics, naphthalenes, and cyclic alkanes (GC-MS-FID, GCxGC). 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) depolymerized to give a liquid biofuel with the po-

tential to be a source for interesting bulk chemicals after fractionation. This opens up new avenues for the development of added value outlets for humins beyond use as a solid fuel. Thus, these will have a positive effect on the technoeconomic viability of biorefinery schemes involving the conversion of C₆ sugars into biobased chemicals such as LA and HMF.

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