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Liquefaction of humins from C6-sugar conversions using heterogeneous catalysts

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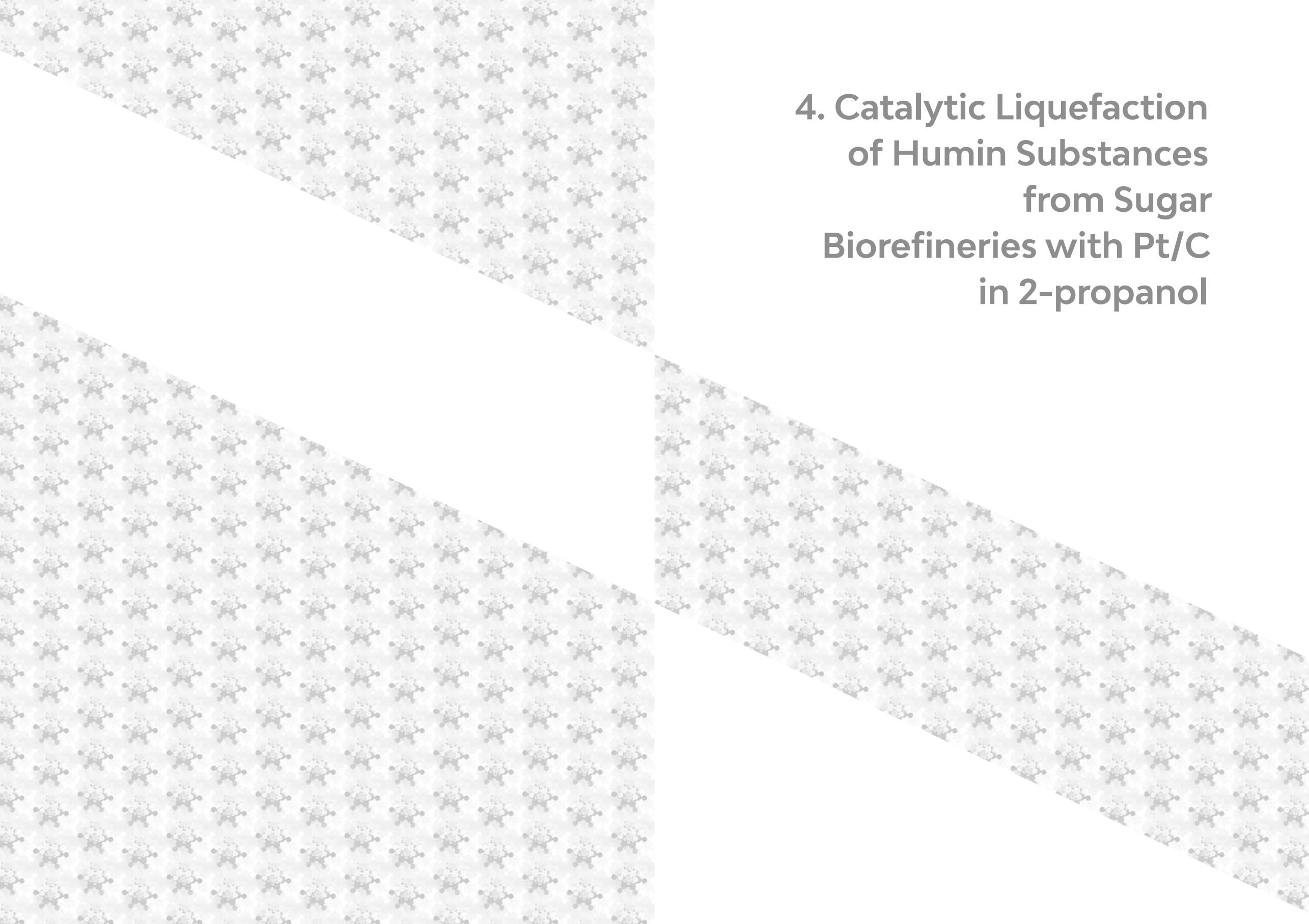
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**4. Catalytic Liquefaction
of Humin Substances
from Sugar
Biorefineries with Pt/C
in 2-propanol**

ABSTRACT

The catalytic liquefaction of humins, the solid byproduct from the conversion of C₆ sugars (glucose, fructose) to 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), using a supported Pt/C catalyst in isopropanol (IPA) as the solvent was investigated. At benchmark conditions (400°C, 7 h, 27 wt% catalyst on humin intake, 21 wt% humin on total intake (IPA and humins), about 60% of the humins was converted to a humin oil. This oil was analysed in detail (GC-MS, GC×GC-FID, GPC) and shown to consist of a mixture of monomers and oligomers belonging to various product classes (alkylphenolics, aromatics, aliphatic hydrocarbons). IPA was shown to be reactive under the prevailing reaction conditions and acts as a hydrogen donor for the humin depolymerisation/hydrodeoxygenation reactions. A systematic study according to a central composite design (19 experiments) was performed to optimise the reaction conditions (T, humin intake, catalyst intake and batch time) to obtain the highest humin conversion and alkylphenolics yield. Highest humin conversion was 72%, whereas the highest amounts of alkylphenolics was 14% (based on GC detectables in the liquid phase after reaction). A reaction network is proposed based on structural proposals for humins and the main reaction products.

Keywords: humins liquefaction, biobased chemicals, alkylphenolics, optimisation

Y. Wang, S. Agarwal, H. J. Heeres, Catalytic Liquefaction of Humin Substances from Sugar Biorefineries with Pt/C in 2-propanol, *ACS Sustainable Chemistry & Engineering*, 2017, 5 (1), 469–480.

4.1. INTRODUCTION

Biobased platform chemicals are of high interest for the chemical industry, amongst others to serve as building blocks for biobased polymers.^[1-12] Well known examples of platform chemicals are 5-hydroxymethylfurfural (HMF) and levulinic acid (LA).^[13] However, the commonly used production routes, *viz.* the acid catalytic hydrolysis of C₆-sugars, inevitably leads to the formation of solid byproduct, also known as humins. The humin yield can be as high as 40% based on feed intake.^[14, 15] Humin formation is undesirable, as it reduces the desired product yield and leads to operational issues like fouling and blocking of valves and piping in the process. As such, there is a large incentive to convert the solid humins to liquified products (rich in phenolics, aromatics and naphthalenes) with a higher value that could for instance serve as a biofuel (additive) or as a source for biobased chemicals. For instance, mixtures of alkylphenolics have shown potential to be used as a phenol replacement in various phenol based resins (e.g. phenol-formaldehyde).^[16-17] Also, it has been shown that the phenolic mixture can be used as a fuel additive to increase the octane number.^[18]

For the design of efficient catalytic conversion strategies, insights in the molecular structure of humins is of high importance. A number of structural studies have appeared in literature for humins obtained from monomeric sugars.^[14, 19-21] Most imply that the humins consist of a furan rich polymeric network with furan fragments linked by aliphatic chains with several functional groups (aldehydes, beta-hydroxy acids, see Figure 4-1 for details).

A number of technologies have been explored for the valorisation of humin byproducts with the main aim to depolymerise the structure to low molecular weight components. Examples include (catalytic) thermochemical pathways like gasification and pyrolysis.^[22-23] The liquid yield after thermal pyrolysis was limited and mainly char was obtained, making the process economically unattractive.

Our focus in the development of efficient humin depolymerisation technologies is centered around the use of heterogeneous catalysts in

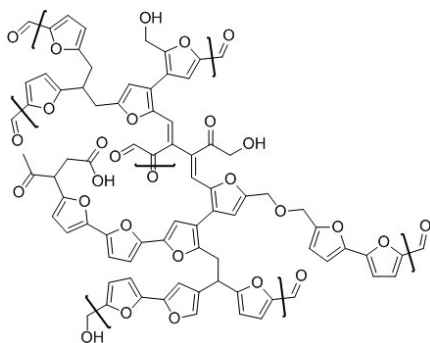


Figure 4-1. Proposed molecular structure of humins from low molecular weight sugars.^[21]

combination with a hydrogen source (molecular hydrogen, formic acid (FA), isopropanol (IPA)). We have recently shown that humins can be depolymerised using a hydrotreatment with Ru/C in an IPA/FA mixture. The reaction was carried out at 400 °C and humin conversions up to 69% could be achieved.^[24] In this case, it was shown that both FA and IPA serve as the hydrogen sources. The oils, with higher heating values up to 38 MJ/kg, were shown to consist of both mono- and oligomeric compounds. The major GC detectable compounds were alkylphenolics, aromatics (mono and with multiple fused rings) and cyclic alkanes. Motivated by these results, an extensive catalyst screening investigation was performed for the depolymerisation of humins via catalytic hydrotreatment. Promising unpublished results were obtained with Pt catalysts using IPA as the hydrogen source.

In this paper, we report a detailed study on the depolymerisation of humins using a supported Pt catalyst with IPA as the hydrogen source in the absence of formic acid. The latter, despite being an excellent hydrogen donor, has a negative effect on the process economics due to its price and corrosiveness, requiring special construction materials. Initial experiments were conducted at benchmark conditions (400 °C, 7 h, 27 wt% catalyst on humin intake, 21 wt% humin on total intake (IPA and humins)), and the product oils were quantified and characterised in detail using advanced GC techniques and GPC. Subsequently, the effect of process conditions on

humin conversion, gas yield and product composition was quantified using an experimental design approach and optimum conditions were identified. Finally, the results were rationalised using a reaction network.

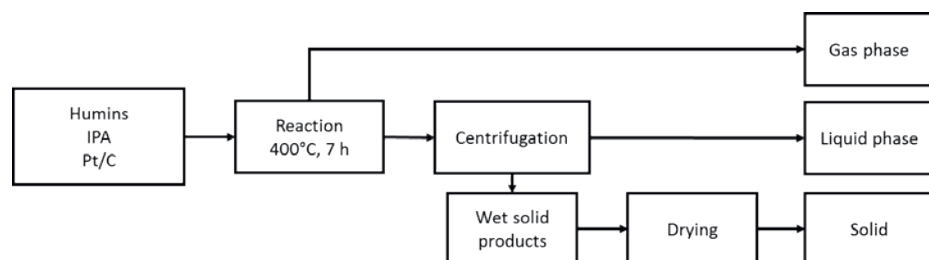
4.2. MATERIALS AND METHODS

Chemicals. All chemicals used in this work were of analytical grade and used without further purification. Tetrahydrofuran (THF), 2-propanol (isopropanol (IPA), 99.8%) and Pt/C were obtained from Sigma Aldrich. The catalyst was not pre-activated and used as such.

Humin synthesis. The humins used in this study were synthesised by the hydrothermal conversion of D-glucose, as reported in literature.^[14] 500 mL of an aqueous solution of glucose (1 M) and sulphuric acid (0.01 M) was transferred to a stainless steel autoclave (1 L) equipped with an overhead stirrer. The solution was subjected to the hydrothermal treatment for 6 h at 180 °C (heating rate: 1.3 °C/min) at a stirring rate of 120 rpm. After the reaction, the reactor was cooled to room temperature and the precipitate (humins) was separated by vacuum filtration followed by washing with 3 L of deionised water. The obtained solids were vacuum dried for 24 h at 60 °C. After drying, the humins were grinded using an electric grinder and then purified by Soxhlet extraction for 24 h using water as the solvent. Finally, the purified humins were vacuum dried for 24 h at 70 °C and were further crushed into a powder. The elemental composition of the humin was determined (64.64 wt% carbon, 4.38 wt% hydrogen and 30.98 wt% oxygen by difference, H/C: 0.81 and O/C: 0.36 mol/mol, which agrees well with reported values).^[14]

CATALYTIC HUMIN LIQUEFACTION REACTIONS

Experimental set-up. The hydrogenation experiments were performed in a batch autoclave (100 mL, maximum operating conditions: 350 bar and



Scheme 4-1. Overview of the experimental procedure for a catalytic liquefaction experiment.

500 °C) equipped with electric heating and water cooling, an overhead stirrer and a temperature control system. The stirring speed for all experiments was set at 1400 rpm.

EXPERIMENTAL PROCEDURE

A representative example of an experiment is given in Scheme 4-1. The reactor was charged with a humin sample (4.0 g), IPA (15.0 g) and Pt/C (1.07 g). 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 7 h. After reaction, the reactor was cooled to room temperature and the pressure was recorded for determination of the total moles of gas (using ideal gas law) formed during the reaction. Calculation details are given in the Supplementary information. The pressure was released and the gas phase was collected in a 3 L plastic gas bag and was analysed with GC-TCD (*vide infra*). The suspension was removed from the reactor, weighed and placed in a centrifuge tube (50 mL). After 45 min of centrifugation at 4500 rpm, the liquid phase and solid phase were separated and weighed. The solid residue (unreacted humins and catalyst) was dried at 70 °C, 0.03 bar for 12 h and weighed for mass balance calculations. The organic phase was analysed

by GC-MS, GC×GC-FID and GPC. The elemental composition of the liquid phase was obtained after the removal of residual amounts of solvent (IPA) and low molecular products derived thereof (e.g. acetone) at 70 °C, 0.03 bar for 2h. This organic phase after solvent evaporation is designated as the humin oil throughout this paper.

DEFINITIONS

The liquid, solids and gas yields are on a mass basis and based on total reactor intake (IPA and humins). The definitions are given in Equations 4-1 to 4-3:

$$\text{Solid yield}(\%) = \frac{\text{Mass of solid product} - \text{catalyst intake}}{\text{Humin intake} + \text{solvent intake}} \cdot 100\% \quad (4-1)$$

$$\text{Liquid yield} (\%) = \frac{\text{Mass of liquid phase}}{\text{Humin intake} + \text{solvent intake}} \cdot 100\% \quad (4-2)$$

$$\text{Gas yield} (\%) = \frac{\text{Mass of gas phase}}{\text{Humin intake} + \text{solvent intake}} \cdot 100\% \quad (4-3)$$

The humin conversion is calculated based on humin intake and the solid products isolated after reaction. It assumes that the solid residue consists of unconverted humins, and as such solid formation due to re-polymerisation reactions of reactive intermediates is not taken into account.

$$\text{Humin conversion} (\%) = \frac{\text{Humin intake} - (\text{Mass of solid after reaction} - \text{Catalyst intake})}{\text{Humin intake}} \cdot 100\% \quad (4-4)$$

The alkylphenolics yield was determined by GC×GC-FID and is provided as the amount based on total GC-detectables in the liquid phase after reaction.

STATISTICAL MODELING AND OPTIMISATION

Non-linear multi-variable regression was used to model the experimental data and for this purpose the Design Expert Version 8.0.0 software package was used. The experimental data were modeled using Equation 4-5.

$$y = b_0 + \sum_{i=1}^4 b_i x_i + \sum_{i=1}^4 b_{ii} x_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^4 b_{ij} x_{ij} + e \quad (4-5)$$

Where y is the dependent variable (humin conversion, gas yield and alkylphenolics yield), x_i and x_j are the independent variables (catalyst intake (g), humin intake (g), temperature (°C) and reaction time (h)), b_0 , b_i , b_{ii} and b_{ij} are the regression coefficients of the model, whereas e is the error of the model. The regression equations were obtained by backward elimination of statistically non-significant parameters. A parameter was considered statistically relevant when the p value was less than 0.05.

ANALYTICAL INSTRUMENTS AND PROCEDURES

GC-MS. GC-MS spectra were recorded on a Hewlett-Packard 5890 gas chromatograph (GC) connected with a quadrupole Hewlett-Packard 6890 MSD selective with a Restek RTX-1701 column (60 m × 0.25 mm i.d. and 0.25 μm film thickness). Electron ionisation was performed at 70 eV. The injector and oven temperature were set at 280 °C. Analysis was performed using an oven temperature heating profile (from 40 to 250 °C at a rate of 3 °C/min). Typically, the oil (0.12 g) was dissolved in tetrahydrofuran (1.5 g) before injection. Peak identification was done using the NIST05a mass spectra library.

TWO-DIMENSIONAL GAS CHROMATOGRAPHY (GC×GC).

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 ionisation detector (FID) was used. A dual-jet modulator was applied using carbon dioxide to trap the samples using the analysis. Helium was used as the carrier gas (flow rate of 0.8 mL/min). The injector temperature and FID temperature were set at 280 °C. The oven temperature was kept at 40 °C for 5 min and then heated to 250 °C with a rate of 3 °C/min. The pressure was set at 0.7 bar. The modulation time was 6 s.

From the GC×GC-FID chromatograms, the amount of aromatics, alkylphenolics, ketones, alkanes, naphthalenes and acids were calculated based on total GC detectable components. The identification of main GC×GC component groups (e.g. alkanes, aromatics, alkylphenolics) in the humin 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. Quantification of alkylphenolics was performed by using an average relative response factor (RRF) for the various alkylphenolics present in the sample with di-n-butyl ether (DBE) as the internal standard. All the samples were diluted in THF before the analysis.

GAS PHASE ANALYSES.

The gas phase samples were collected in a gasbag (SKC Tedlar 3 L sample bag 9.5" × 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 Al₂O₃/Na₂SO₄ 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 temperature were set at 110 °C and 200 °C respectively. The oven temperature was kept at 40 °C for 3 minutes then heated to 90 °C at the rate of 20 °C min⁻¹ and kept at this temperature for another 7.5 min. For identification and quantification, a reference gas mixture (55.19% H₂, 19.70% CH₄, 3.00% CO, 18.10% CO₂, 0.51% ethylene, 1.49% ethane, 0.51% propylene and 1.50% propane) was used.

4.3. RESULTS AND DISCUSSION

4.3.1. BENCHMARK EXPERIMENTS

In the first stage of experimentation, an experiment was carried out using a humin sample from D-glucose in IPA (21 wt% humins) with Pt/C as the catalyst. This benchmark reaction was carried out in a batch autoclave at 400 °C for a reaction time of 7 h. During heating, the pressure in the reactor increased typically to 120-130 bar when the temperature approached 400 °C, likely due to the catalytic decomposition of IPA to gasphase components (*vide infra*). After reaction and work-up, a transparent, single liquid phase was obtained. The product yields (gas, liquid phase and solids) were determined gravimetrically and the results are shown in Table 4-1. Here, the results for three experiments (entry 1, 2 and 3 in Table 4-1) performed at the same bench mark conditions, the average values for these experiments and the results for a blank experiment are provided.

Mass balance closures for the reactions involving humins were satisfactorily (> 82 wt%), the main issue being the relatively large amounts of gas phase components formed. These are cumbersome to quantify very accurately. For instance, part of the CO₂ is expected to have a considerable solubility in the liquid phase. As such, it is only partly included in the gas-phase composition. In addition, it will evaporate during liquid phase work-up and as such is also not taken into account for the determination of the amount of the liquid phase. The reproducibility of the benchmark reaction

Table 4-1. Product yields and compositions for the catalytic liquefaction of humins in IPA using a Pt/C catalyst^a

Experiment	1	2	3	Average	4 blank (no humins)
Humins intake, wt% on total feed	21	21	21	21	-
Liquid yield, wt% on total feed	62	59	64	62	76
Solids, wt% on total feed	9.0	8.8	8.6	8.8	-
Humins conversion, wt%	57	58	59	58	-
Gas phase, wt% on total feed	11	13	11	12	3
Carbon dioxide, mol%	30.4	25.9	24.2	26.8	18.1
Carbon monoxide, mol%	< 1	< 1	< 1	< 1	3
Ethylene, mol%	< 1	< 1	< 1	< 1	< 1
Ethane, mol%	1.2	< 1	2.1	1.7	1.5
Propylene, mol%	< 1	< 1	< 1	< 1	< 1
Propane, mol%	22.9	11.9	15.0	16.6	1.5
Methane, mol%	36.7	38.7	33.8	36.4	19.7
Hydrogen, mol%	8.2	22.3	24.4	18.3	55.1-
Mass balance closure	82	81	84	82	79
Elemental composition humin (wt%)					
Carbon	85.52	86.69	85.70	85.97	-
Hydrogen	9.28	8.91	8.49	8.89	-
Oxygen ^b	5.20	4.41	5.82	5.14	-

^a400°C for 7 h, 27 wt% catalyst on humin intake, 21 wt% humin on total reactor intake (IPA and humins) ^bby difference

was determined by performing three experiments at similar reaction conditions and the results are given in Table 4-1. The product distributions as well as the mass balance closures are within 3%, showing that the reproducibility of the reaction is good.

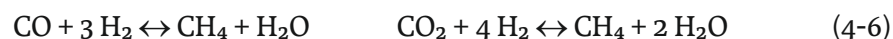
The liquid phase yield on total intake (humins and IPA) was on average 62% wt%. Also a substantial amount of a gasphase was obtained (about 12 wt% on feed intake), indicating that part of the humins and the solvent IPA are converted to gasphase components. The formation of gas phase components from IPA was confirmed by performing a reaction in the absence of humins, i.e. a catalytic experiment with IPA and Pt/C only

(Table 4-1, entry 4). Considerable amounts of gasphase components were indeed formed (3 wt% on total reactor intake).

The humin conversion is on average 58% for the bench mark experiment. Thus, we can conclude that humins can indeed be solubilised to a significant extent by a catalytic liquefaction reaction using IPA as the solvent.

GAS PHASE COMPOSITION

The composition of the gas phase for the benchmark reaction with IPA was determined (Table 4-1). The main gas phase component is methane (36 mol%), followed by CO₂ (27 mol%), hydrogen (18 mol%) and propane (17 mol%). Methane may either be formed by reactions involving the humins, e.g. cleavage of alkyl substituents, and/or by subsequent gasphase hydrogenation reactions of CO_x with hydrogen (Equation 4-6). These methanation reactions are known to be catalysed by supported Pt catalysts.^[25]



The blank reaction (IPA and Pt/C only, no humins) also shows the formation of considerable amounts of methane (19.7 mol%), indicating that methane formation by gas phase methanation is indeed occurring to a significant extent.

The hydrogen is likely formed by the dehydrogenation of IPA to acetone, catalysed by Pt/C.^[26-29] Acetone was indeed detected in the liquid phase (*vide infra*), which is a strong indication for the occurrence of this pathway. In addition, the blank reaction also showed the presence of substantial amounts of hydrogen in the gas phase. Thus, IPA is not solely acting as a solvent but is also a hydrogen donor and as such plays a major role in the conversion of the humin to lower molecular weight components. Besides the conversion to acetone, IPA also dehydrates to propylene and subsequently to propane, as is evident for the presence of considerable amounts of propane in the gas phase (17 mol%, Table 4-1).

LIQUID PHASE COMPOSITION

The molecular composition of the liquid phase from the benchmark experiment using IPA as the solvent was determined using GC-MS and GC×GC-FID. A typical GC/MS spectrum of the liquid phase is shown in Figure 4-2. Numerous products were observed that belong to various organic product classes, the major ones being ketones, phenolics and aromatics as well as aliphatic hydrocarbons. IPA is still present in considerable amounts, indicating that its conversion at the prevailing reaction conditions is not quantitative.

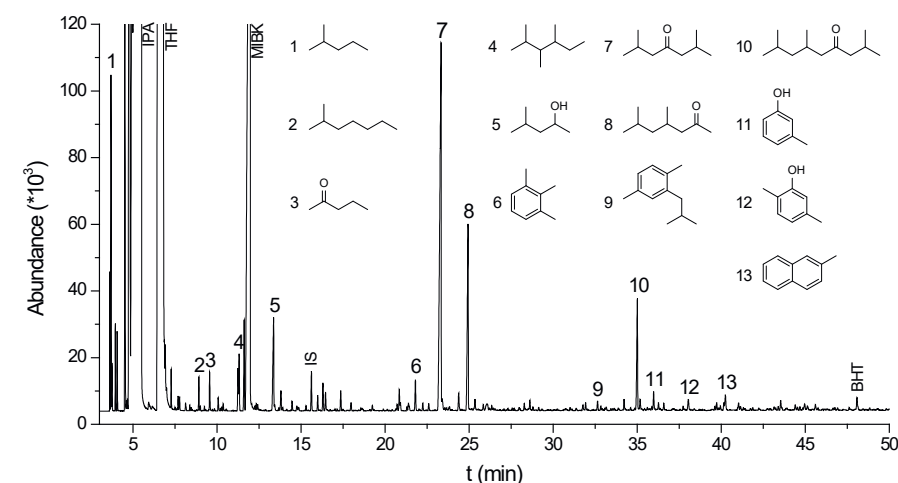
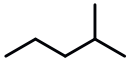
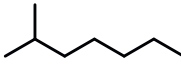
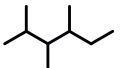
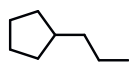
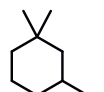
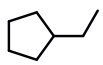

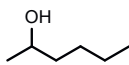
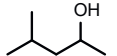
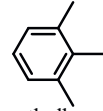
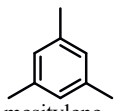
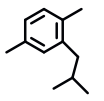
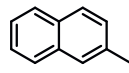
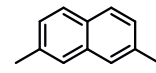
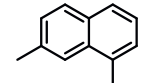
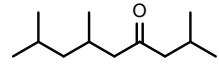
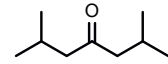
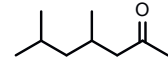
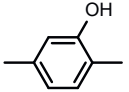
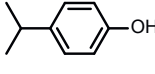
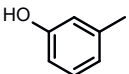


Figure 4-2. GC-MS spectrum of the liquid phase of a benchmark experiment (Table 4-1, entry 1: IPA, Pt/C, 7 h, 400 °C, BHT is the stabilizer in the THF, IS is the internal standard). The exact position of substituents on the aromatic ring for 6, 9, 11, 12 and 13 could not be established unequivocally by the GC-MS database

An overview of the various individual components in the discrete organic component classes (aromatics, alkylphenolics etc.) by GC-MS is given in Table 4-2.

The presence of these component classes was further confirmed by GC×GC-FID analyses (Figure 4-3). This GC technique is very suitable to rapidly determine various organic compound classes present in a bioliquid as these

Table 4-2. Major component classes and representative individual components in the liquid phase obtained at benchmark conditions (GC-MS^a).

Alkanes			
	2-methylpentane	2-methylheptane	2,3,4-trimethylhexane
Cycloalkanes			
	propylcyclopentane	1,1,3-trimethylcyclohexane	ethylcyclopentane
Alcohols			
	propan-2-ol	hexan-2-ol	4-methylpentan-2-ol
Aromatics			
	1,2,3-trimethylbenzene	mesitylene	2-isobutyl-1,4-dimethylbenzene
Naphthalenes			
	2-methylnaphthalene	2,7-dimethylnaphthalene	1,7-dimethylnaphthalene
Ketones			
	2,6,8-trimethylnonan-4-one	2,6-dimethylheptan-4-one	4,6-dimethylheptan-2-one
Phenolics			
	2,5-dimethylphenol	4-isopropylphenol	<i>m</i> -cresol

^athe exact position of substituents on aromatic rings could not be established unequivocally by the GC-MS database

are visible in discrete regions in the GC×GC-FID plots with good separation.^[30] The main components in the various product groups for the liquid phase obtained for the benchmark experiment were in agreement with GC-MS results.

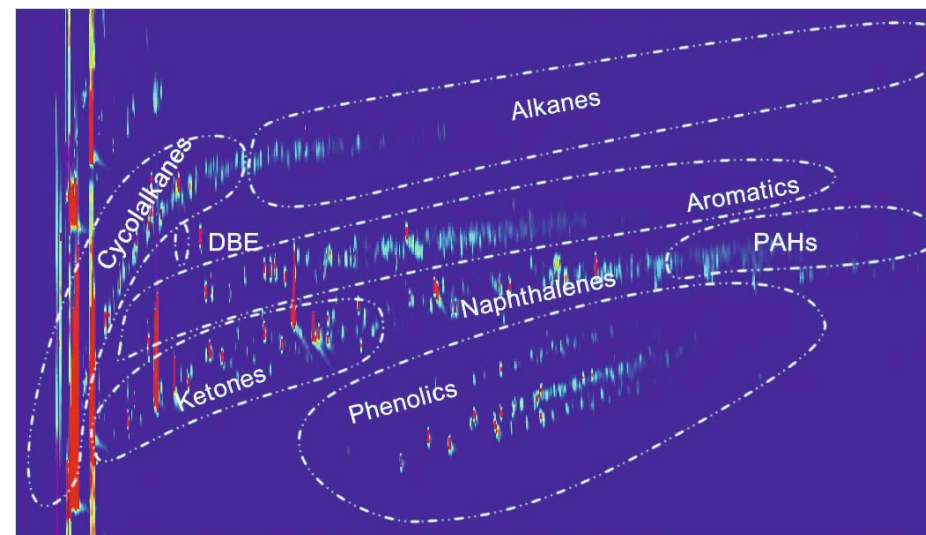


Figure 4-3. GC×GC-FID plot of the liquid phase from (Table 4-1, entry 1: Pt/C, 400 °C, 7 h, crude reaction mixture before solvent evaporation). DBE: internal standard.

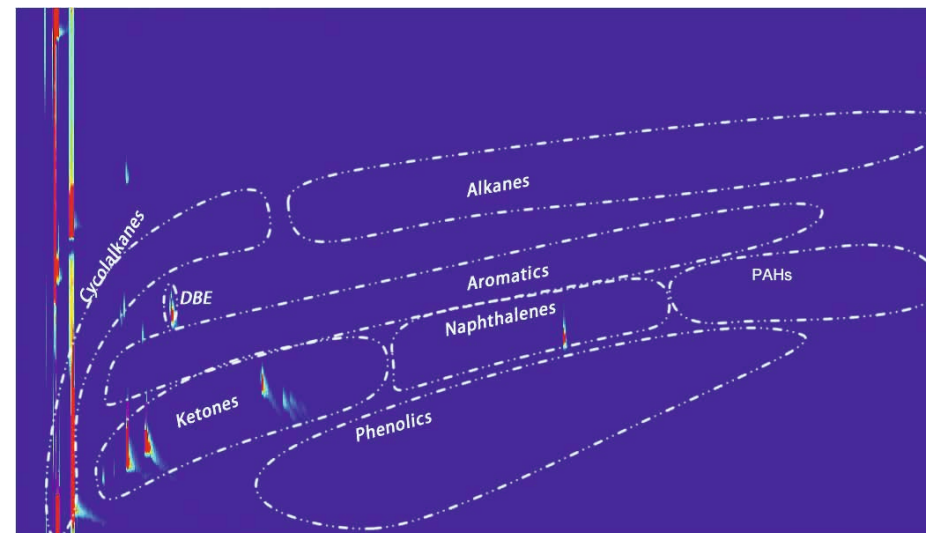


Figure 4-4. GC×GC-FID plot of the liquid phase of a blank reaction (Table 4-1, entry 4: Pt/C, 400 °C, 7 h, no humins, crude reaction mixture).

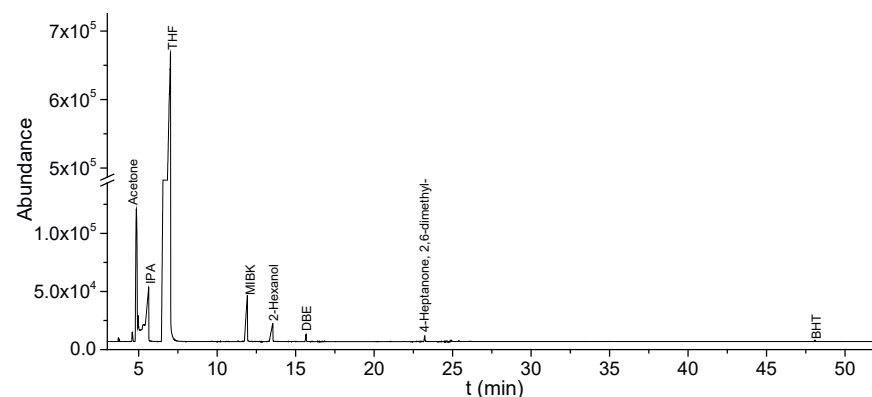
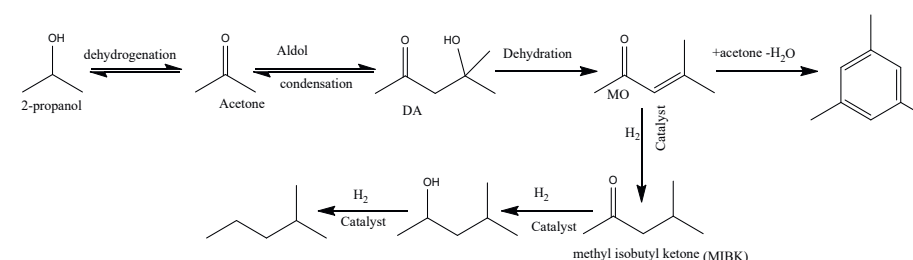


Figure 4-5. GC-MS-FID plot of the liquid phase of a blank reaction (Table 4-1, entry 4: Pt/C, 400 °C, 7 h. THF is the solvent used for dilution of the samples, DBE is the internal standard and BHT is the stabilizer in THF).

IPA is not inert under reaction conditions, as proven by the formation of gas phase components (*vide supra*), and by analysing the liquid phase after a blank reaction (IPA and catalyst in the absence of humins, Figure 4-4 and 4-5). Acetone, methylisobutylketone (MIBK), 2-hexanol and 2,6-dimethyl-4-heptanone were observed in substantial amounts.

The ketones and alcohols are likely formed from IPA by a reaction pathway provided in Scheme 4-2.^[31] 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 ketones may also be hydrogenated under the prevailing reaction conditions in the presence of Pt to give the corresponding alcohols. Similar reactivity of IPA has been observed by Kleinert *et al.*^[18] 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.^[32]

When comparing the product composition of the liquid phase for a blank reaction with a reaction in the presence of humins, it is clear that the phenolics, naphthalenes and aromatics are formed from humins. The amount of alkylphenolics on total GC detectables in the humin oil was determined using



Scheme 4-2. Possible reaction pathway for IPA (400 °C, Pt/C).

GC×GC-FID (internal standard method) and the use of an average response factor for alkylphenolics). This resulted in a total alkylphenolics yield of about 7 wt% on GC detectables in the liquid phase after reaction (Table 4-3).

Table 4-3. Overview of the composition of the liquid phase (GC×GC-FID).^a

Experiment	1	2	3	Average	4 blank (no humin)
Alkylphenolics (%) ^a	8.9	6.2	6.2	7.1	<1.0
Aromatics (%)	4.9	6.9	4.6	5.5	<1.0
Linear/branched alkanes (%)	2.0	1.9	1.3	1.7	<1.0
Cyclic alkanes (%)	6.0	7.2	4.0	5.7	10.8
Ketones/alcohol (%)	66.9	67.2	71.4	68.5	88.0

^a% based on GC detectables in the liquid phase; experimental conditions: Pt/C, 400 °C, 7 h. Minor component belonging to other product classes are not provided (e.g. organic acids)

It is interesting to notice that furanics are absent in the liquid phase, despite the fact that the humin structure contains significant amounts of substituted furan fragments (Figure 4-1). The furanics are likely converted during the liquefaction procedure at elevated temperatures and pressures to, for example, aromatics and alkylphenolics. Similar reactivity was observed for the catalytic hydrotreatment of humins using IPA/formic acid mixtures with Ru/C as the catalyst.^[24]

A GPC chromatogram of the liquid phase after reaction is given in Figure 4-6. The presence of substantial amounts of low molecular weight products along with a molecular weight tail can be seen. As such, it reveals that the conversion to solely low molecular weight components is not yet complete and that the liquid phase also contains higher molecular weight components that are not GC detectable.

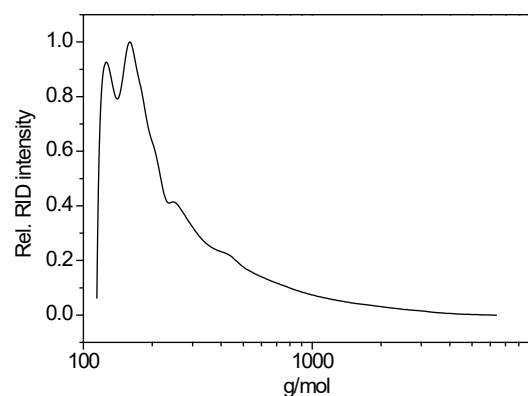
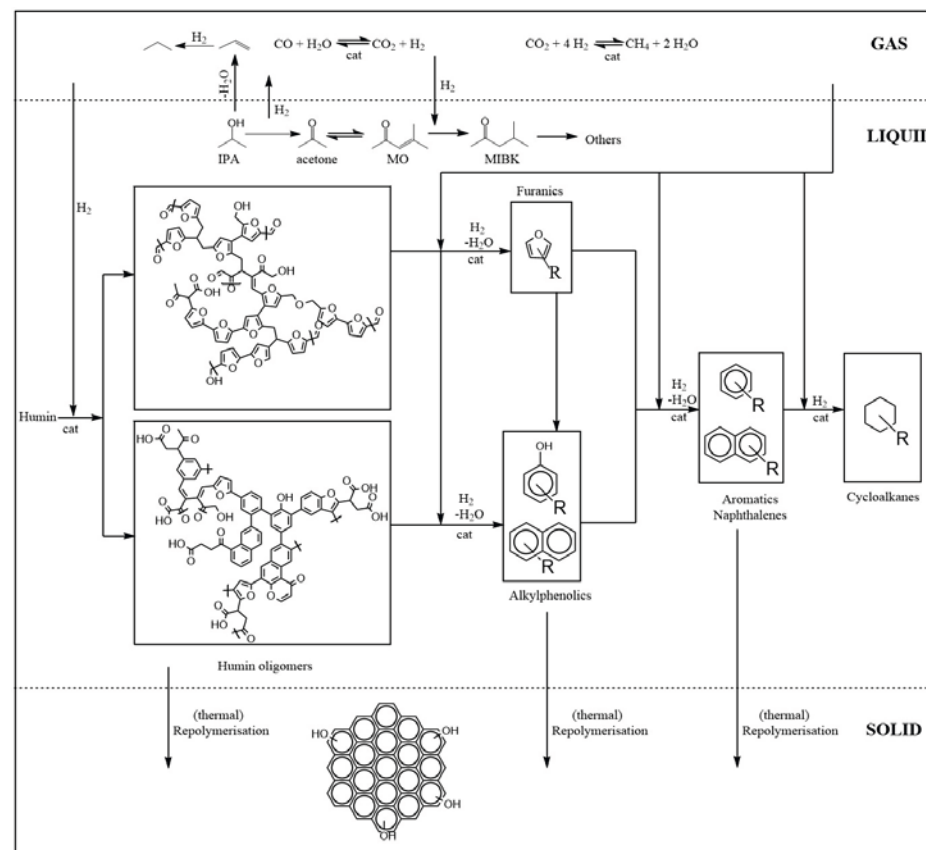


Figure 4-6. GPC chromatogram of a representative liquid phase after a catalytic liquefaction reaction.

REACTION PATHWAYS

On the basis of the experimental findings, supported by earlier studies on catalytic humin depolymerisation/liquefaction using Ru/C in combination with formic acid/IPA,^[24] a reaction network is proposed to explain the formation of various products in the gas and liquid phase (Scheme 4-3). The humins are depolymerised, either catalytically or thermally or a combination of the two, to form oligomeric furanics and ultimately lower molecular weight furanics. However, furanics were absent in the reaction products and this implies that these are rapidly converted into mainly aromatics and/or alkylphenolics. Both pathways are feasible according to recent literature.^[33-34] Alternatively, the furanic structure is dehydrated during heating



Scheme 4-3. Proposed reaction network for humin depolymerisation/liquefaction using Pt/C in IPA.

of the reaction mixture to a more condensed structure with aromatic and alkylphenolic units,^[33-34] which is subsequently depolymerised to alkylphenolics and aromatics. Both aromatisation of the humin structure and depolymerisation may also occur in parallel.

The presence of alkanes in the reaction mixture is (partly) due to the catalytic hydrogenation of the formed aromatics from the humins with molecular hydrogen. The latter, though not deliberately added to the reaction, is *in situ* formed by the dehydrogenation of IPA to acetone, which was proven experimentally by performing blank reactions with IPA (*vide supra*). The

majority of the ketones in the reaction products are formed from IPA by subsequent (aldol) condensations of acetone, which is confirmed by the blank reactions. The reactions always lead to some solid formation (9 wt% on feed for the benchmark reactions), which were not identified in detail. These can be either residual humins (most likely aromatised and not containing a large amount of furanic units) or solid products from the thermal repolymerisation of intermediates. Further research including detailed analyses of the solid products (elemental composition, solid state 2D-NMR) will be required to provide more definite answers, which is outside the scope of this manuscript.

4.3.2. SYSTEMATIC STUDIES USING PT/C AND IPA

To assess the impact of relevant process variables on humin conversion, liquid yield and the amount of alkylphenolics in the liquid phase, a systematic study according to a central composite design involving 19 experiments was performed. The ranges for the process variables are given in Table 4-4, the results of all experiments are provided in Table 4-5.

The centerpoint of the design was measured in triplicate (run 6, 9, 14 in Table 4-4), and showed good reproducibility. For instance, the average humin conversion was 58 wt% with a standard deviation of 1 wt%.

To quantify the effects of the process variables (temperature, catalyst intake, humin intake and reaction time) on the humin conversion, liquid yield and amount of alkylphenolics in the product oil were modeled using an expression given in Equation 4-1. All regression coefficients (b_i and b_{ij}) and the intercept (b_0) were calculated using the Design Expert® software package.

4.3.2.1. HUMIN CONVERSION

The experimental data given in Table 4-5 were used as input for the development of multi-variable non-linear regression model for the humin

Table 4-4. Process conditions for the design of experiment study on the catalytic humin liquefaction using Pt/C in IPA

Variable	Abbreviation	Benchmark (entry 6, 9, 14)	Systematic study
Catalyst intake (g)	Cat _{in}	1.07	0.15-2.01
Humin intake (g)	H _{in}	4	1-7
Time (h)	t	7	2-12
Temperature (°C)	T	400	375-450
IPA intake (g)		15	constant at 15

Table 4-5. Overview of experiments for the catalytic liquefaction of humins using Pt/C in IPA

Run	Catalyst Intake (g)	Humin intake (g)	Temperature (°C)	Time (h)	Humin conversion (%)	Liquid yield (%)	Amount of alkylphenolics (%) ^a
1	0.62	2.5	375	9.5	70	78	9
2	0.62	5.5	425	4.5	53	47	13
3	1.07	4.0	400	12	61	60	9
4	1.01	7.0	400	7	57	48	13
5	1.07	4.0	400	2	56	70	9
6 ^b	1.07	4.0	400	7	58	62	9
7	0.15	4.0	400	7	57	78	14
8	1.54	5.5	375	4.5	52	65	12
9 ^b	1.07	4.0	400	7	58	60	6
10	1.54	5.5	375	9.5	54	63	6
11	1.07	4.0	450	7	58	23	10
12	1.07	1.0	400	7	61	68	2
13	0.61	5.5	425	9.5	56	49	10
14 ^b	1.07	4.0	400	7	60	64	6
15	1.07	4.0	350	6	52	69	7
16	1.54	2.5	425	4.5	61	54	6
17	2.01	4.0	400	7	55	47	3
18	1.54	2.5	425	9.5	72	44	5
19	0.61	2.5	375	4.5	57	74	7

^a% based on GC detectables in the liquid phase after reaction (GC×GC-FID), ^bbench mark reaction conditions.

conversion as a function of process conditions. The coefficients for the regression model are provided in Table S4-1 (Supplementary information) and relevant statistical data are given in Table S4-2 (Supplementary information). The model relation between process conditions and humin conversion is given in Equation 4-7.

$$\text{Humin conversion} = 46.03 - 159.50\text{Cat}_{in} + 3.76H_{in} + 0.34T + 3.53t + 0.40\text{Cat}_{in}T - 0.63H_{in}t - 0.00089T^2 \quad (4-7)$$

The p-value of the model is very low ($< 10^{-4}$) which indicates that the model is statistically significant. The parity plot (Figure 4-7) shows that the model fits the experimental data reasonably well.

The effects of the relevant process variables on the humin conversion are provided in a three-dimensional response surface plot provided in Figure 4-8. The effect of the humin intake on the humin conversion was limited (Figure not shown for brevity). Both the catalyst loading and the temperature have a larger effect on the humin conversion. The highest conversion, up to 72%, was obtained at the highest temperature (450 °C) and catalyst intake (2.01 g) within the experimental range of the experimental design. As expected, at a high catalyst intake and temperature, a positive effect on humin conversion is observed. However, at low catalyst intake and low temperature, the conversion is also relatively high, though not as high as at the highest catalyst intake and temperature in the range. These findings may be related to the two possible depolymerisation mechanisms proposed in Scheme 4-3, the first involving cleavage of the linkages between the furanic fragments leading to monomeric furanics, the second to the formation of an aromatised structure,^[22, 35] followed by cleavage to low molecular weight aromatics. The model suggests that at low temperature and low catalyst intake, the first mechanism prevails. Upon a progressive increase in catalyst intake and temperature the conversion drops, possibly due to (catalytic) aromatisation of the humin structure, which is likely more difficult to depolymerise. At the high range of the temperature and catalyst intake, the

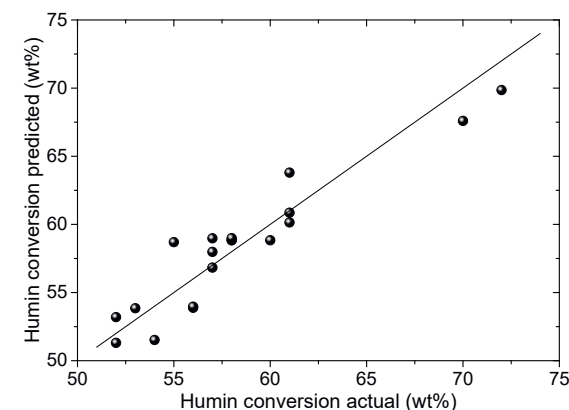


Figure 4-7. Parity plot for the regression model of humin conversion.

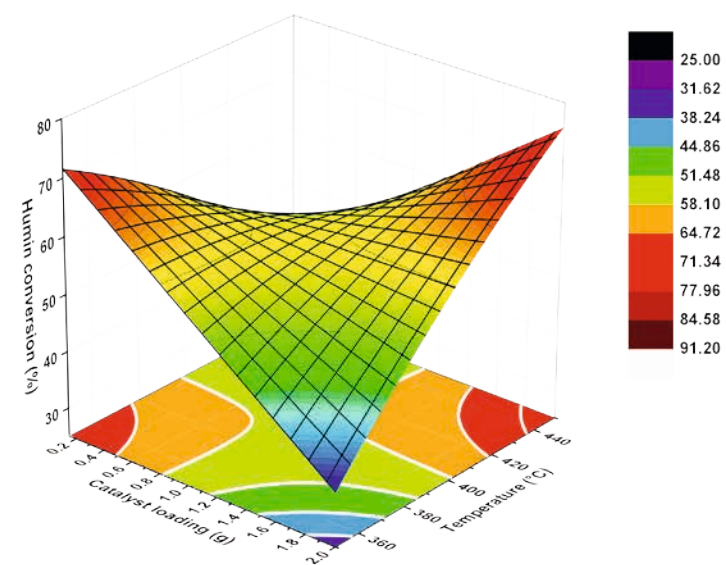


Figure 4-8. 3D surface plot of humin conversion as a function of temperature and catalyst intake.

humin yield increases again due to enhanced catalytic cleavage rates of the aromatised humin structure to form aromatic monomers. In addition, catalyst deactivation at the timescale of the reaction at elevated temperatures

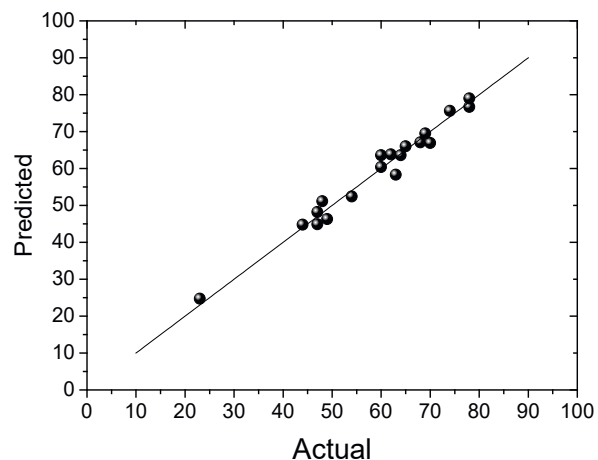


Figure 4-9. Parity plot for the regression model of the liquid yield.

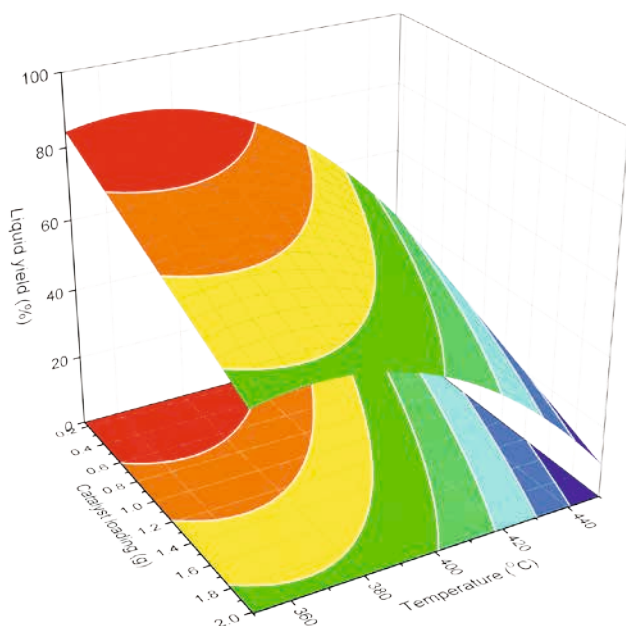


Figure 4-10. 3D surface plot for the liquid yield versus temperature and catalyst intake.

may also play a role. This effect will be more pronounced when using lower catalyst intakes and explains a reduction in the humin yield as a function of the temperature when using low catalyst intakes. Further studies, beyond the scope of this paper, to gain insights in catalyst stability are in progress.

4.3.2.2. LIQUID YIELD

The coefficients for the regression model for the liquid yield are provided in Table S4-1 (Supplementary information) and relevant statistical data are given in Table S4-3 (Supplementary information). The relation between process conditions and liquid yield is given in Equation 4-8.

$$\text{Liquid yield} = -1035 - 2.97Cat_{in} + 54.11H_{in} + 5.46T + 1.45t - 1.49Cat_{in}t - 0.13H_{in}T - 0.57H_{in}^2 - 0.007T^2 \quad (4-8)$$

The p-value of the model is very low ($< 10^{-4}$) which indicates that the model is statistically significant. The parity plot (Figure 4-9) shows that the model fits the experimental data well.

The effects of the process variables on the liquid yield are provided in a three-dimensional response surface plot provided in Figure 4-10. The liquid yield is primarily a function of the temperature and catalyst intake and highest liquid yields are predicted at the lowest temperature and catalyst intake. At these conditions, reactions leading to gas phase components, both involving humins and IPA, are slower than at higher temperatures and catalyst intakes, leading to higher liquid yields.

4.3.2.3. ALKYLPHENOLICS YIELD

The coefficients for the regression model for the alkylphenolics are provided in Table S4-1 (Supplementary information) and relevant statistical data are

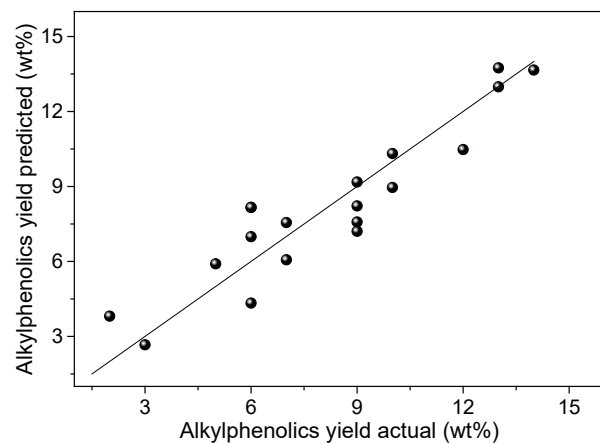


Figure 4-11. Parity plot for the regression model for the alkylphenolics yield.

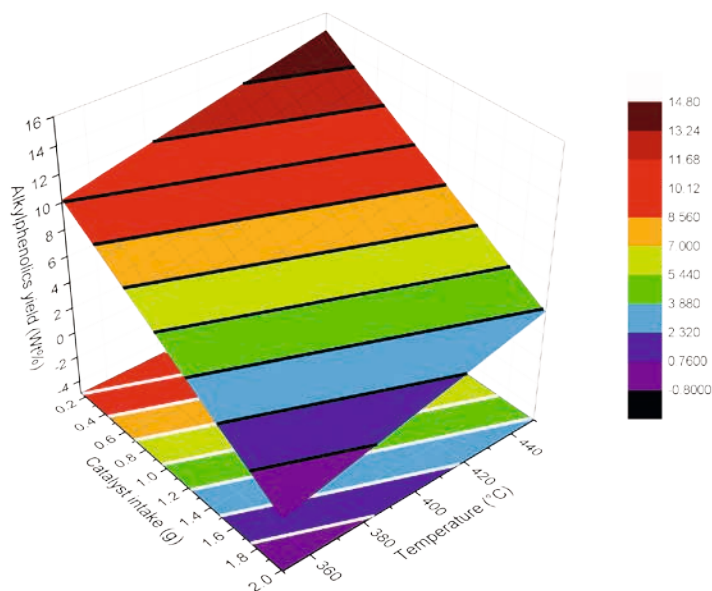


Figure 4-12. 3D surface plot of the alkylphenolics yield as a function of temperature and catalyst intake.

given in Table S4-4 (Supplementary information). The relation between process conditions and alkylphenolics is given in Equation 4-9.

$$\text{Alkylphenolics yield} = -69.13 - 5.91Cat_{in} + 19.66H_{in} + 0.17T + 1.16t - 0.04H_{in}T - 0.34H_{in}t \quad (4-9)$$

The p-value of the model is very low ($< 10^{-4}$) which indicates that the model is statistically significant. The parity plot (Figure 4-11) shows that the model fits the experimental data reasonably well.

The effects of the process variables on the alkylphenolics yield are provided in a three-dimensional response surface plots provided in Figure 4-12. Analysis shows that both the temperature and humin intake are of less significance on the alkylphenolics yield and that particularly the catalyst intake is of primary importance. These findings can be rationalised by considering that alkylphenolics are intermediates in the reaction pathway and will be further converted at the prevailing reaction conditions to aromatics and aliphatic hydrocarbons (Scheme 4-2). These hydrodeoxygenation/hydrogenation reactions are catalysed by Pt/C and as such are expected to be more pronounced at higher catalyst intake.^[36-37]

Thus, we can conclude that the experimental and modeling results regarding the effect of process conditions on humin conversion and liquid yield, as well as the alkylphenolics yield are in line with the mechanistic proposal given in Scheme 4-2.

4.4. CONCLUSIONS

We have shown that (model) humins, the solid byproducts from the conversion of C₆ sugars (glucose, fructose) to 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), can be converted to a liquid product (humin oil) using a supported Pt/C catalyst with IPA as the solvent. The highest humin conversion was 72% (425°C). IPA is not inert and acts as a hydrogen donor by

a Pt catalysed dehydrogenation reaction to acetone. As such, the product oil also contains IPA derived products, mainly ketones (MIBK) and alcohols derived thereof. The main products from the humins are aromatics, alkylphenolics and aliphatic hydrocarbons, which was confirmed by performing blank reactions with IPA and Pt/C in the absence of humins. These findings imply that the solid, recalcitrant humins may be (partly) depolymerised to a liquid oil, which may serve as a biofuel (component) and, after separation, also as a source for valuable biobased chemicals. The oils also contains substantial amounts of particularly ketones derived from IPA, which also have added value after a separation step. For instance MIBK is used for the manufacture of lube oil additives, and is widely used as an industrial solvent in paint, resin, varnishes and lacquers. A reaction network is proposed to explain the formation of products and further rationalised by performing experiments at a range of process conditions. Highest amounts of alkylphenolics, which are important intermediates in the petrochemical industry, were 14% (based on GC detectables in the liquid phase after reaction), obtained at low catalyst intakes. The latter was rationalised by considering that the alkylphenolics are intermediates in the reaction network that are converted to aromatics and alkanes.

4.5. REFERENCES

- 1 Beckham GT, Johnson CW, Karp EM, Salvachúa D, Vardon DR. Opportunities and Challenges in Biological Lignin Valorization. *Current Opinion in Biotechnology*. 2016; 42: 40-53.
- 2 Yung MM. Catalytic Conversion of Biomass to Fuels and Chemicals. *Topics in Catalysis*. 2015; 59(1): 1.
- 3 Nicklaus CM, Minnaard AJ, Feringa BL, de Vries JG. Synthesis of Renewable Fine-Chemical Building Blocks by Reductive Coupling between Furfural Derivatives and Terpenes. *ChemSusChem*. 2013; 6(9): 1631-1635.
- 4 Jong ED, Dam MA, Sipos L, Gruter GJM. Furanicarboxylic Acid (FDCA), a Versatile Building Block for a Very Interesting Class of Polyesters. *American Chemical Society*, 2012, 1-13.
- 5 Lee SB, Kim SK, Hong YK, Jeong GT. Optimization of the Production of Platform Chemicals and Sugars From the Red Macroalga, *Kappaphycus Alvarezii*. *Algal Research-Biomass Biofuels and Bioproducts*. 2016; 13: 303-310.
- 6 Yuan ZQ, Long JX, Zhang XH, Xia Y, Wang TJ, Ma LL. Catalytic Conversion of Lignocellulose Into Energy Platform Chemicals. *Progress in Chemistry*. 2016; 28(1): 103-110.
- 7 Yan K, Jarvis C, Gu J, Yan Y. Production and Catalytic Transformation of Levulinic

- Acid: A Platform for Speciality Chemicals and Fuels. *Renewable & Sustainable Energy Reviews*. 2015; 51: 986-997.
- 8 Dumeignil F, Capron M, Katryniok B, Wojcieszak R, Lofberg A, Girardon JS, Desset S, Araque-Marin M, Jalowiecki-Duhamel L, Paul S. Biomass-Derived Platform Molecules Upgrading through Catalytic Processes: Yielding Chemicals and Fuels. *Journal of the Japan Petroleum Institute*. 2015; 58(5): 257-273.
- 9 Isikgor FH, Becer CR. Lignocellulosic Biomass: A Sustainable Platform for the Production of Bio-Based Chemicals and Polymers. *Polymer Chemistry*. 2015; 6(25): 4497-4559.
- 10 Luterbacher JS, Alonso DM, Dumesic JA. Targeted Chemical Upgrading of Lignocellulosic Biomass to Platform Molecules. *Green Chemistry*. 2014; 16(12): 4816-4838.
- 11 Novodarszki G, Retfalvi N, Dibo G, Mizsey P, Csefalvay E, Mika LT. Production of Platform Molecules From Sweet Sorghum. *RSC Advances*. 2014; 4(4): 2081-2088.
- 12 Giang CH, Osatiashiani A, Dos Santos VC, Lee AF, Wilson DR, Waldron KW, Wilson K. Valorisation of Vietnamese Rice Straw Waste: Catalytic Aqueous Phase Reforming of Hydrolysate from Steam Explosion to Platform Chemicals. *Catalysts*. 2014; 4(4): 414-426.
- 13 Zhou C, Xia X, Lin C, Tong D, Beltramini J. Catalytic Conversion of Lignocellulosic Biomass to Fine Chemicals and Fuels. *Chemical Society Reviews*. 2011; 40: 5588-5617.
- 14 van Zandvoort I, Wang Y, Rasrendra CB, van Eck ERH, Bruijninx PCA, Heeres HJ, Weckhuysen BM. Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem*. 2013; 6(9): 1745-1758.
- 15 Funke A, Ziegler F. Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering D-6457-2011. *Biofuels Bioproducts & Biorefining-Biofpr*. 2010; 4(2): 160-177.
- 16 Kleinert M, Barth T. Phenols From Lignin. *Chemical Engineering & Technology*. 2008; 31(31): 736-745.
- 17 Stewart D. Lignin as a Base Material for Materials Applications: Chemistry, Application and Economics. *Industrial Crops & Products*. 2008; 27(2): 202-207.
- 18 Kleinert M, Barth T. Towards a Lignocellulosic Biorefinery: Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel. *Energy & Fuels*. 2008; 22(2): 1371-1379.
- 19 Patil S, Heltzel J, Lund C. Comparison of Structural Features of Humins Formed Catalytically from Glucose, Fructose, and 5-Hydroxymethylfurfuraldehyde. *Energy & Fuels*. 2012; 26(8): 5281-5293.
- 20 Sumerskii IV, Krutov SM, Zarubin MY. Humins-Like Substances Formed Under the Conditions of Industrial Hydrolysis of Wood. *Russian Journal of Applied Chemistry*. 2010; 83(2): 320-327.
- 21 van Zandvoort I, Koers EJ, Weingarth M, Bruijninx PCA, Baldus M, Weckhuysen BM. Structural Characterization of ¹³C-enriched Humins and Alkali-Treated ¹³C Humins by 2D Solid-State NMR. *Green Chemistry*. 2015; 17: 4383-4392.
- 22 Hoang TMC, Lefferts L, Seshan K. Valorization of Humins-Based Byproducts From Biomass Processing-a Route to Sustainable Hydrogen. *ChemSusChem*. 2013; 6(9): 1651-1658.
- 23 Rasrendra CB, Windt M, Wang Y, Adisasmito S, Makertihartha I, van Eck E, Meier D, Heeres HJ. Experimental Studies On the Pyrolysis of Humins From the Acid-Catalysed Dehydration of C6-sugars. *Journal of Analytical and Applied Pyrolysis*. 2013; 104: 299-307.
- 24 Wang Y, Agarwal S, Kloekhorst A, Heeres HJ. Catalytic Hydrotreatment of Humins in Mixtures of Formic Acid/2-Propanol with Supported Ruthenium Catalysts. *ChemSusChem*. 2016; 9(9): 951-961.
- 25 Gao J, Liu Q, Gu F, Liu B, Zhong Z, Su F. Recent Advances in Methanation Catalysts for the Production of Synthetic Natural Gas. *RSC Advances*. 2015; 5(29): 22759-22776.
- 26 Karakuş Y, Aynacı F, Kıpçak E, Akgün M. Hydrogen Production From 2-Propanol Over Pt/Al₂O₃ and Ru/Al₂O₃ Catalysts in Supercritical Water. *International Journal of Hydrogen Energy*. 2013; 38(18): 7298-7306.
- 27 Ukisu Y, Miyadera T. Dehydrogenation of 2-Propanol with Suspended Noble Metal

- Catalysts: Activity Enhancement by the Addition of Sodium Hydroxide. *Reaction Kinetics and Catalysis Letters*. 2004; 81(2): 305-311.
- 28 Ando Y, Yamashita M, Saito Y. Reaction Mechanism of 2-Propanol Dehydrogenation with a Carbon-Supported Ru-Pt Composite Catalyst in the Liquid Phase. *Bulletin of the Chemical Society of Japan*. 2003; 76(10): 2045-2049.
- 29 Mooksuwan W, Kumar S. Study On 2-Propanol/Acetone/Hydrogen Chemical Heat Pump: Endothermic Dehydrogenation of 2-Propanol. *International Journal of Energy Research*. 2000; 24(12): 1109-1122.
- 30 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 Chromatography and Time-Of-Flight Mass Spectrometry. *Journal of Chromatography a*. 2008; 1188(1): 17-25.
- 31 Sakurai M, Honda H, Kameyama H. Fundamental Study of a Non-Steady Operation for 2-Propanol De-Hydrogenation. *International Journal of Hydrogen Energy*. 2007; 32(9): 1303-1308.
- 32 Kloekhorst A, Shen Y, Yie Y, Fang M, Heeres HJ. Catalytic Hydrodeoxygenation and Hydrocracking of Alcell® Lignin in Alcohol/Formic Acid Mixtures Using a Ru/C Catalyst. *Biomass & Bioenergy*. 2015; 80(0): 147-161.
- 33 Bottari G, Kumalaputri AJ, Krawczyk KK, Feringa BL, Heeres HJ, Barta K. Copper-Zinc Alloy Nanopowder: A Robust Precious-Metal-Free Catalyst for the Conversion of 5-Hydroxymethylfurfural. *ChemSusChem*. 2015; 8(8): 1323-1327.
- 34 Buntara T, Noel S, Phua P, Melián-Cabrera I, de Vries J, Heeres H. From 5-Hydroxymethylfurfural (HMF) to Polymer Precursors: Catalyst Screening Studies On the Conversion of 1,2,6-Hexanetriol to 1,6-Hexanediol. *Topics in Catalysis*. 2012; 55(7-10): 612-619.
- 35 Hoang TMC, van Eck ERH, Bula WP, Gardeniers JGE, Lefferts L, Seshan K. Humin Based By-Products From Biomass Processing as a Potential Carbonaceous Source for Synthesis Gas Production. *Green Chemistry*. 2015; 17(2): 959-972.
- 36 Xu W, Miller SJ, Agrawal PK, Jones CW. Depolymerization and Hydrodeoxygenation of Switchgrass Lignin with Formic Acid. *ChemSusChem*. 2012; 5(4): 667-675.
- 37 Güvenatam B, Kurşun O, Heeres EHV, Pidko EA, Hensen EJM. Hydrodeoxygenation of Mono- and Dimeric Lignin Model Compounds On Noble Metal Catalysts. *Catalysis Today*. 2014; 233(13): 83-91.

4.6. SUPPLEMENTARY INFORMATION

Calculation procedure for the amount of gas phase components formed during the hydrotreatment reactions

After reaction, the reactor content was cooled to room temperature and the pressure was recorded. Subsequently, the reactor was vented to atmospheric pressure and the gas phase was collected in a gas bag. The volume of the gas was measured by immersing the gas bag into a vessel with water. The total amount of gas in the gasbag (in moles) was calculated using the ideal gas law. The composition of the gas was determined using GC (see experimental procedure) and this allowed calculation of the amounts of the individual gas phase component (in gram).

Table S4-1: Coefficients for the various regression model for the dependent variables

Variable	Humin conversion	Liquid yield	Amount of alkylphenolics
Model	Quadratic	Quadratic	2FI
Constant	46.03325	-1035.33615	-69.13143
Humin intake (H)	3.76039	54.11154	19.65895
Temperature (T)	0.33714	5.46252	0.17423
Reaction time (t)	3.52577	1.45291	1.15762
Catalyst intake (C)	-159.50444	-2.97122	-5.911
H.T	-	-0.13091	-0.039569
H.t	-0.63343	-	-0.33727
H.C	-	-	-
T.t	-	-	-
T.C	0.39838	-	-
t.C	-	-1.94133	-
H ²	-	-0.57287	-
T ²	-0.000899193	-0.00672611	-
t ²	-	-	-
C ²	-	-	-

Table S4-2 ANOVA data for the humin conversion

	SS	DF	MS	F	p-value	R ² values	
Model	443	7	63	11.86	< 0.0002	R ²	0.88
Error	59	11	5.34			R ² _{adjusted}	0.81
Total	502	18				R ² _{predicted}	0.63

Table S4-3. ANOVA data for the liquid yield

	SS	DF	MS	F	p-value	R ² values	
Model	3308	8	413	49.63	< 0.0001	R ²	0.98
Error	8	1	8			R ² _{adjusted}	0.96
Total	3391	18				R ² _{predicted}	0.89

Table S4-4. ANOVA for the alkylphenolics yield

	SS	DF	MS	F	p-value	R ² values	
Model	173	6	28.8	12.09	< 0.0002	R ²	0.86
Error	29	12	2.38			R ² _{adjusted}	0.79
Total	202	18				R ² _{predicted}	0.66