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Catalytic Liquefaction of Humin Substances from Sugar Biorefineries with Pt/C in 2-Propanol

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S Supporting Information

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 bench mark 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 analyzed in detail (GC-MS, GCxGC-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 depolymerization/hydrodeoxygenation reactions. A systematic study according to a central composite design (19 experiments) was performed to optimize the reaction conditions (T , humin intake, catalyst intake, and batch time) to obtain the highest humin conversion and alkylphenolics yield. The highest humin conversion was 72%, whereas the highest amount 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, Optimization

■ INTRODUCTION

Biobased platform chemicals are of high interest for the chemical industry, among 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 the 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 1 for details).

A number of technologies have been explored for the valorization of humin byproducts with the main aim to depolymerize the structure to low molecular weight components. Examples include (catalytic) thermochemical pathways

Figure 1. Proposed molecular structure of humins from low molecular weight sugars.²¹

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Scheme 1. Overview of the Experimental Procedure for a Catalytic Liquefaction Experiment

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 depolymerization technologies is centered around the use of heterogeneous catalysts in combination with a hydrogen source (molecular hydrogen, formic acid (FA), isopropanol (IPA)). We have recently shown that humins can be depolymerized 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 depolymerization 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 depolymerization of humins using a supported Pt catalyst with IPA as the hydrogen source in the absence of formic acid. The latter, though 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 bench mark 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 characterized 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 are rationalized using a reaction network.

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 preactivated and used as such.

Humin Synthesis. The humins used in this study were synthesized by the hydrothermal conversion of D-glucose, as reported in the literature.¹⁴ A total of 500 mL of an aqueous solution of glucose (1 M) and sulfuric 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 deionized 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 Setup. The hydrogenation experiments were performed in a batch autoclave (100 mL, maximum operating conditions: 350 bar and 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 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 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, 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 Supporting Information. The pressure was released, and the gas phase was collected in a 3 L plastic gas bag and was analyzed 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 and 0.03 bar for 12 h and weighed for mass balance calculations. The organic phase was analyzed by GC-MS, GCxGC-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 and 0.03 bar for 2 h. 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 eq 1–3:

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

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

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

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 repolymerization reactions of reactive intermediates is not taken into account.

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

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

Statistical Modeling and Optimization. Nonlinear multivariable 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 eq 5.

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

where y is a dependent variable (humin conversion, liquid yield, and alkylphenolics yield); x_i and x_j are the independent variables (catalyst intake (g), humin intake (g), temperature ($^{\circ}\text{C}$), 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 nonsignificant 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 $\times$ 0.25 mm i.d. and 0.25 μm film thickness). Electron ionization was performed at 70 eV. The injector and oven temperature were set at 280 $^{\circ}\text{C}$. Analysis was performed using an oven temperature heating profile (from 40 to 250 $^{\circ}\text{C}$ at a rate of 3 $^{\circ}\text{C}/\text{min}$). 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 (GCxGC). GCxGC-FID analyses were performed on a Trace GCxGC system from Interscience equipped with a cryogenic trap and two columns (30 m $\times$ 0.25 mm-i.d. and 0.25 μm -film RTX-1701 capillary column connected to a 120 cm $\times$ 0.15 mm-i.d. and 0.15 μm -film Rxi-5Sil MS column). A flame ionization detector (FID) was used. A dual-jet modulator was applied using carbon dioxide to trap the samples 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 $^{\circ}\text{C}$. The oven temperature was kept at 40 $^{\circ}\text{C}$ for 5 min and then heated to 250 $^{\circ}\text{C}$ with a rate of 3 $^{\circ}\text{C}/\text{min}$. The pressure was set at 0.7 bar. The modulation time was 6 s.

From the GCxGC-FID spectra, the amounts of aromatics, alkylphenolics, ketones, alkanes, naphthalenes, and acids were calculated based on total GC detectable components. The identification of main GC $\times$ 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 $\times$ 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 gas bag (SKC Tedlar 3 L sample bag 9.5" $\times$ 10" with a polypropylene septum fitting) after the hydrotreatment reaction. The gaseous products were analyzed using a GC (Hewlett-Packard 5890 Series II equipped with a Poraplot Q $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ column and a molecular sieve (5 $\text{\AA}$) column) and a thermal conductivity detector (TCD). Both columns were maintained at the same temperature. The injector and detector temperature were set at 110 and 200 $^{\circ}\text{C}$, respectively. The oven temperature was kept at 40 $^{\circ}\text{C}$ for 3 min then heated to 90 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C min}^{-1}$ and kept at this temperature for another 7.5 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.

RESULTS AND DISCUSSION

Bench Mark Experiments. In the first stage of experimentation, an experiment was carried out using a

Table 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)
humin 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	
humin 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 oil (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 $^{\circ}\text{C}$ for 7 h, 27 wt % catalyst on humin intake, 21 wt % humin on total reactor intake (IPA and humins). ^bBy difference.

humin sample from D-glucose in IPA (21 wt % humins) with Pt/C as the catalyst. This bench mark reaction was carried out in a batch autoclave at 400 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$, likely due to the catalytic decomposition of IPA to gas-phase components (*vide infra*). After reaction and workup, 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 1. Here, the results for three experiments (entry 1, 2, and 3 in Table 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 satisfactory (>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 CO_2 is expected to have a considerable solubility in the liquid phase. As such, it is only partly included in the gasphase composition. In addition, it will evaporate during liquid phase workup 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 was determined by performing three experiments at similar reaction conditions, and the results are given in Table 1. The product distributions as well as the mass balance closures are within 3%, showing that the reproducibility of the reaction is good.

Figure 2. GC-MS spectrum of the liquid phase of a bench mark experiment (Table 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.

Table 2. Major Component Classes and Representative Individual Components in the Liquid Phase Obtained at Bench Mark 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.

The liquid phase yield on total intake (humin and IPA) was on average 62 wt %. Also a substantial amount of a gas phase

was obtained (about 12 wt % on feed intake), indicating that part of the humins and the solvent IPA are converted to gas-

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

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

phase 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 1, entry 4). Considerable amounts of gas-phase 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 solubilized to a significant extent by a catalytic liquefaction reaction using IPA as the solvent.

Gas Phase Composition. The composition of the gasphase for the bench mark reaction with IPA was determined (Table 1). The main gasphase 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 gas-phase hydrogenation reactions of CO_x with hydrogen (eq 6). These methanation reactions are known to be catalyzed 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, catalyzed 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

Figure 5. GC-MS-FID plot of the liquid phase of a blank reaction (Table 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.

Scheme 2. Possible Reaction Pathway for IPA (400 °C, Pt/C)

Table 3. Overview of the Composition of the Liquid Phase (GCxGC-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).

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

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 1).

Liquid Phase Composition. The molecular composition of the liquid phase from the bench mark experiment using IPA as the solvent was determined using GC-MS and GCxGC-FID. A typical GC-MS spectrum of the liquid phase is shown in Figure 2. Numerous products were observed that belong to various organic product classes; the major ones are 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.

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

The presence of these component classes was further confirmed by GCxGC-FID analyses (Figure 3). This GC technique is very suitable to rapidly determining various organic compound classes present in a bioliquid as these are visible in discrete regions in the GCxGC-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.

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

Scheme 3. Proposed Reaction Network for Humin Depolymerization/Liquefaction Using Pt/C in IPA

Table 4. Process Conditions for the Design of Experiment Study on the Catalytic Humin Liquefaction Using Pt/C in IPA

variable	abbreviation	bench mark (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)	<i>t</i>	7	2–12
temperature (°C)	<i>T</i>	400	375–450
IPA intake (g)		15	constant at 15

The ketones and alcohols are likely formed from IPA by a reaction pathway provided in Scheme 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 and Barth¹⁸ for the noncatalytic 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 GCxGC-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 the reaction (Table 3).

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 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 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.

Table 5. Overview of Experiments for the Catalytic Liquefaction of Humins Using Pt/C in IPA

run	catalyst intake (g)	humins intake (g)	temperature (°C)	time (h)	humins 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 (GCxGC-FID). ^bBench mark reaction conditions.

Figure 7. Parity plot for the regression model of humins conversion.

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

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

Reaction Pathways. On the basis of the experimental findings, supported by earlier studies on catalytic humins

depolymerization/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 3). The humins are depolymerized, 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 of the reaction mixture to a more condensed structure with aromatic and alkylphenolic units,^{33,34} which is subsequently depolymerized to alkylphenolics and aromatics. Both aromatization of the humin structure and depolymerization 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*

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

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

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 solids formation (9 wt % on feed for the bench mark reactions), which were not identified in detail. These can be either residual humins (most likely aromatized and not containing a large amount of furanic units) or solid products from the thermal repolymerization 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.

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; the results of all experiments are provided in Table 5.

The centerpoint of the design was measured in triplicate (runs 6, 9, and 14 in Table 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 eq 5. All regression coefficients (b_i and b_{ij}) and the intercept (b_0) were calculated using the Design Expert software package.

Humin Conversion. The experimental data given in Table 5 were used as input for the development of a multivariable nonlinear regression model for the humin conversion as a function of process conditions. The coefficients for the regression model are provided in Table S1 (Supporting Information), and relevant statistical data are given in Table S2 (Supporting Information). The model relation between process conditions and humin conversion is given in eq 7.

Humin conversion

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

The p value of the model is very low ($<10^{-4}$), which indicates that the model is statistically significant. The parity plot (Figure 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 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 depolymerization mechanisms proposed in Scheme 3, the first involving cleavage of the linkages between the furanic fragments leading to monomeric furanics, the second to the formation of an aromatized 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) aromatization of the humin structure, which is likely more difficult to depolymerize. At the high range of the temperature and catalyst intake, the humin yield increases again due to enhanced catalytic cleavage rates of the aromatized humin structure to form aromatic monomers. In addition, catalyst deactivation on the time scale of the reaction at elevated temperatures 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.

Liquid Yield. The coefficients for the regression model for the liquid yield are provided in Table S1 (Supporting Information), and relevant statistical data are given in Table S3 (Supporting Information). The relation between process conditions and liquid yield is given in eq 8.

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

$$\begin{aligned} \text{liquid yield} = & -1035 - 2.97\text{Cat}_{\text{in}} + 54.11\text{H}_{\text{in}} + 5.46T \\ & + 1.45t - 1.49\text{Cat}_{\text{in}}t - 0.13\text{H}_{\text{in}}T - 0.57\text{H}_{\text{in}}^2 \\ & - 0.007T^2 \end{aligned} \quad (8)$$

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

Alkylphenolics Yield. The coefficients for the regression model for the alkylphenolics are provided in Table S1 (Supporting Information), and relevant statistical data are given in Table S4 (Supporting Information). The relation between process conditions and alkylphenolics is given in eq 9.

$$\begin{aligned} \text{Alkyl phenolics yield} \\ = & -69.13 - 5.91\text{Cat}_{\text{in}} + 19.66\text{H}_{\text{in}} + 0.17T + 1.16t \\ & - 0.04\text{H}_{\text{in}}T - 0.34\text{H}_{\text{in}}t \end{aligned} \quad (9)$$

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

provided in Figure 12. Analysis shows that both the temperature and humin intake are of less significant on the alkylphenolics yield and that particularly the catalyst intake is of prime importance. These findings can be rationalized 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 3). These hydrodehydrogenation/hydrogenation reactions are catalyzed 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 3.

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 catalyzed 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) depolymerized 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 contain 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 rationalized by performing experiments at a range of process conditions. The 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 rationalized by considering that the alkylphenolics are intermediates in the reaction network that are converted to aromatics and alkanes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b01834.

Tables with the coefficients and ANOVAs for the various regression models (PDF)

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Notes

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