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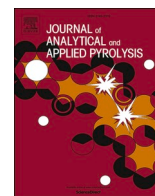
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Valorization of humin type byproducts from pyrolytic sugar conversions to biobased chemicals

R.M. Abdilla-Santes^{a,b}, S. Agarwal^{a,c}, X. Xi^a, H. Heeres^d, P.J. Deuss^a, H.J. Heeres^{a,*}

^a Green Chemical Reaction Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands

^b Department of Chemical Engineering, University of Brawijaya, MT. Haryono 167, Malang, 65145, Indonesia

^c Catalytic Processes and Materials, MESA+ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE, Enschede, the Netherlands

^d Biomass Technology Group, Josink Esweg 34, 7545 PN, Enschede, the Netherlands

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ABSTRACT

The pyrolytic sugar fraction, obtained by an aqueous extraction of pyrolysis oil, is an attractive source for sugar-derived platform chemicals. However, solids (humin) formation occurs to a significant extent during hydrolysis and subsequent acid-catalyzed conversion processes. In this study, we report investigations on possible conversion routes (pyrolysis, liquefaction) of such humin byproducts to biobased chemicals. Experiments were carried out with a model humin made from a representative technical pyrolytic sugar and the product was characterized by elemental analysis, GPC, TGA, HPLC, GC-MS, FT-IR and NMR. The obtained humin sample is soluble in organic solvents (dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and isopropanol (IPA)), in contrast to typical more condensed humins from glucose and fructose, allowing characterization using NMR and GPC. All analyses reveal that the humins are oligomeric in nature (M_w of about 900 g/mol) and consist of sugar and furanic fragments linked with among others (substituted) aliphatic, ester units and, in addition, phenolic fragments with methoxy groups. The humins were used as a feed for catalytic pyrolysis and catalytic liquefaction experiments. Catalytic pyrolysis experiments (mg scale, programmable temperature vaporizer (PTV)-GC-MS, 550 °C) with HZSM-5–50 as the catalyst gave benzene-toluene-xylene-naphthalene-ethylbenzene mixtures (BTXNE) in 5.1 wt% yield based on humin intake. Liquefaction experiments (batch reactor, 350 °C, 4 h, isopropanol as both the solvent and hydrogen donor and Pt/CeO₂ (4.43 wt% Pt) catalyst) resulted in 80 wt% conversion of the humin feed to a product oil with considerable amounts of phenolics and aromatics (ca. 24.7 % based on GC detectables in the humin oil). These findings imply that the techno-economic viability of pyrolysis oil biorefineries can be improved by converting humin type byproducts to high value, low molecular weight biobased chemicals.

1. Introduction

Lignocellulosic biomass is considered a promising alternative feedstock for renewable carbon-based transportation fuels (e.g., bioethanol, biodiesel) and biobased chemicals [1–3]. In the last decade, major breakthroughs have been realized regarding the conversion of the carbohydrate fraction from lignocellulosic biomass. For example, an attractive valorization route involves the conversion into biobased platform chemicals like 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) [4,5].

The cellulose and hemicellulose fractions in lignocellulosic biomass typically need to be depolymerized/pre-treated to obtain monomeric

sugars like glucose and xylose before further conversion into biobased chemicals and biofuels [6]. Well known approaches are enzymatic and acid-catalyzed depolymerization. A less developed route is the use of fast pyrolysis technology as a pre-treatment process. In fast pyrolysis processes, the biomass is rapidly heated to 450–600 °C in the absence of oxygen, leading to significant deconstruction and depolymerization. The main product is a liquid known as pyrolysis liquid (oil) or bio-oil and depending on the process parameters, the oil yield can be as high as 70–80 wt% on a dry-feed basis [7,8]. Pyrolysis oils are composed of several hundreds of small organic compounds in combination with considerable amounts of higher molecular weight (non GC detectable) compounds [9,10]. A main disadvantage is its low thermal stability,

* Corresponding author at: Green Chemical Reaction Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands.

E-mail address: h.j.heeres@rug.nl (H.J. Heeres).

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Table 1
Low molecular weight components detected in PS fractions.

Compound	Rice husk [15]	Acid-leached pine wood [17]	Untreated pinewood [17]	PS used in this study ^a [18]
Levoglucofan	28.9 mg/g	10.0 ± 0.6 wt%	3.4 ± 0.2 wt %	16 wt%
Cellobiosan	10.2 mg/g			
Xylose	3.7 mg/g			
Arabinose	1.2 mg/g			
Glucose	2.6 mg/g			
Total sugars		21.8 wt%	13 wt%	
Glycoaldehyde				10.8 wt%
Acids				2.5 wt%
Ketones				1.4 wt%
Phenolics				0.4 wt%
Other low molecular weight component (mostly phenolics and aromatics)		4.5 wt%	7.5 wt%	
Water	65.2 wt%	73.7 ± 0.7 wt%	79.5 ± 0.5 wt %	14.5 wt%

^a Concentrated by evaporation, see experimental section.

which precludes separation by distillation. However, pyrolysis oils are easily fractionated into three product fractions using a combination of precipitation, extraction and fractionation approaches [11]. The following fractions are obtained, i) an organic so-called pyrolytic lignin fraction (products mostly derived from lignin), ii) an aqueous phase containing mostly monomeric and oligomeric sugars and iii) a low molecular weight oxygenate stream containing among others acetic acid. The aqueous sugar-rich phase can be concentrated to obtain a thick syrup, commonly addressed as pyrolytic sugars (PS), in yields up to 30 wt% of the original pyrolysis oil [11]. This separation procedure is the basis for a pyrolysis biorefinery, where the pyrolysis liquid is separated into fractions, followed by tailored, dedicated conversions of each fraction into value added products.

The PS contain a number of sugars and sugar-derived chemicals. When using pure cellulose as the fast pyrolysis feedstock, the main product is 1,6-anhydro- β -D-glucopyranose, commonly known as levoglucosan, and the yield can be as high as 59 wt% [12]. It is also the main component in the PS fraction when using a typical lignocellulosic biomass as the feed (Table 1). Other products are 1,

6-anhydro- β -cellobiose (cellobiosan) and higher molecular weight sugars. Levoglucosan is readily hydrolyzed to glucose using acid catalysts [13,14], which subsequently can be converted to numerous bio-based chemicals including HMF and LA.

Examples on the use of PS as a feed for LA and HMF synthesis are scarce. In a recent study, Zhang et al. [15] reported the hydrolysis of the water soluble fraction (WSF) of pyrolysis oil using H₂SO₄ (1 wt%) as the catalyst at 170 °C giving LA in low yields (2.3 mol%). We have recently investigated the acid-catalyzed conversion of pine wood-derived PS (see Table 1 for its chemical composition) with 0.5 M H₂SO₄ catalyst at 180 °C [16]. HMF was detected in the earlier stage of the reaction (around 5 min, 1 wt% yield) whereas LA was the main detectable product (10 wt%) after 60 min. However, considerable amounts of insoluble brown products (humins) were formed. In addition, heating of the pine wood-derived PS in the absence of a catalyst also leads to significant amounts of such humins (32 wt% based on the initial PS feed). As such, the use of such PS fractions to obtain biobased chemicals has been hampered by the fact that significant amounts of humins are formed. Evidently, optimization studies to obtain higher yields of HMF/LA are required (catalyst and solvent selection, biphasic systems), although it is unlikely that humin formation can be avoided completely. As such, there is an incentive to convert these humins into valuable chemicals.

It has been shown in the literature that humins from monomeric sugars (fructose, glucose) are carbonaceous, heterogeneous, poly-disperse and typically highly insoluble materials consisting of a furan-rich polymer network with different oxygen containing functional groups [6,19–21]. A number of valorization routes for such humins have been suggested in the literature. Examples are the use as an energy source by combustion [21], use in composites based on PFA (poly-furfuryl alcohol) [22] and valorization approaches involving depolymerization of the humin structure to low-molecular weight-components, which are subsequently transformed into biobased chemicals (Fig. S1, Supporting information) [23].

In this paper, we describe experimental studies on the conversion of humins, obtained from a technical PS fraction, by catalytic pyrolysis and liquefaction approaches to depolymerize the humins and to obtain high amounts of monomeric products. All reactions were carried out using a humin sample derived from the PS fraction of a pine-based pyrolysis oil. This humin was characterized in detail (elemental analysis, GPC, TGA, HPLC, GC-MS, FT-IR, and NMR) to gain insights in its chemical structure and to rationalize its reactivity.

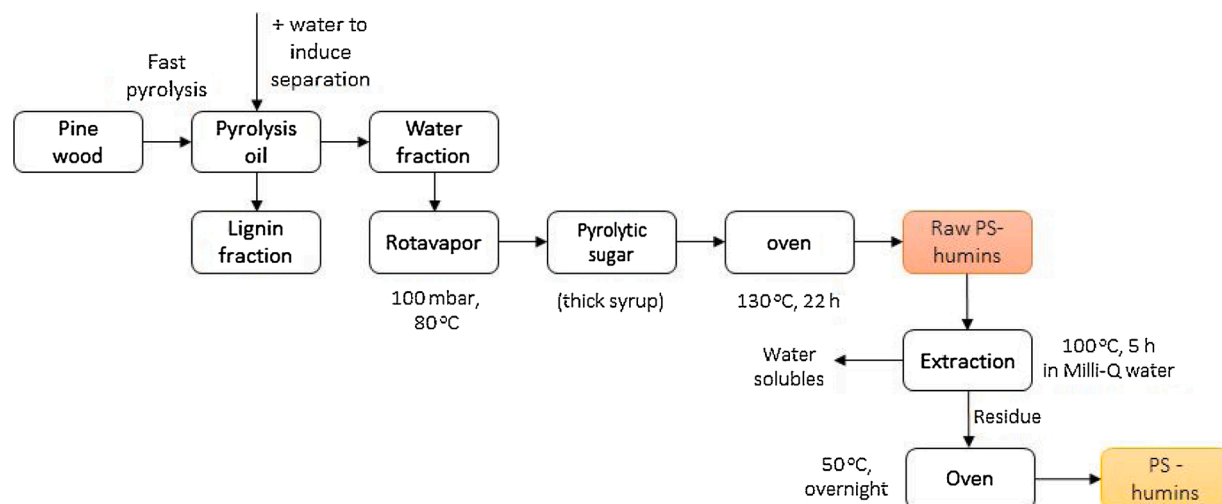


Fig. 1. Schematic illustration of the synthesis of PS-humins.

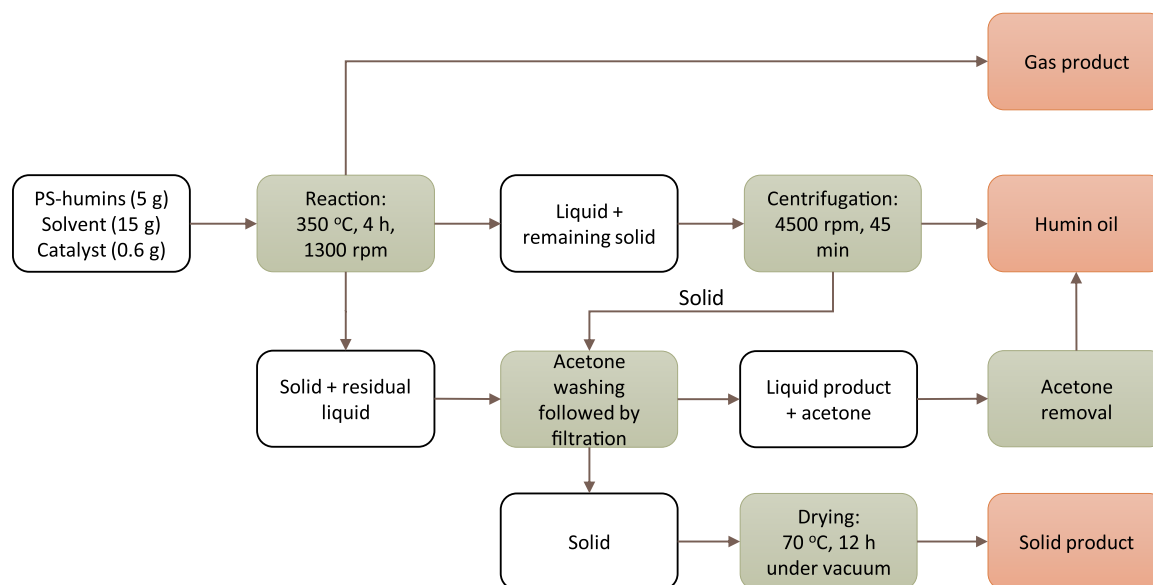


Fig. 2. Schematic representation of the catalytic liquefaction procedure.

2. Experimental section

2.1. Chemicals

All chemicals used in this work were of analytical purity and used without further purification, unless stated otherwise. Gases used in this study were supplied by Linde Gas (Schiedam, the Netherlands) and were of analytical grade. Tetrahydrofuran (THF), toluene and acetone were supplied by Boom B.V. (Meppel, the Netherlands). Isopropanol (IPA, anhydrous, 99.5 %), di-*n*-butylether (DBE) and CeO₂ (Sigma No. 544841-50 G) were obtained from Sigma Aldrich. Platinum(II) acetylacetonate was acquired from Merck (8.14689.0001).

2.2. Humin synthesis

The pyrolysis oil was provided by Biomass Technology Group (BTG, Enschede) and obtained from the fast pyrolysis of pine wood. The pyrolysis oil was fractionated by the addition of water, resulting in phase separation and the formation of an insoluble fraction (mostly lignin-derived) and a water phase (containing sugars, see Fig. 1 for details). The water phase was concentrated using a rotavapor (100 mbar, at 80 °C) until water evaporation ceased, to give a thick PS syrup. Subsequently, the PS fraction was thermally treated for 22 h in an oven at 130 °C under atmospheric pressure. The resulting dark brown product (designated as *raw PS-humins* in this study) was extracted with Milli-Q water (2.5 g sample in 80 mL water) at 100 °C for 5 h to remove (trapped) solubles. After water extraction, the insoluble part of the sample was filtered and dried overnight at 50 °C in an oven at atmospheric pressure. This residue was ground into a powder and used as the feed in this study (*PS-humins*).

2.3. Synthesis of the Pt/CeO₂ catalyst for catalytic liquefaction reactions

The Pt/CeO₂ (with a target content of 5 wt% Pt) catalyst was synthesized by a wet impregnation procedure. Pt(Acac)₂ (0.404 g, 0.2018 g Pt) was dissolved in acetone (78 mL) under stirring and the appropriate amount of pre-calcined (500 °C) CeO₂ (4.004 g) was added. The acetone was then slowly removed from the suspension by heating the suspension at 40 °C under atmospheric pressure (about 8 h). The remaining solid was collected and calcined in a muffle furnace under air (heating profile: from room temperature to 300 °C with a heating rate of 5 °C min⁻¹ for 2 h followed by heating to 500 °C with a rate of 5 °C min⁻¹ for 1 h followed

by cooling to 50 °C). After calcination, the catalyst was reduced in a tubular glass oven with a sweep gas consisting of 7 vol% hydrogen and 93 vol% nitrogen (heating profile: room temperature to 400 °C with a heating rate of 5 °C min⁻¹, 6 h at 400 °C and then cooled to 50 °C).

2.4. Experimental procedures

2.4.1. Thermal and catalytic pyrolysis

Pyrolysis and catalytic pyrolysis of the PS-humins were performed following a procedure described by Agarwal, et al. [24]. The experiments were conducted using a PTV injector (programmable temperature vaporizer, Model: Optic2 from Atlas) placed on a HP 5890 GC Series II system in combination with a HP 5972 MS detector (PTV-GC-MS) controlled by an Optic 2 device. Typically, for thermal pyrolysis 0.6–0.8 mg of the humin sample was used. For catalytic pyrolysis, a humin to catalyst ratio of 0.05 w/w was used, loading first the PS-humins followed by the catalyst. The (catalytic) pyrolysis temperature was set at 550 °C. The oven was programmed to ramp from 40 °C to 550 °C with a rate of 16 °C min⁻¹ and kept at 550 °C for 60 s. After (catalytic) pyrolysis in the injector was completed, the products were transferred to a capillary column (Agilent Technologies VF-5 ms, 30 m × 0.25 mm × 1.0 μm film thickness, split ratio of 50:1). Helium was used as the carrier gas at a flow rate of 1 mL min⁻¹. The initial temperature was set at 40 °C and kept for 60 s followed by heating to 250 °C with a rate of 10 °C min⁻¹. The MS detector was operated in the scan range of *m/z* 35–400 using ionization mode (70 eV) with an interface temperature of 280 °C. The NIST-05a mass spectra library was used to identify the pyrolysis products. Subsequently, the total ion chromatogram (TIC) peak areas acquired from the MS detector were used as a semi-quantitative estimation of the concentration of GC-MS detectable compounds, assuming a linear correlation between the concentration and the TIC peak area percentage as often applied when reporting the composition of biomass-derived pyrolysis product streams. The semi-quantitative yields of each compound/group of compounds were calculated by dividing the corresponding TIC peak area percentage to the total TIC peak area of all the GC detectables. For simplicity, except BTXNE, the compounds were classified based on chemical functionalities, e.g., aromatic derivatives (substituted benzene and polycyclic aromatics), furans and derivatives, naphthalenes (naphthalene and substituted naphthalenes), (substituted) phenolic derivatives, and others (mainly alkanes, alkenes, acetic acid, indanes, etc). An external standard solution with known quantities of BTXNE was used to calculate the response factor of BTXNE to determine

the yields of BTXNE. Again, it was assumed that the concentration of the compounds is linearly related to the TIC peak area. A measurement using an external standard solution was performed prior to each set of experiments. A schematic representation of the PTV-GC-MS setup is provided in the Supporting information (Fig. S2).

2.4.2. Catalytic liquefaction experiments

The catalytic liquefaction of the PS-humins were performed in a 100 mL batch autoclave (Parr reactor system) with maximum operating conditions of 350 °C and 200 bar, surrounded with an electrically heated metal block and equipped with an overhead stirrer (Rushton type turbine with a gas induced impeller). Prior to an experiment, the reactor was weighed and then charged with a humin sample (5.0 g), IPA (15 g), and the metal catalyst (0.6 g, 12 wt% on humin intake). The reactor was closed and tested for leakage by pressurizing it with 50–80 bar of nitrogen. The pressure was released and the reactor was subsequently flushed twice with nitrogen gas. Subsequently, the stirring was started (1300 rpm) and the reactor was heated to 350 °C at a rate of about 5 °C min⁻¹, giving a final pressure of typically 80–90 bar. After reaction (4 h), the reactor was cooled to room temperature, the pressure was recorded and the gas phase collected in a 3 L plastic gas bag (SKC Tedlar, with polypropylene septum fitting) for GC analysis. The reactor was weighed and the reactor content was transferred to a centrifuge tube and weighed again. The product mixture was centrifuged at 4500 rpm for 45 min and the liquid phase (product oil) was separated from the solid phase (unreacted humins and catalyst). The reactor and the stirrer were thoroughly rinsed with acetone several times to collect the remaining solids. The combined acetone fraction (containing small amount of remaining product oil, unreacted humins and catalyst) was passed through a filter paper (to collect the solids) and collected in a beaker. The acetone in the mixture was then removed by evaporation in air and the resulting product (the remaining product oil) was weighted and added to the previously obtained product oil. The solid residue of unreacted humins and catalyst (from filter paper and centrifuge tube) was dried at 70 °C under vacuum overnight and subsequently weighted for mass balance calculations. The obtained product oil is a single phase liquid and designated as *humin oil* in this study. An overview of the product work-up is shown in Fig. 2.

The conversion of humins and yields of humin oil are reported on a mass basis and were calculated using Eqs. (1)–(3). In Eq. (3), the total feed intake represents the humin and solvent intake excluding catalyst.

$$\text{Humin conversion} = \frac{\text{Humin}_{in} - (\text{Total solid}_{out} - \text{catalyst intake})}{\text{Humin}_{in}} \times 100 \% \quad (1)$$

$$\text{Humin oil yield (based on humin intake)} = \frac{\text{Total humin oil}}{\text{humin intake}} \times 100 \% \quad (2)$$

$$\text{Humin oil yield (based on total intake)} = \frac{\text{Total humin oil}}{\text{Total feed intake}} \times 100 \% \quad (3)$$

2.5. Analytical methods

2.5.1. Thermogravimetric analysis (TGA)

TGA data of the humins (raw PS-humins and PS-humins) were obtained using a Mettler–Toledo analyzer (TGA/SDTA851e). The samples were heated in a nitrogen atmosphere from 30 to 900 °C with a heating rate of 10 °C min⁻¹.

2.5.2. Elemental analysis

The elemental composition (C, H, N, O, and S content) of the humins (raw PS-humins and PS-humins) were analyzed using an automated Euro Vector EA3000 CHNS analyzer with acetanilide as the calibration reference. The oxygen content was determined by the difference of CHNS. Each sample was analyzed at least in duplicate and the average

value is reported.

2.5.3. Heteronuclear single quantum coherence (HSQC) NMR

NMR spectra of the humins samples were acquired at 25 °C using an Agilent 400 MHz spectrometer. Approximately 0.3 g of each sample was dissolved in 0.7 g of DMSO-*d*₆. ¹H–¹³C HSQC spectra were acquired using a standard pulse sequence with a spectral width of 160 ppm, 16 scans and 512 increments in the F1 dimension. The data were processed using the MestReNova software.

2.5.4. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the humins samples were recorded on a Shimadzu IR Tracer-100 by attenuated total reflection (ATR) method in the range of 4000–600 cm⁻¹. Small amount of samples were placed on the sample unit (Graseby Specac Golden Gate with diamond crystal top with 45 degree angle) and the IR-spectra were recorded.

2.5.5. High performance liquid chromatography (HPLC)

Components in the water phase (after water extraction of raw PS-humins) were identified by an HPLC system consisting of an Agilent 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87 H), a refractive index detector and an ultraviolet detector. The HPLC column was operated at 60 °C and aqueous sulfuric acid (5 mM) was used as the mobile phase with a flow rate of 0.55 mL min⁻¹. Identification of compounds in the mixture were determined by comparison of retention time of known, pure compounds.

2.5.6. Gas phase analysis

The composition of the gas phase obtained after reaction was determined by GC-TCD. The instrument consists of a Hewlett Packard 5890 Series II GC with a thermal conductivity detector (TCD) equipped with a CP Poraplot Q Al₂O₃/Na₂SO₄ column (50 m x 0.5 mm, 10 μm film thickness) and a CP molecular sieve 5 Å column (25 m x 0.53 mm, 50 μm film thickness). Both columns were maintained at the same temperature. The injector and detector temperature were set at 150 °C and 90 °C respectively. The oven temperature was kept at 40 °C for 2 min, heated up to 90 °C at a rate of 20 °C min⁻¹ and kept at this temperature for another 2 min. Helium was used as the carrier gas. The columns were flushed for 30 s with reference and sample gas prior the measurement. For peak identification and quantification, a reference gas mixture containing H₂, CH₄, CO, CO₂, ethylene, ethane, propylene and propane with known concentration (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.

2.5.7. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analyses of the humin oil were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a quadrupole Hewlett-Packard 6890 MSD selective detector and a 30 m x 0.25 mm, i. d. and 0.25 μm film sol-gel capillary column. The injector temperature was set at 250 °C. The oven temperature was kept at 60 °C for 5 min, then increased to 250 °C at a rate of 3 °C/min, and then held at 250 °C for 10 min.

2.5.8. Two-dimensional gas chromatography-flame ionization detector (GCxGC-FID)

GCxGC-FID analyses of the humin oil were performed on a Trace GCxGC system from Interscience equipped with a cryogenic trap and two columns (RTX-1701 capillary column, 30 m x 0.25 mm i.d. and 0.25 μm film thickness connected by Meltfit to a Rxi-5Sil MS column, 120 cm x 0.15 mm i.d. and 0.15 μm film thickness). A flame ionization detector (FID) was used. A dual-jet modulator was applied using carbon dioxide to trap the samples. The lowest possible operating temperature for the cold trap was 60 °C. Helium was used as the carrier gas (flow rate of 0.6 mL min⁻¹). The injector temperature and FID temperature were set at 250 °C. The oven temperature was kept at 60 °C for 5 min and then

increased to 250 °C with a rate of 3 °C min⁻¹. The pressure was set at 0.7 bar and the modulation time was 6 s. For these measurements, a certain amount of humin oil was mixed with THF solution in a 1:1 v/v ratio. The THF solution contained 500 mg/L of di-*n*-butyl ether (DBE) as the internal standard (IS). From the GCxGC-FID spectra, the yields of aromatics, phenolics, ketones, alkanes, naphthenes and acids were calculated based on the humin intake. Quantification was performed by using an average relative response factor (RRF) per component group with DBE as the IS. Details of the procedure can be found elsewhere [23].

2.5.9. Gel permeation chromatography (GPC)

GPC analyses of the humins (raw PS-humins and PS-humins) and the humin oil were performed using an Agilent HPLC 1100 system equipped with three MIXED-E columns (length 300 mm, i.d. 7.5 mm, PLgel 3 mm) in series and a GBC LC 1240 refractive index (RI) detector. The average molecular weights were determined using the PSS WinGPC Unity software from Polymer Standards Service. Polystyrene samples with different molecular weights were used as a calibration standard. For the measurements, the system was operated at 140 bar pressure, a column temperature of 42 °C, with THF as eluent at a flow rate of 1 mL min⁻¹ and injection volume of 20 mL with sample concentrations of *circa* 10 mg mL⁻¹. For the analyses purpose, the samples were diluted with THF and two drops of toluene were added as a flow marker prior to injection. For analyses of the humin oil, the residual solvent (IPA) as well as low molecular products derived thereof (*e.g.*, acetone) were removed by heating the sample at 70 °C, 50 mbar, for 2 h prior to dissolution in THF.

2.6. Characterization of the Pt/CeO₂ catalyst

Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the actual Pt content of the catalyst. The analyses were performed on a Perkin Elmer 4300 DV device. Samples were calcined at 900 °C and subsequently dissolved in an aqueous HNO₃ (2% wt). Transmission electronic microscopy (TEM) images were obtained using a Philips CM12 operated at an acceleration voltage of 120 kV. A small amount of sample was placed in a glass vial and 5 mL ethanol was added. Subsequently, the mixture was ultrasonically dispersed for about 15 min. The resulting suspension was then deposited on a copper grid coated with carbon and subsequently analyzed. The images were taken with a slow scanning CCD camera.

3. Results and discussion

3.1. Synthesis and characterization of the PS-derived humins

The PS-derived humins used in this study were obtained by thermal treatment of a technical PS (obtained from pine wood pyrolysis) at 130 °C for 22 h. The synthesis was performed without the addition of an acid catalyst, as typically done for humin synthesis, as PS already contain some organic acids like acetic acid (Table 1). Typically, this procedure gives 73 wt% of solids (referred to as raw PS-humins). The resulting sample was either used as such or extracted with water to remove any entrapped low molecular weight compounds. After water extraction, the final purified humin yield (PS-humins) was about 32 wt%. Surprisingly, the PS-humins are soluble in typical organic solvents like DMSO and THF. This is in contrast with previously reported humin samples obtained from glucose and fructose upon heating in the presence of an acid [6,25]. The higher solubility of the PS-humins prepared in this study is likely due to a lower molecular weight and less condensed structure compared to the typical humins from glucose/fructose, supported by analyses (*vide infra*). This solubility in selected organic solvents allows a more detailed study on the molecular structure of the PS-humins sample by GPC and HSQC-NMR techniques, instead of the typically used solid state analysis techniques for highly insoluble humins.

The PS-humins contain 59 wt% [C], 35 wt% [O] and 5.5 wt% [H],

Table 2

Elemental composition of humins samples from this study and literature data.

Element (wt%)	Raw PS-humins	PS-humins	Glucose-derived humins [24]	Fructose-derived humins [6]	HMF ^a
C	54	59	65.7	66.4	57.1
H	6	5.5	4.4	4.2	4.8
N	0.07	0.36	n/a	n/a	n/a
S	< 0.01	< 0.01	n/a	n/a	n/a
O	40	35	29.9	32	38.1

^a As reference.

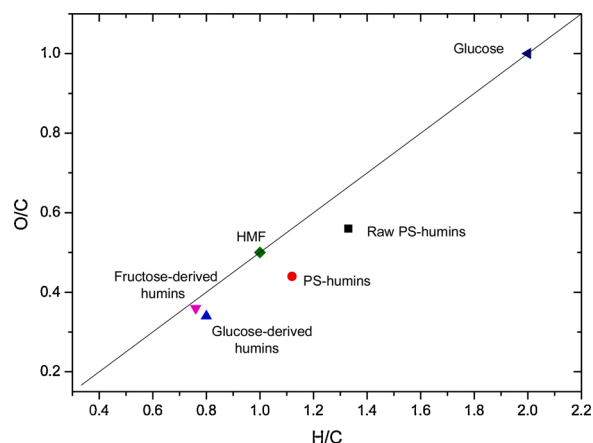


Fig. 3. Van Krevelen plot of the different types of humins given in Table 2. Solid line represents the dehydration line.

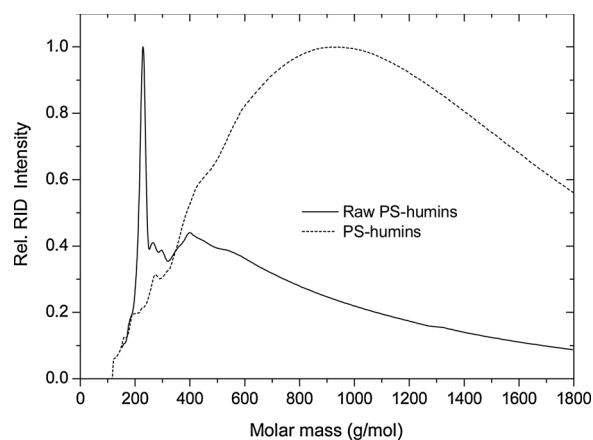


Fig. 4. Molecular weight distribution of PS-derived humins as measured by GPC (THF) using polystyrene standards.

which is in the range with reported values for glucose-derived humins and HMF (see Table 2 for details). A van Krevelen plot with H/C and O/C molar ratios of the humins is given in Fig. 3. The results indicate that the PS-humins used in this study is less dehydrated and thus likely less condensed than the typical humins from glucose (*vide infra*).

Molecular weight distribution for both raw PS-humins and PS-humins are given in Fig. 4. The average molecular weight (M_w) for the purified humins was about 900 g/mol, which suggests that on average about 8–10 sugar/furan units are present. When comparing both distributions, it is evident that a large amount of low molecular weight components are removed by the water extraction procedure. Analysis of the liquid extract (by HPLC technique) after water extraction of the raw PS-humins, reveals the presence of low molecular weight sugars like levoglucosan and cellobiosan (see Supporting information, Fig. S3).

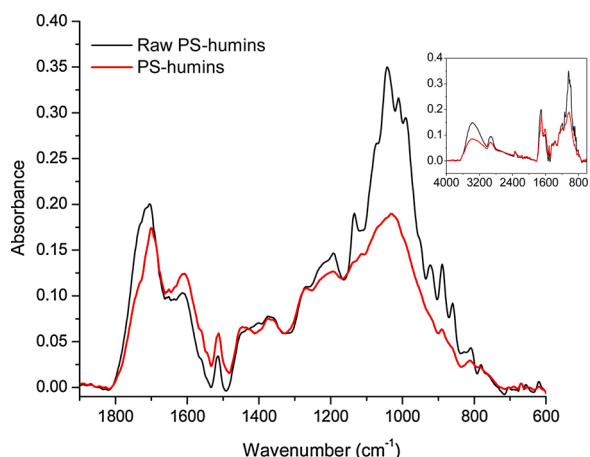


Fig. 5. FT-IR spectra of raw (black) and purified PS humins (red). Inset plot is from 4000 – 600 cm^{-1} region.

FT-IR analyses were performed to investigate the functionalities and chemical linkages in the humin samples before and after water extraction (Fig. 5). The spectrum for the PS-humins sample shows strong similarities with those reported for humins derived from glucose and fructose [6,26]. A broad peak at 3200–3400 cm^{-1} is present, which originates from the C–O stretch vibration of alcohols and possibly some residual water. Strong broad bands are present in the 1800–1600 cm^{-1} region corresponding to C=O stretch vibrations of acids, esters, aldehydes and ketones as well as substituted furanic rings (about 1600 cm^{-1}). A comparison of the spectra for the raw PS-humins (before extraction) and PS-humins (after extraction) shows that the peak intensities in the 3400–3000 cm^{-1} , 1800–1600 cm^{-1} and particularly the 1100–900 cm^{-1} region is higher for the former. This is due to a reduction of the amount of sugar-based molecules after extraction (glucose and levoglucosan, which show strong bands in the 1100–900 cm^{-1} region), in accordance with HPLC data for the water phase after extraction (Fig. S3).

To further understand the chemical composition of the PS-humins,

two-dimensional ^1H – ^{13}C HSQC-NMR was performed using deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as the solvent (Fig. 6). Major chemical groups can be clearly identified on the basis of the available literature [6,18,25,27]. In line with the FT-IR analysis, NMR analysis confirms that the PS-humins contains aliphatic C–H bonds, aliphatic (sugar) CH–O(H) motifs and aromatic (furanics) C–H bonds. In addition, a clear OMe signal is present, which is likely due to the presence of some residual guaiacol units in the structure. It is possible that covalently bound carbohydrate- and lignin fragments, either from the biomass feed or formed during pyrolysis, end up in the PS fraction and thus ultimately in the humin structure. Another possibility is the incorporation of monomeric phenolics, which are known to be present in the PS due to incomplete separation from the pyrolytic lignins. Estimations for the amounts of combined phenolics/aromatics in PS have been reported in the literature and are between 4.5 and 7.5 wt% [17], see Table 1 for details. The amount of low molecular weight phenolics in the PS fraction used in this study was estimated by GC at 0.4 wt% [18], and as such, it is possible that monomeric phenolics may participate in the condensation reactions that contribute to the insoluble products formed during thermal

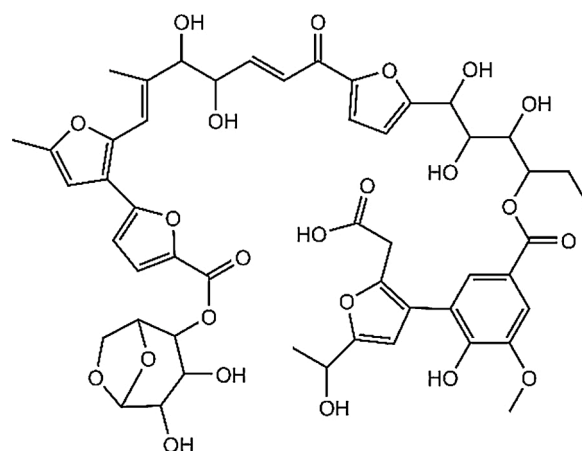


Fig. 7. Proposed molecular structure of PS-humins.

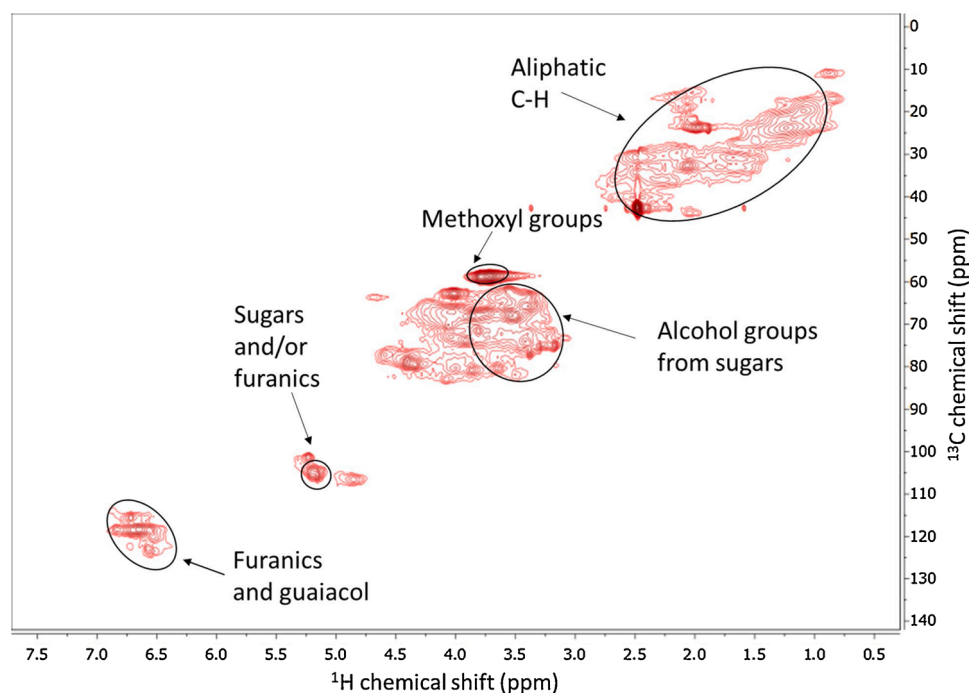


Fig. 6. HSQC spectra of PS-humins (400 MHz, $\text{DMSO-}d_6$).

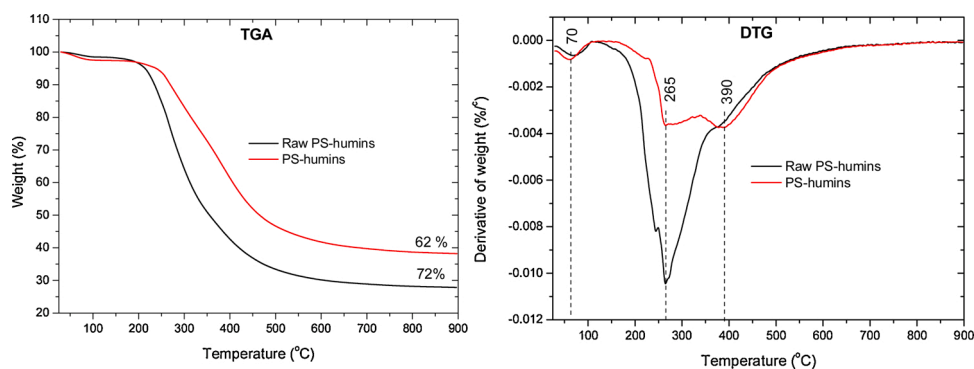


Fig. 8. TGA (left) and DTG (right) plots of raw PS-humins (black line) and PS-humins (red line).

treatment of the PS fraction.

To obtain information on the presence of other carbonyl groups in the humin structure e.g., from ketones/acids/esters, a 1D ^{13}C -NMR spectrum of the PS-humins sample was acquired (Fig. S5, Supporting information). It indeed shows (broad) resonances in the 170–180 range from the carbonyl groups of acids and esters.

On the basis of the NMR results, FT-IR and GPC analyses, a proposal for the structure of the PS-humins is provided in Fig. 7. It consists of sugar and furanic fragments linked with among others (substituted) aliphatic and ester units. In addition, a phenolic fragment with a -OMe group is added, in line with the HSQC-NMR data and Py-GC-MS analyses (*vide infra*).

3.2. Thermal pyrolysis

3.2.1. TGA studies

The thermal behavior of the humins were studied using TGA under N_2 (Fig. 8). The total weight loss was about 72 wt% for the raw PS-humins and 62 wt% for the PS-humins. This difference is likely due to the presence of low molecular weight, volatile compounds in the raw PS-humins, supported by HPLC measurements (*vide supra*). For both humin samples, three distinct weight loss stages were observed in the derivative thermo-gravimetric, DTG image (Fig. 8, right). The first stage started at around 70 °C and is likely due to the evaporation of very small entrapped volatile organics. Subsequently, two major peaks were observed, one at about 265 and another at about 380 °C. The ratio of the

peak heights differs considerably for both samples. The peak at 265 °C is highest for the raw PS-humins, and considerably lower for PS-humins. As such, this peak is likely due to the decomposition and evaporation of volatile, low molecular weight and sugar-like components (e.g., levoglucosan). TGA data for highly condensed and insoluble humins derived from glucose and fructose were reported by Rasrendra et al. [20]. Here, a maximum mass loss was observed at 450 °C, which is much higher than found for our samples, and suggest indeed that the PS-humins are less condensed than those reported for glucose/fructose. In addition, and in line with this statement, lower overall weight losses (50 %) were reported for those glucose/ fructose-derived humins.

3.2.2. Pyrolysis experiments

Thermal (non-catalytic) pyrolysis of the PS-humins was performed in a mg scale (PTV-GC-MS) to gain insights in the composition of the vapor phase. The TGA data imply that 400–500 °C is sufficient to volatilize the majority of the feed. To ensure highest volatiles formation, a pyrolysis temperature of 550 °C was selected for further studies. A typical chromatogram of the volatiles is shown in Fig. S6 (Supporting information) and shows that phenolics are the main products, together with furanics and substituted cyclopentanones. Interestingly, D-glucose-derived humins mainly gave furanics such as 2-methylfuran, 2,5-dimethylfuran and 1,2-furanylethanone upon thermal pyrolysis [24]. This observation confirms that the PS-humins used in this study also contain some phenolic structures besides furan and sugars units. This is also supported by NMR data (*vide supra*), which showed the presence of methoxy

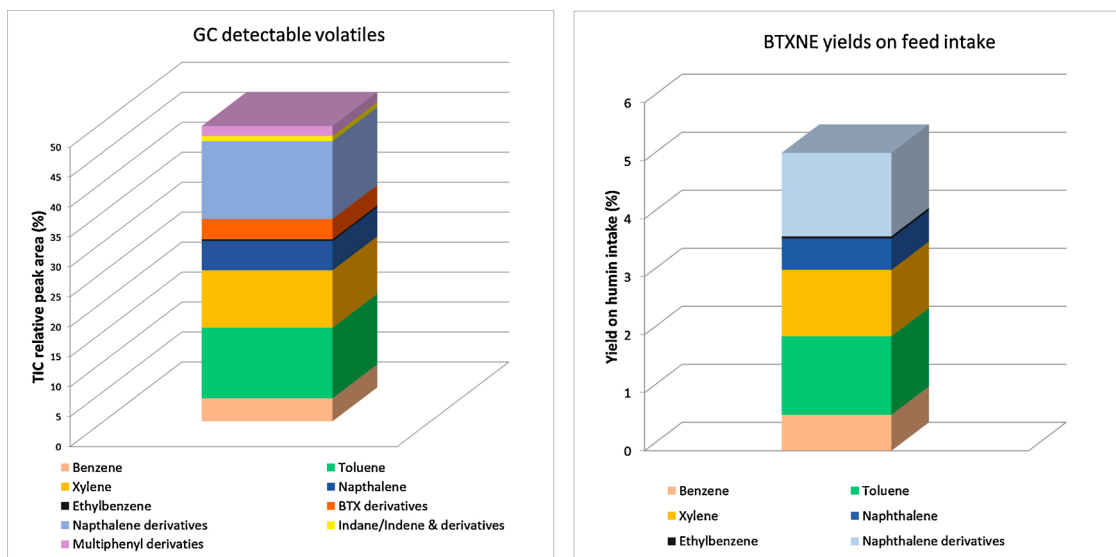


Fig. 9. Representative GC detectable monomers for the catalytic pyrolysis of PS-humins with HZSM-5-50 as the catalyst (humin to catalyst ratio of 0.05 w/w) at 550 °C (left) and BTXNE yields based on PS-humins intake (right).

Table 3

Product yields and compositions for the catalytic liquefaction of PS-humins in IPA^a.

	Run 1	Run 2
Humins intake, wt% on total feed	24.4	24.2
Humin oil yields, wt % on total feed	79.6	79.2
Solid residue, wt% on total feed	4.8	4.2
Humins conversion, wt% on total humin intake	81.1	83.2
Gas phase, wt% on total feed	14.2	11.7
Mass balance closure	98.6	95.3

^a Reaction condition: 350 °C, 4 h, 1300 rpm, with Pt/CeO₂ (12 wt% on humin intake).

groups, in line with the presence of significant amounts of 4-methylguaiacol in the chromatogram (compound 7, Fig. S6). However, it should be noted that some phenolics may also be formed by the (thermal) decomposition of sugar derivatives, a well-known example is the formation of 1,2,4-benzenetriol from HMF [28].

3.3. Catalytic pyrolysis

Catalytic pyrolysis was investigated to determine the possibility to convert the PS-humins into industrially relevant aromatics like BTXNE. Experiments with PS-humins were performed in a PTV-GC-MS unit at 550 °C with a humin to catalyst ratio of 0.05 w/w. Based on previous studies [29], HZSM-5–50 (SiO₂/Al₂O₃ ratio of 50) was selected as the catalyst. Considerable amounts of BTXNE (61.6 % on total GC detectable monomers) were formed, corresponding to 5.1 wt% based on the PS-humins feed (Fig. 9). Other GC detectable products were CO₂ and higher aromatics such as substituted naphthalenes, indanes and indenenes. The BTXNE yield is considerably higher than for glucose-derived humins (1.5 wt%) obtained at similar pyrolysis conditions, and comparable to the yields obtained for kraft lignin (6 wt%) [24]. The latter is considered a promising feed for BTXNE [24]. These results indicate that PS-humins have the potential to be converted to biobased aromatics *via* catalytic pyrolysis.

3.4. Catalytic liquefaction using a Pt/CeO₂ catalyst

PS-humins liquefaction experiments were carried out in a batch set-up with isopropanol (IPA) as the solvent and H₂ donor using a Pt/CeO₂ catalyst (see Supporting information for catalyst characterization) at

350 °C for 4 h with the objective to depolymerize the humin structure and obtain low molecular weight aromatics. All experiments were performed in duplicate, showing a very good reproducibility for the experimental procedure (Table 3). Mass balance closures for the PS-humins liquefaction experiments were excellent (> 95 wt %). A liquid product was obtained in about 79 % yield. The PS-humins conversion, calculated based on the amounts of solids isolated after reaction and corrected for catalyst intake, was of about 80 %. Hence, these experiments show that humins derived from PS can indeed be liquefied to a large extent using Pt/CeO₂ as the catalyst in combination with IPA.

The humin oil composition was determined using GC-MS, GCxGD-FID and GPC. GCxGC-FID analyses (Fig. 10) show the presence of numerous products belonging to various organic product classes *viz.* ketones, phenolics, and aromatics as well as aliphatic hydrocarbons. The presence of these components classes was further confirmed by GC-MS analyses (see Supporting information, Fig. S7). IPA is still present in considerable amounts, indicating that its conversion at the prevailing reaction conditions is far from quantitative. Typical reaction products of IPA (*e.g.*, acetone and (hydrogenated) aldol condensation products derived thereof like methyl isobutyl ketone (MIBK), 2-hexanol, and 2,6-dimethyl-4-heptanone) were detected [30]. Phenolics, naphthalenes, and aromatics in the humin oil are most likely formed from humins and not from IPA [31,32]. The amounts of the individual component classes in the humin oil were determined an average response factor for each group (Table 4). Among the humin-derived products, phenolics (phenol, methoxyphenol and dihydroxybenzene) were present in the largest amounts, with a total yield of about 14.1 % based on the GC detectables in the humin oil. Aromatics (mono-aromatics, naphthalenes) were the second main product (10.6 %). Interestingly, considerable amounts of

Table 4
Overview of the humin oil composition from catalytic liquefaction of PS-humins (GCxGC-FID).

Component class	Amount (%) ^a
Phenolics	14.1
Aromatics	10.6
Linear/branched alkanes	0.6
Cycloalkanes	2.6
Organic acids	7.9
Ketones/alcohols	64.2

^a Based on GC detectables in the humin oil, values are average from duplicate experiments at 350 °C for 4 h.

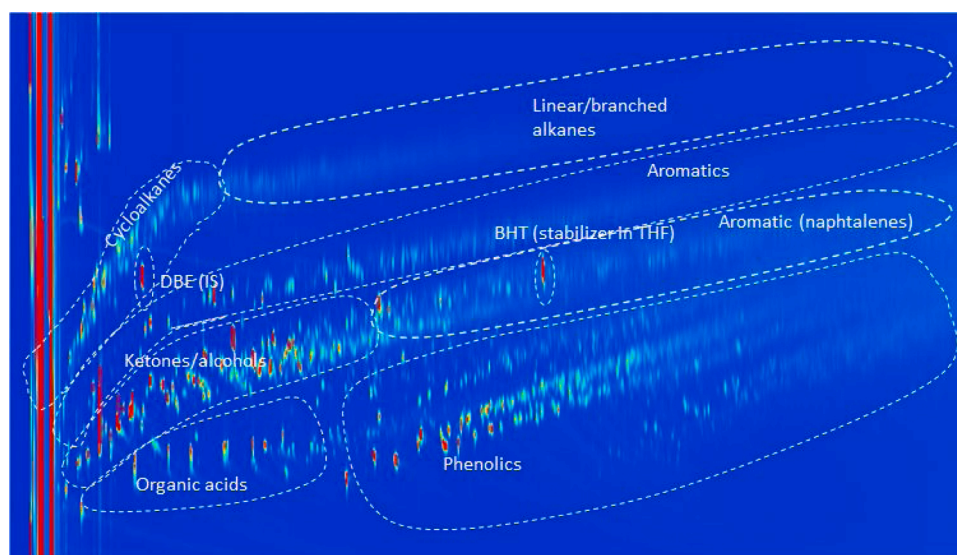
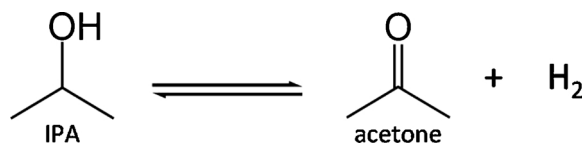


Fig. 10. GCxGC-FID of the humin oil from PS-humins reaction with IPA and Pt/CeO₂ catalyst at 350 °C for 4 h (crude reaction mixture before solvent evaporation). DBE: internal standard (IS).



Scheme 1. IPA dehydrogenation to acetone and hydrogen.

organic acids – possibly propionic, acetic and formic acid, were detected. These organic acids may be formed from residual sugars present in the PS-humins (Fig. 7). A GPC chromatogram of the liquid phase after removal of residual IPA shows the presence of substantial amounts of low molecular weight products along with a higher molecular weight tail (Supporting information, Fig. S8). It shows that the catalytic liquefaction procedure indeed results in significant depolymerization of the PS-humins structure by cleavage of inter unit bonds.

A substantial amount of gaseous products were obtained (on average around 12.5 wt% based on feed intake), indicating that part of the solvent (IPA) and the PS-humins are converted to gas components. The composition of the gas phase was determined by GC/TCD (Table S1) and was shown to consist of propane (41.5 mol%), carbon dioxide (20.5 mol %), methane (12.1 mol%), and hydrogen (11 mol%). Hydrogen is likely formed from IPA dehydrogenation (Scheme 1), a well-known reaction catalyzed by Pt.

Wang et al. proposed a reaction network to explain the formation of various products in the humin oil and gas phase during the catalytic liquefaction of humins using Pt/C and IPA, see Supporting information (Scheme S1). [32]. Although the starting material and temperature used in this work are different, it is likely also applicable for the results presented here.

4. Conclusions

In this work, we have prepared humins (PS-humins) from a technical PS fraction of a commercial pyrolysis oil, characterized them in detail, and explored the potential to convert them to low molecular weight biobased compounds. Unlike typical sugar (glucose, fructose)-derived humins reported in the literature, PS-humins obtained from this PS under relatively mild conditions are soluble in common organic solvents. This allows for the characterization of the materials by GPC and NMR. All characterization data show that these humins have a relatively low molecular weight (Mw about 900 g/mol) and consist of furanics and sugar-like fragments. Thus, the results suggest the formation of relatively uncondensed (and therefore still relatively soluble) humins that are the result of the relatively mild conditions applied.

The PS-humins can be converted to liquid products (humin oil) using catalytic pyrolysis and treatment with Pt/CeO₂ in IPA. Catalytic pyrolysis using a HZSM-5 (SiO₂/Al₂O₃ = 50) catalyst at 550 °C gave an BTXNE yield of 5.1 wt% based on PS-humins intake, which is close to that obtained for Kraft lignin under similar conditions. Catalytic liquefaction using IPA as solvent and hydrogen donor and Pt/CeO₂ catalyst at 350 °C resulted in significant depolymerization and liquefaction of the PS-humins. Humin oil analysis using GCxGC-FID showed that low molecular weight components, particularly phenolics and aromatics (estimated 24.7 % based on GC detectables in the humin oil) are present, together with higher molecular weight fragments (observed by GPC). As such, this study has shown that PS-humins may be (partly) depolymerized to liquid products, containing significant amounts of low molecular components. These findings imply that the techno-economic viability of pyrolysis oil biorefineries can be improved by converting humin type byproducts to high value, low molecular weight biobased chemicals.

CCRediT authorship contribution statement

R.M. Abdilla-Santes: Investigation, Funding acquisition, Writing -

original draft. S. Agarwal: Supervision, Validation, Investigation, Writing - original draft. X. Xi: Investigation, Writing - original draft. H. Heeres: Investigation, Conceptualization, Writing - original draft. P.J. Deuss: Conceptualization, Supervision, Validation, Writing - review & editing. H.J. Heeres: Conceptualization, Funding acquisition, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jaap.2020.104963>.

References

- [1] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr., J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Timpler, T. Tschaplinski, The path forward for biofuels and biomaterials, *Science* (New York, N.Y.) 311 (2006) 484–489.
- [2] A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, *Chem. Rev.* 107 (2007) 2411–2502.
- [3] J.J. Bozell, Feedstocks for the future—biorefinery production of chemicals from renewable carbon, *Clean-Soil, Air, Water* 36 (2008) 641–647.
- [4] B. Girisuta, B. Danon, R. Manurung, L. Janssen, H. Heeres, Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid, *Bioresour. Technol.* 99 (2008) 8367–8375.
- [5] R. van Putten, Jan C. van der Waal, E. De Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, *Chem. Rev.* 113 (2013) 1499–1597.
- [6] I. van Zandvoort, Y. Wang, C.B. Rasrendra, E.R. van Eck, P.C. Bruijninx, H. J. Heeres, B.M. Weckhuysen, Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions, *ChemSusChem* 6 (2013) 1745–1758.
- [7] R. Venderbosch, W. Prins, Fast pyrolysis technology development, *Biofuels Bioprod. Biorefining* 4 (2010) 178–208.
- [8] N.M. Bennett, S.S. Helle, S.J. Duff, Extraction and hydrolysis of levoglucosan from pyrolysis oil, *Bioresour. Technol.* 100 (2009) 6059–6063.
- [9] K. Sipilä, E. Kuoppala, L. Fagernäs, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils, *Biomass Bioenergy* 14 (1998) 103–113.
- [10] A. Oasmaa, S. Czernik, Fuel oil quality of biomass pyrolysis oils state of the art for the end users, *Energy Fuels* 13 (1999) 914–921.
- [11] Bio-materials & chemicals, <http://www.btgworld.com/en/rtd/technologies/bio-materials-chemicals>, 31-07-2020.
- [12] N. Kuzhiyil, D. Dalluge, X. Bai, K.H. Kim, R.C. Brown, Pyrolytic sugars from cellulosic biomass, *ChemSusChem* 5 (2012) 2228–2236.
- [13] S. Helle, N.M. Bennett, K. Lau, J.H. Matsui, S.J. Duff, A kinetic model for production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oil, *Carbohydr. Res.* 342 (2007) 2365–2370.
- [14] R. Abdilla, C. Rasrendra, H. Heeres, Kinetic studies on the conversion of levoglucosan to glucose in water using Brønsted acids as the catalysts, *Ind. Eng. Chem. Res.* 57 (2018) 3204–3214.
- [15] Y. Zhang, Y. Wang, H. Cui, P. Zhao, F. Song, X. Sun, Y. Xie, W. Yi, L. Wang, Effects of hydrolysis and oxidative hydrolysis pretreatments on upgrading of the water-soluble fraction of bio-oil via decarboxylation, *Appl. Energy* 226 (2018) 730–742.
- [16] R.M. Abdilla-Santes, H. Heeres, H.J. Heeres, Acid Catalysis Conversion of Pyrolytic Sugars, Manuscript in preparation, 2019.
- [17] X. Li, L.C. Luque-Moreno, S.R.G. Oudenhoven, L. Rehmman, S.R.A. Kersten, B. Schuur, *Bioresour. Technol.* 216 (2016) 12–18.
- [18] W. Yin, R.H. Venderbosch, M.V. Alekseeva, M.B. Figueiredo, H. Heeres, S. A. Khromova, V.A. Yakovlev, C. Cannilla, G. Bonura, F. Frusteri, H.J. Heeres, Hydrotreatment of the carbohydrate-rich fraction of pyrolysis liquids using

- bimetallic Ni based catalyst: catalyst activity and product property relations, *Fuel Process. Technol.* 169 (2018) 258–268.
- [19] J. Horvat, B. Klaić, B. Metelko, V. Šunjić, Mechanism of levulinic acid formation, *Tetrahedron Lett.* 26 (1985) 2111–2114.
- [20] C. Rasrendra, M. Windt, Y. Wang, S. Adisasmito, I. Makertihartha, E. Van Eck, D. Meier, H. Heeres, Experimental studies on the pyrolysis of humins from the acid-catalysed dehydration of C6-sugars, *J. Anal. Appl. Pyrolysis* 104 (2013) 299–307.
- [21] T.M.C. Hoang, L. Lefferts, K. Seshan, Valorization of humin-based byproducts from biomass processing—a route to sustainable hydrogen, *ChemSusChem* 6 (2013) 1651–1658.
- [22] J. Pin, N. Guigo, A. Mija, L. Vincent, N. Sbirrazzuoli, Jan C. van der Waal, E. De Jong, Valorization of biorefinery side-stream products: combination of humins with polyfurfuryl alcohol for composite elaboration, *ACS Sustain. Chem. Eng.* 2 (2014) 2182–2190.
- [23] Y. Wang, S. Agarwal, A. Kloekhorst, H.J. Heeres, Catalytic hydrotreatment of humins in mixtures of formic acid/2-propanol with supported ruthenium catalysts, *ChemSusChem* 9 (2016) 951–961.
- [24] S. Agarwal, D. van Es, H.J. Heeres, Catalytic pyrolysis of recalcitrant, insoluble humin byproducts from C6 sugar biorefineries, *J. Anal. Appl. Pyrolysis* 123 (2017) 134–143.
- [25] I. van Zandvoort, E.J. Koers, M. Weingarth, P.C. Bruijninx, M. Baldus, B. M. Weckhuysen, Structural characterization of 13 C-enriched humins and alkali-treated 13 C humins by 2D solid-state NMR, *Green Chem.* 17 (2015) 4383–4392.
- [26] S. Wang, H. Lin, Y. Zhao, J. Chen, J. Zhou, Structural characterization and pyrolysis behavior of humin by-products from the acid-catalyzed conversion of C6 and C5 carbohydrates, *J. Anal. Appl. Pyrolysis* 118 (2016) 259–266.
- [27] I. van Zandvoort, E.R. van Eck, P. de Peinder, H.J. Heeres, P.C. Bruijninx, B. M. Weckhuysen, Full, reactive solubilization of humin byproducts by alkaline treatment and characterization of the alkali-treated humins formed, *ACS Sustain. Chem. Eng.* 3 (2015) 533–543.
- [28] A.J. Kumalapati, C. Randolph, E. Otten, H.J. Heeres, P.J. Deuss, Lewis acid catalyzed conversion of 5-hydroxymethylfurfural to 1, 2, 4-benzenetriol, an overlooked biobased compound, *ACS Sustain. Chem. Eng.* 6 (2018) 3419–3425.
- [29] J. Jae, G.A. Tompsett, A.J. Foster, K.D. Hammond, S.M. Auerbach, R.F. Lobo, G. W. Huber, Investigation into the shape selectivity of zeolite catalysts for biomass conversion, *J. Catal.* 279 (2011) 257–268.
- [30] M. Sakurai, H. Honda, H. Kameyama, Fundamental study of a non-steady operation for 2-propanol de-hydrogenation, *Int. J. Hydrogen Energy* 32 (2007) 1303–1308.
- [31] Y. Wang, S. Agarwal, Z. Tang, H.J. Heeres, Exploratory catalyst screening studies on the liquefaction of model humins from C6 sugars, *RSC Adv.* 7 (2017) 5136–5147.
- [32] Y. Wang, S. Agarwal, H.J. Heeres, Catalytic liquefaction of humin substances from sugar biorefineries with Pt/C in 2-propanol, *ACS Sustain. Chem. Eng.* 5 (2016) 469–480.