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Catalytic Hydrotreatment of Biomass-Derived Fast Pyrolysis Liquids Using Ni and Cu-Based PRICAT Catalysts

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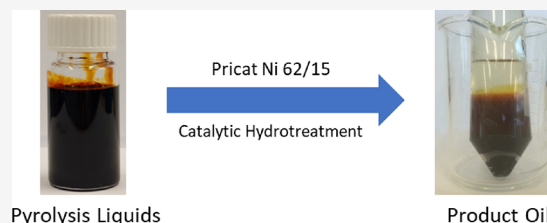


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ABSTRACT: Biomass-derived fast pyrolysis liquids (PLs) are not directly applicable as transportation fuels due to their high oxygen content and limited storage stability. Catalytic hydrotreatment is an efficient technology to convert such PLs to finished fuels or intermediates that can be used as a co-feed for existing oil refinery units. In this paper, we report catalyst screening studies for the mild hydrotreatment of PLs using commercially available Ni and Cu-based PRICAT catalysts at rather mild conditions (200 °C, initial 140 bar H₂ pressure) in a batch setup for 4 h. Among all catalysts, PRICAT NI 62/15 showed the best performance for mild catalytic hydrotreatment in terms of product properties (highest H/C ratio and lowest TG residue). The best catalysts were also tested for deep hydrotreatment at more severe conditions (350 °C, initial 100 bar H₂ pressure). Here, the PRICAT NI catalysts showed better performance than the benchmark Picula Ni-Mo catalyst when considering oil yield and H/C ratio. Advantageously, the hydrogen consumption during deep hydrotreatment is also reduced, rationalized by a lower methanation activity.



1. INTRODUCTION

Biomass is the only sustainable material that contains renewable carbon to (partly) replace fossil-based crude oil.¹ It mainly consists of three biopolymers, viz., cellulose, hemicellulose, and lignin with a large variation in composition.² However, the use of biomass as a feed for fuels and chemicals has some major disadvantages such as its solid nature and a large amount of oxygen, both resulting in a low volumetric energy density, typically ten times lower than crude oil.³

Fast pyrolysis is a versatile technology to convert solid biomass into liquid energy carriers, known as fast pyrolysis liquids (PLs). Generally, fast pyrolysis of biomass is carried out at 450–600 °C under atmospheric pressure in the absence of oxygen. A short vapor residence time (<2 s) in combination with high biomass heating rates ensures a high yield of liquid product, which can be up to 70 wt % on dry biomass feed.^{4–6} The obtained PLs have a higher volumetric energy density and are easier for transportation than solid biomass. Fast pyrolysis technology is moving to maturity and is on the verge of commercial exploitation, e.g., BTG-Bioliquids in the Netherlands.⁷

However, fast PLs have some negative properties such as a low H/C ratio and limited stability during storage and upon heating.^{8,9} As such, technologies have been explored in detail to improve the product properties and, as such, allow a wider spectrum of applications of such PLs. Catalytic hydrotreatment is a promising technology to convert PLs to intermediates, known as stabilized pyrolysis oils ('SPOs'), which have potential as a co-feed with crude oil cuts like vacuum gas oil

(VGO) in the existing oil refinery processes (e.g., in a fluidized catalytic cracking (FCC) unit).^{10–16}

The catalytic hydrotreatment of PLs is typically carried out in the presence of a hydrotreatment catalyst, typically at elevated temperatures (80–400 °C) and using a high hydrogen pressure (100–300 bar).^{17,18} Due to the thermal instability of PLs, the direct hydrotreatment of PLs at temperatures higher than 300 °C is not preferred as it leads to repolymerization of thermal labile components in PLs, especially carbonyl and sugar molecules, ultimately giving considerable amounts of solids. To circumvent this, a two (or more)-step hydrotreatment process for the upgrading of PLs was developed and reported by many researchers, for example, by Elliott *et al.*^{19,20} and Venderbosch *et al.* The process is characterized by two stages performed at two temperature regimes.

In the low-temperature stabilization step (<250 °C), the objective is to convert thermally labile oxygenated compounds (e.g., aldehydes) to more stable ones (e.g., alcohols). The main reactions occurring in this stage involve the water-soluble fractions of PLs (pyrolytic sugar fractions).¹⁷ Good catalysts for the stabilization step give product oils with a higher H/C ratio and better thermal stability. Thus, when screening catalysts for mild stabilization of PLs by catalytic hydrotreat-

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ment, the criteria for catalyst selection are (i) a higher H/C ratio obtained by elemental analysis and (ii) higher thermal stability, as determined by thermogravimetric analysis (TGA)^{21–23} or microcarbon residue testing (MCRT).¹⁰

The high-temperature step is generally carried out at a temperature of 350 °C or higher. After this step, the resulting product oils have a strongly reduced oxygen content, typically below 10 wt %. In this step, hydrogen consumption is substantial, especially when methanation occurs.

Catalysis is key for both the mild stabilization and deep hydrotreatment stage, and there is ample room for improved catalysts. We have performed extensive catalyst development studies.^{24,25} Proprietary Ni-based catalysts with a high Ni content ('Picula' catalysts) were developed and showed good performance for, particularly, mild hydrotreatment. Stability tests in a continuous setup have shown that such catalysts have a relatively good long-term stability (>500 h).²⁶ Deep hydrotreatment studies produce a deoxygenated oil with around 10 wt % oxygen with potential use as a co-feed. However, H₂ consumption levels are higher than 300 NL/kg PLs due to the methanation reaction, which is not preferred when considering the techno-economic viability of the process. In addition, the Picula catalysts are not commercially available and time-consuming development trajectories are required for further catalyst scale-up.

As such, there is significant interest in the use of commercially available catalysts for the hydrotreatment of PLs, both for the mild and deep hydrotreatment steps. Well-known commercial hydrotreatment catalysts are NiMo and CoMo-based ones.^{19,20} A major disadvantage of these catalysts is the requirement of the presence of S in the reactor to keep the catalysts in the active, sulfided form. PLs do not contain a significant amount of S and thus need continuous S addition in the feed for improved hydrotreatment performance. This adds to the costs and also may lead to undesired S contamination of the product oils. Thus, there is an incentive to apply catalysts that do not require S for activity. In this study, a series of commercially available PRICAT CU and NI catalysts from Johnson Matthey (JM, UK) with high Ni and Cu contents (> 30 wt %), which do not require S for activation/promotion, were screened for use in the mild and deep hydrotreatment of PLs. These catalysts have a broad application range in industry, for instance, for the hydrogenation of aldehydes, ketones, and aldoses to the corresponding alcohols and the selective hydrogenation of phenol to cyclohexanol. These reactions are also of high relevance for the hydrotreatment of PLs and those involving aldehydes/ketones in particular for the stabilization phase.⁹ The performance of the PRICAT catalysts will be compared with our benchmark Picula catalysts. The main criteria for catalyst selection are high H/C ratios of the product oils, a low hydrogen consumption level, and a low charring/coking tendency. The mild stabilization step was carried out in a batch setup at 200 °C, 140 bar H₂ pressure for 4 h, and the deep hydrotreatment was performed in the same batch setup at 350 °C, 100 bar H₂ for 4 h. The properties and molecular composition of the product oils were determined using various analytical techniques such as elemental analysis, gel permeation chromatography (GPC), TGA, 1D/2D-nuclear magnetic resonance (NMR), and GC × GC-FID. Finally, the performance of the PRICAT catalysts will be compared with a benchmark Picula Ni-Mo catalyst with a Ni content in the range of the PRICAT catalysts though with Mo as the promoter. It is among one of the most widely

studied catalysts from the Picula family and is the most attractive catalyst for mild hydrotreatment (stabilization) of the pyrolytic sugar fractions from PLs and deep hydrotreatment of PLs at 350 °C.^{27,28}

2. EXPERIMENTAL SECTION

2.1. Materials. The PL used in this study is derived from Pinewood and was supplied by the Biomass Technology Group (BTG, Enschede, the Netherlands). Relevant properties are shown in Table 1.

Table 1. Relevant Properties of the PL Used in This Study

property	value
water content (wt %)	27.83
elemental composition on a dry basis (wt %)	
C	55.22
H	6.58
O (by difference)	38.20
N	<0.01
H/C molar, dry	1.43
O/C molar, dry	0.52

Hydrogen, nitrogen, and helium were obtained from Linde and were all of analytical grade (>99.99%). Reference gas containing H₂, CH₄, ethylene, ethane, propylene, propane, CO, and CO₂ with known composition for gas-phase calibration was purchased from Westfalen AG, Münster, Germany. The commercially available catalysts were supplied as a powder by JM, UK. Detailed compositional data as reported in the literature are given in Table 2. The PRICAT catalysts as provided by the catalyst manufacturer are reduced and air-passivated before shipment to customers.

Table 2. Chemical Composition of the PRICAT Catalysts Used in This Study^a

catalyst code	active metal	metal content (%)	support
PRICAT CU 50/8	Cu	60	Al ₂ O ₃ -SiO ₂
PRICAT NI 55/5	Ni	55	MgO-Kieselguhr
PRICAT NI 62/15	Ni	60	Al ₂ O ₃ -Kieselguhr

^aCatalyst information provided by JM, UK.

Picula Ni-Mo was selected as the benchmark catalyst for this study. Compositional data for this catalyst are provided in Table 3, and

Table 3. Active Metal and Support of Reference Catalyst Picula Ni-Mo²⁸

catalyst	active metal, wt %		support, wt %	
Picula Ni-Mo	Ni	Mo	SiO ₂	Al ₂ O ₃
	41	7.4	13.3	24

detailed characterization data are given in ref 28. The catalyst was reduced at 500 °C under a H₂ flow (100 mL/min) for 2 h in a tubular oven,²⁸ passivated with 1% O₂ in N₂ in 4 h, and then transferred to the autoclave for testing.

2.2. Experimental Procedures. **2.2.1. Catalytic Hydrotreatment of PLs.** Catalyst studies were performed in a 100 mL batch autoclave (Parr, see Scheme S1 in the Supporting Information for details). 1.25 g of catalyst was loaded in the reactor followed by an *in situ* reduction under 20–30 bar H₂ at 200 °C (400 °C for Picula Ni-Mo) for 1 h. After reduction, the reactor was cooled to room temperature. 25.0 g of PLs (5 wt % catalyst/feed ratio) was fed to the reactor, which was flushed 3 times with 20 bar H₂ to remove the air and then pressurized to 140 bar (for mild hydrotreatment, 100 bar for

deep hydrotreatment) by H_2 . During the catalytic hydrotreatment in the batch reactor, the total pressure in the reactor is not constant as the consumed hydrogen is not compensated for during the experiments. The initial hydrogen pressure at room temperature was selected in such a way to ensure that the maximum reactor pressure was 200 bar at the desired temperature, corresponding to an initial pressure of 140 bar for the 200 °C and 100 bar for the 350 °C experiments.

To start the reaction, the reactor was heated to 200 °C (or 350 °C for deep hydrotreatment) at 10 °C/min, while the liquids were stirred at 1400 rpm. After reaction for 4 h at the pre-set temperature, the reactor was cooled to room temperature. The gas phase was collected using a 3 L gas bag and analyzed by GC-TCD (see Section 2.2.3 for details). The liquid and solid phases were transferred to a 50 mL centrifuge tube and separated by centrifugation at 4500 rpm for 30 min. The liquid phase after reaction consisted of a separate aqueous and oil phase for both mild and deep hydrotreatment of PLs.

In the case of mild hydrotreatment experiments, typically 30 wt % of the organic carbon is present in the aqueous phase.²⁹ To include this organic carbon in the carbon balances, the aqueous phase was heated to 120 °C at atmospheric pressure to evaporate the excess water. The organic residue was added to the oil phase (both together are referred to as total organics). For the deep hydrotreatment experiments, an organic oil on top of the water phase was obtained using the Picula Ni-Mo (so-called 'top oil'), while the PRICAT catalysts yielded an organic phase that was heavier than water ('bottom oil').

Each liquid phase was collected by using a glass pipette and weighed. The reactor was thoroughly rinsed with acetone, and the acetone was subsequently removed by evaporation. The organic residue was added to the oil phase for mass balance calculations. The solid residue in the reactor combined with the solids in the centrifuge tube was washed repeatedly with acetone, filtered, and dried in an oven at 100 °C for 24 h until constant weight. The amount of char formed is defined as the recovered solids after reaction minus the fresh catalyst intake. The hydrogen consumption was calculated by considering the pressure in the reactor before and after the reaction; details about the calculation procedure are given in ref 27.

2.2.2. Catalyst Recycling Experiments. To gain insights into the stability of the PRICAT catalysts, catalyst recycling experiments (3 successive runs) were carried out using PRICAT NI 62/15 at 200 °C. The first experiment was performed with a fresh catalyst, and the two successive ones were with a spent catalyst. After reaction, the spent catalyst was washed thoroughly with acetone and ethanol (5 and 2 times, respectively) and subsequently dried at 50 °C overnight. Finally, the dried spent catalyst was loaded to the reactor together with 25.0 g of fresh PLs for a subsequent run. Hydrogen consumption was used as the indicator for the performance. The results are given in Figure S1, and product distributions are provided in Table S1.

2.2.3. Product Analysis. **2.2.3.1. Gas-Phase Analysis.** The gas phase obtained after catalytic hydrotreatment of PLs was sampled using a 3 L gas bag, the composition of the gas phase was determined using a Hewlett Packard 5890 Series II GC equipped with a CP Poraplot Q Al_2O_3/Na_2SO_4 column (50 m \times 0.5 mm, a film thickness of 10 μ m) and a CP-Molsieve 5 Å column (25 m \times 0.53 mm, film thickness of 50 μ m), and He was used as the carrier gas. The temperature for the injector was set at 150 °C, and the oven temperature profile was 40 °C for 2 min, then increased to 90 °C at a heating rate of 20 °C/min, and maintained at this temperature for 2 min. The detector temperature was set at 90 °C. A calibration gas with a known composition of H_2 , CH_4 , CO, CO_2 , ethylene, ethane, propylene, and propane was used for component identification and quantification. The columns of the GC were flushed by calibration gas and sample gas for 30 s before each analysis.

2.2.3.2. Elemental Composition. The determination of the C, H, and N content in the PL feed and product oils was carried out using an elemental analysis using a EuroVector EA3400 Series CHNS-O with acetanilide as the reference. The oxygen content was determined by the difference. All analyses were carried out in duplicate, and the average value is reported.

2.2.3.3. Water Content. The water content in the PL feed and the product oils was determined by Karl–Fischer titration (Metrohm 702 SM Titrino titration setup). For this purpose, 0.01 g of sample was injected into an isolated chamber with Hydranal solvent (Riedel de Haen) and titrated with Hydranal titrant 5 (Riedel de Haen). Milli-Q water was used to calibrate the results. All analyses were carried out in triplicate, and the average value is reported.

2.2.3.4. Molecular Weight Distributions. Gel permeation chromatography (GPC) using an Agilent HPLC 1100 system equipped with three mixed type E columns in series (length, 300 mm; i.d., 7.5 mm) and a refractive index detector was used to determine the molecular weight distributions of the PL feed and product oils. Tetrahydrofuran (THF) was used as the mobile phase, and standard polystyrene samples with known MW distributions were used for calibration. A 10 mg/mL PL feed or product oil sample in THF was prepared by dissolving 50 mg of PLs/product oil sample in 5 mL of THF. Subsequently, 2 drops of toluene were added as a flow marker and the sample was filtered using a 0.2 μ m syringe filter before injection.

2.2.3.5. Thermal Stability. Thermal stability is used to gain information on the 'charring tendency' of the liquids, being one of the most important properties for PLs and related product oils. A TGA 7 (Perkin-Elmer) was used for this purpose. The samples were heated from room temperature to 900 °C under a nitrogen atmosphere with a heating rate of 10 °C/min. The TG residue was defined as the amount of residue at 900 °C.

2.2.3.6. Two-Dimensional Gas Chromatography (GC \times GC-FID). The quantification of volatile components in the PL feed and product oils was carried out on a Trace GC \times GC-FID from Interscience equipped with a cryogenic trap system, an FID detector, and two columns (RTX-1701 capillary column (30 m \times 0.25 mm i.d. and a 0.25 μ m film-thickness) connected to a Rxi-5Sil MS column (120 cm \times 0.15 mm i.d. and a 0.15 μ m film thickness). A dual jet modulator using carbon dioxide was used to trap the samples. He was used as the carrier gas at a flow of 0.6 mL min^{-1} . The injector temperature was set at 250 °C. The following oven temperature profile was used: 40 °C for 5 min, heating to 250 °C at a rate of 3 °C min^{-1} . The FID temperature was set at 250 °C. The pressure was 70 kPa (40 °C), and the modulation time was 6 s. The samples were diluted with tetrahydrofuran (THF) with di-*n*-butyl ether (DBE, 500 ppm) as an internal standard and filtered using a syringe filter with a pore size of 0.2 μ m before injection.

2.2.3.7. 1H -NMR. 1H spectra were recorded on a 400-MHz NMR spectrometer (AMS400, Varian). The samples were dissolved in $DMSO-d_6$ and dried using $MgSO_4$. A total of 64 repetitions and a 1 s relaxation delay were applied.

2.2.3.8. Heteronuclear Single Quantum Coherence (HSQC) NMR. NMR spectra were acquired at 25 °C using an Agilent 400 MHz spectrometer. Approximately 0.5 g of sample was dissolved in 0.5 g of $DMSO-d_6$. 1H - ^{13}C HSQC spectra were acquired using a standard pulse sequence with a spectral width of 160 ppm, 16 scans, and 256 increments in the F1 dimension. The data were processed using the MestReNova software.

3. RESULTS AND DISCUSSION

3.1. Visual Appearance of Typical Products and Product Distribution. The mild and deep hydrotreatments of PLs were carried out in a batch setup with an overhead stirrer. Mild catalytic hydrotreatment experiments were performed at 200 °C and 140 bar initial pressure, deep hydrotreatment at 350 °C, and 100 bar initial pressure. A batch time of 4 h was applied for all experiments. The mild hydrotreatment reactions were carried out using the full set of Ni and Cu-based catalysts (3 in total, see Table 2), whereas the deep hydrotreatments were only performed with the Ni-based catalysts (2 in total). The latter choice was rationalized by considering the relatively low performance of the Cu-based catalysts in the mild hydrotreatment step (*vide infra*).

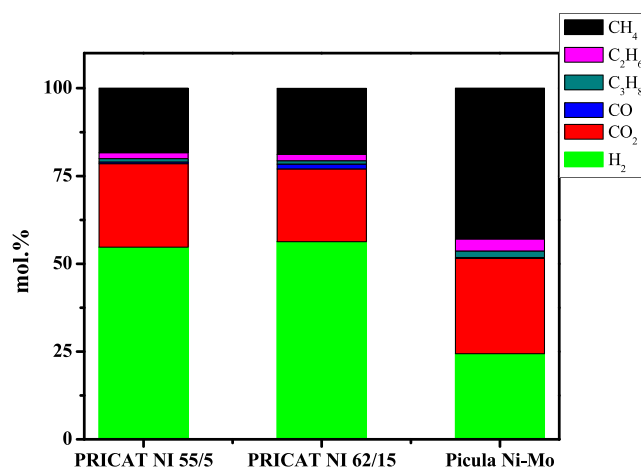
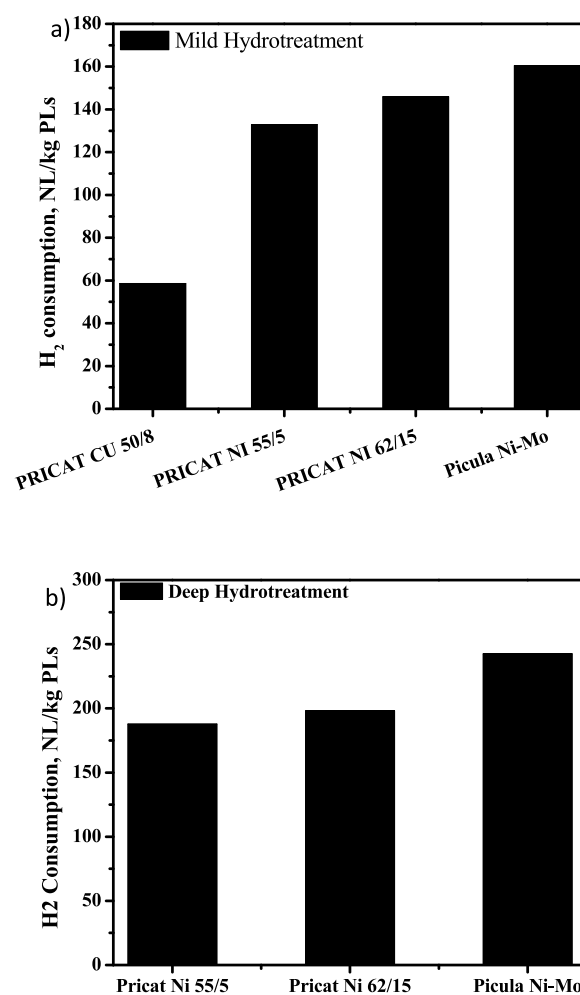
Table 4. Product Distribution Using PRICAT NI/CU and Reference Picula Ni-Mo at 200 °C (Mild Hydrotreatment)

cataylists	PRICAT CU 50/8	PRICAT NI 55/5	PRICAT NI 62/15	Picula Ni-Mo
organic phase (wt % on PLs intake)	50.7	50.4	49.3	44.7
total organics (after work-up of the aqueous phase, wt % on PLs intake)	62.3	65.3	67.3	82.9
water content of oil phase, wt %	8.8	9.6	11.5	16.6
total organics (after work-up of the aqueous phase, wt % on PLs intake, dry basis)	56.8	59.0	59.6	69.1
aqueous phase (wt % on PLs intake)	33.2	39.7	41.1	50.8
solid (wt % on PLs intake)	6.7	4.5	3.9	0.5
gas (wt % on PLs intake)	1.5	0.9	0.8	0.5
carbon dioxide (mol %)	2.5	1.7	1.5	0.6
hydrogen (mol %)	97.5	97.4	97.6	97.9
methane (mol %)	0.0	0.9	0.9	1.5
total mass balance, %	92.1	95.5	95.1	96.5
hydrogen consumption, NL/kg PLs	59	133	146	160
elemental composition of oil phase (dry basis)				
C	59.05	62.30	59.91	60.29
H	7.38	8.28	8.31	8.39
O	33.57	29.42	31.78	31.33
H/C molar, dry	1.50	1.59	1.66	1.67
O/C molar, dry	0.43	0.35	0.40	0.39

Table 5. Product Distribution Using PRICAT NI and Reference Picula Ni-Mo at 350 °C (Deep Hydrotreatment)

cataylists	PRICAT NI 55/5	PRICAT NI 62/15	Picula Ni-Mo
top/bottom oil	bottom	bottom	top
organic phase (wt % on PLs intake)	37.5	41.1	35.7
water content of oil phase, wt %	5.6	5.2	5.4
organic phase (wt % on PLs intake, dry basis)	35.4	39.0	33.8
aqueous phase (wt % on PLs intake)	37.8	36.7	34.5
solid (wt % on PLs intake)	6.1	6.6	0
gas (wt % on PLs intake)	9.3	7.6	14.5
carbon dioxide (mol %)	23.8	20.8	27.1
ethane (mol %)	1.7	1.8	3.4
propane (mol %)	1.0	1.0	1.9
hydrogen (mol %)	54.8	56.3	24.4
methane (mol %)	18.4	18.9	42.9
carbon monoxide (mol %)	0.5	1.4	0.2
total mass balance, %	90.7	92.0	84.7
hydrogen consumption, NL/kg PLs	188	198	243
elemental composition of oil phase (dry basis)			
C	77.21	76.27	79.14
H	9.10	8.74	8.83
O	13.70	14.99	12.03
H/C molar, dry	1.41	1.38	1.34
O/C molar, dry	0.13	0.15	0.11

After hydrotreatment, a gas phase, two liquids phases (heavier organic and lighter aqueous), and a solid residue (including catalyst and char) were obtained. The visual

**Figure 1.** Gas-phase composition from catalytic hydrotreatment of PLs under deep hydrotreatment conditions (350 °C, 100 bar H₂, 4 h).**Figure 2.** Hydrogen consumption from catalytic hydrotreatment of PLs under mild (a, 200 °C, 140 bar H₂, 4 h) and deep hydrotreatment conditions (b, 350 °C, 100 bar H₂, 4 h).

appearance of the liquid phase after catalytic hydrotreatment using a typical PRICAT NI catalyst is given in Figure S2.

Overall, mass balance closures for all experiments were > 90%, the only exception being the Picula Ni-Mo in deep hydrotreatment conditions (85%). For the mild hydrotreatment, the organic phase yield was between 45 and 51 wt % on

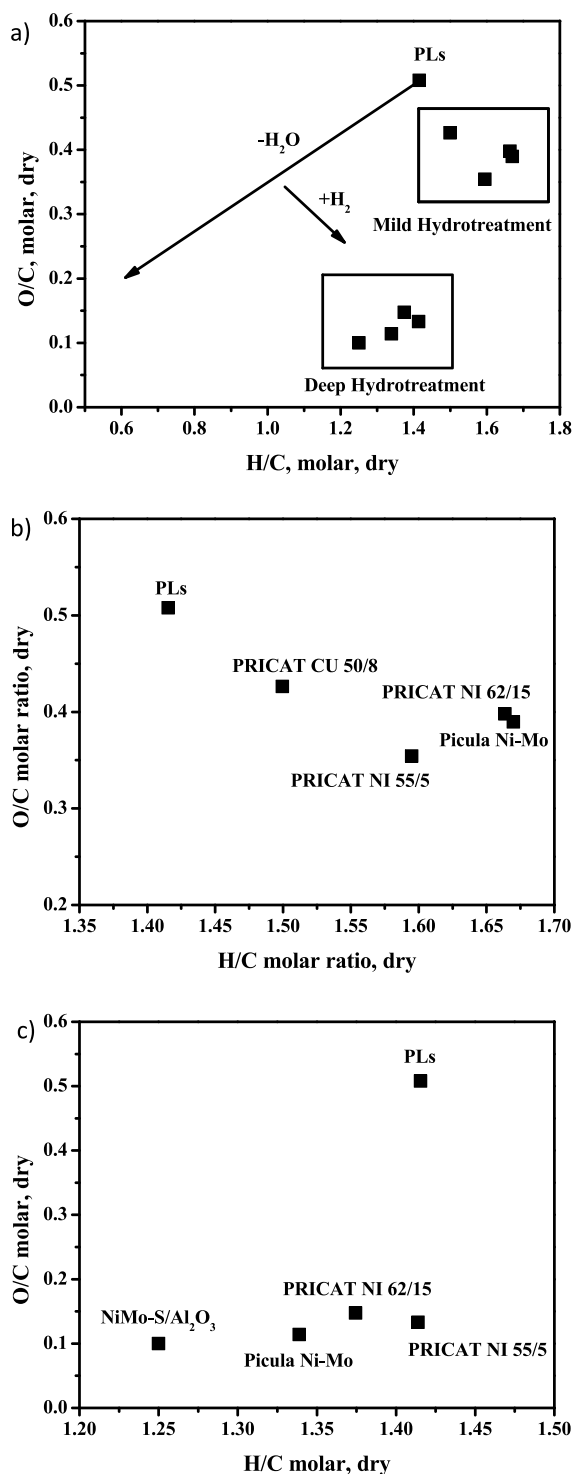


Figure 3. Van Krevelen plot for the PL feed and product oils after catalytic hydrotreatment reaction using PRICAT catalysts and Picula Ni-Mo (a: overview, b: mild hydrotreatment: 140 bar H_2 , 200 °C, 4 h, c: deep hydrotreatment: 100 bar H_2 , 350 °C, 4 h, data for sulfided NiMo-S/ Al_2O_3 from ref 34).

PLs intake (Table 4), whereas the aqueous phase yield was in the range of 33 to 51 wt %. A considerable amount of carbon is present in the aqueous phase. For a proper comparison, the water was removed from the aqueous phase by evaporation (120 °C, atmospheric pressure) and the remaining organics were collected and added to the organic bottom oil phase for

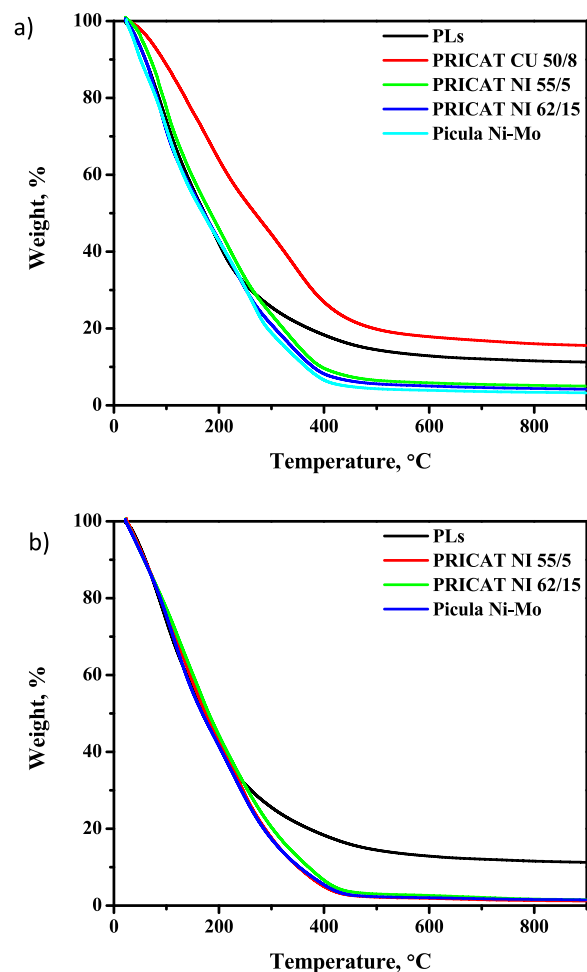


Figure 4. Thermogravimetric analysis (TGA) of the PL feed and product oils using all PRICAT CU/Ni and reference Picula Ni-Mo (a: mild hydrotreatment, 140 bar H_2 , 200 °C, 4 h; b: deep hydrotreatment, 100 bar H_2 , 350 °C, 4 h).

Table 6. TG Residue of the PL Feed and Product Oils Using All PRICAT CU/Ni and Reference Picula Ni-Mo by Thermogravimetric Analysis (TGA)

	conditions	TG residue, wt %
PL feed		11.3
PRICAT CU 50/8	140 bar H_2 , 200 °C	15.6
PRICAT NI 55/5	140 bar H_2 , 200 °C	5.0
PRICAT NI 62/15	140 bar H_2 , 200 °C	4.2
Picula Ni-Mo	140 bar H_2 , 200 °C	3.2
PRICAT NI 55/5	100 bar H_2 , 350 °C	1.2
PRICAT NI 62/15	100 bar H_2 , 350 °C	1.5
Picula Ni-Mo	100 bar H_2 , 350 °C	1.5

analysis and mass balance calculations. After this workup, the organic product yield ranged between 57 and 69 wt % (dry basis). A considerably higher yield of 69 wt % (dry basis) was found for the Picula Ni-Mo catalyst (Table 4). This difference is mainly due to a considerably higher amount (3.9 to 6.7 wt %) of solids formed when using the PRICAT NI and CU catalysts, compared to the 0.5 wt % measured for the Picula Ni-Mo catalyst and 0.7 wt % for Picula Ni-Cu.¹⁷ Among the PRICAT catalysts, the Cu-based ones showed a higher solid yield than any of the Ni catalysts, indicating a higher level of

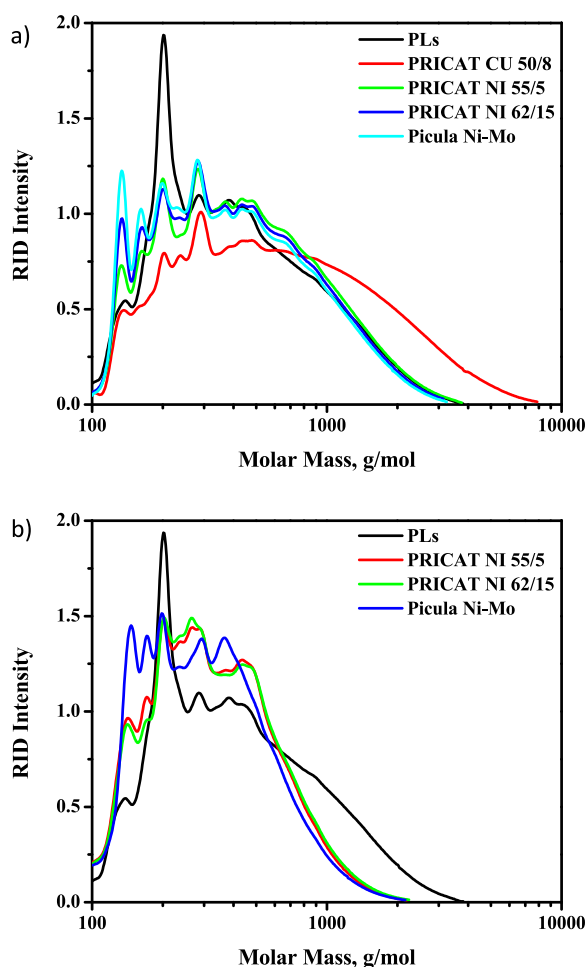


Figure 5. Molecular weight distribution of the PL feed and product oils using the PRICAT and reference Picula Ni-Mo catalysts by GPC (a: mild hydrotreatment, 140 bar H₂, 200 °C, 4 h; b: deep hydrotreatment, 100 bar H₂, 350 °C, 4 h).

repolymerization of reactive organics when using Cu-based PRICAT catalysts.

For the deep hydrotreatments using the Ni-based PRICAT catalysts, the oil phase yields ranged from 34 to 39 wt % (dry basis), which is slightly higher than the oil yields for the Picula Ni-Mo catalyst (Table 5). The solid yields for all the Ni-based PRICAT catalysts are rather similar and in the range of 6.1 to 6.6 wt %. These are comparable with values reported for noble metal catalysts, e.g., Ru/C (3 wt %),³⁰ mono- and bimetallic (Pt, Pd, Rh) catalysts (2 to 7 wt %)²¹ and the bimetallic Ni-Cu/ δ -Al₂O₃ (1 to 5 wt %),²² but higher than the 0.1–0.7 wt % reported for Picula-type catalysts.²⁸

Thus, we can conclude that particularly the Ni-based PRICAT catalysts are suitable catalysts for mild and deep hydrotreatment and that the Cu-based ones have less potential. When considering char yields, it appears that the PRICAT catalysts perform worse than the Picula Ni-Mo benchmark catalyst.

3.2. Gas-Phase Composition and Hydrogen Consumption. In mild hydrotreatment conditions, the main gas-phase components for the PRICAT catalysts and the reference Picula Ni-Mo catalyst are CO₂ and CH₄, in amounts less than 2 wt % (Table 4). CO₂ is the main product of the Cu-based catalysts, likely from decarboxylation of the carboxylic acids, especially from the thermal/catalytic decom-

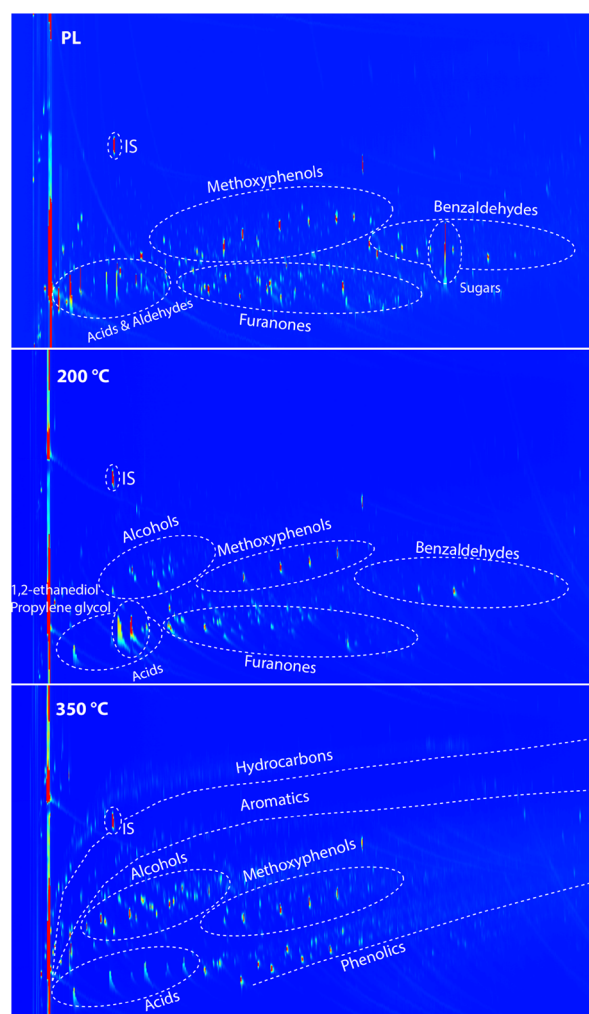


Figure 6. GC \times GC spectrum of PL feed and product oils obtained using PRICAT NI 62/15 (IS: internal standard, di-*n*-butyl ether, a: PL feed, b: mild hydrotreatment, 140 bar H₂, 200 °C, 4 h, c: deep hydrotreatment, 100 bar H₂, 350 °C, 4 h).

position of formic acid.³¹ When using the Ni-based catalysts, also methane is formed, for example, by methanation of CO₂ over Ni or from small oxygenates by Ni-catalyzed aqueous phase reforming reactions³² or by demethoxylation of lignin fragments.³³

The composition of the gas phase for deep hydrotreatment (Table 5) is provided in Figure 1. The gas-phase composition in deep hydrotreatment conditions differs considerably from that in mild conditions. The amount of hydrogen is reduced significantly due to hydrogen-consuming reactions. In addition, more methane is formed for the Ni-based catalysts, indicative of higher rates of methanation reactions. This is an undesired, hydrogen-consuming reaction, and in this respect, the PRICAT catalysts outperform the benchmark Picula catalyst, which shows a by far higher methanation reactivity (Figure 1 and Figure S3).

Recording of the initial and final pressure in combination with the gas-phase composition after reaction allows calculation of the hydrogen consumption for the individual hydrotreatment experiments. This is an interesting number to compare the performance of the catalysts. A high hydrogen consumption indicates a high hydrogenation activity of the catalysts, which is desired for mild hydrotreatment, while a low

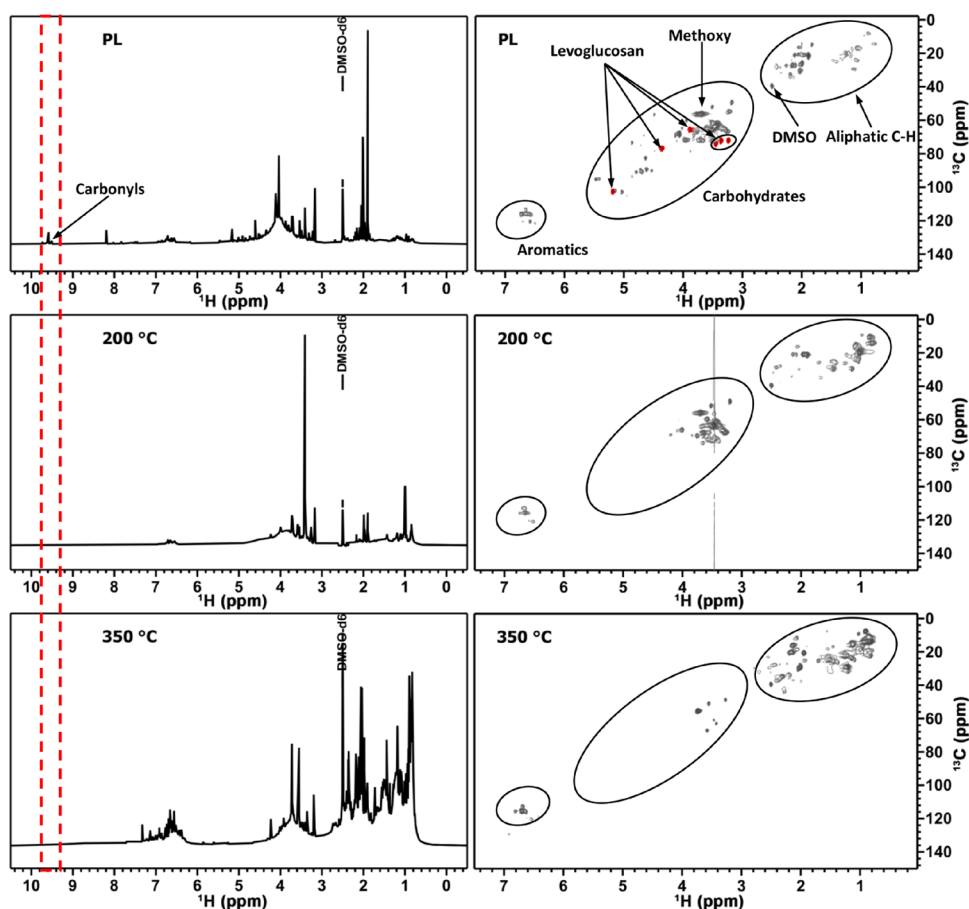
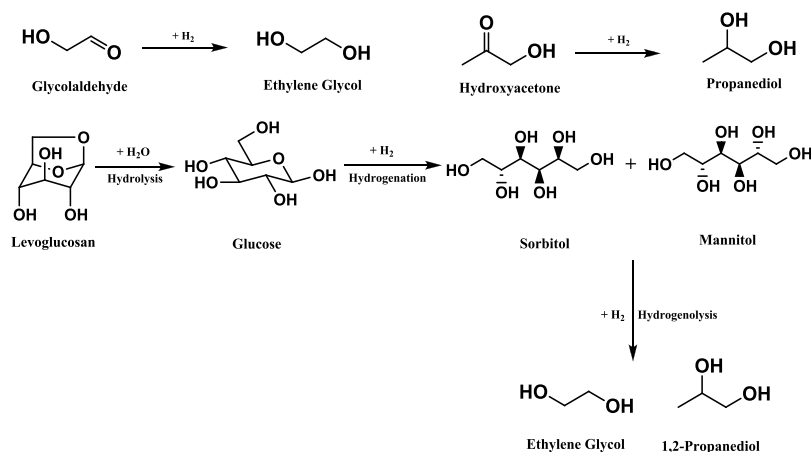


Figure 7. ^1H -NMR, HSQC spectrum of PL feed, and product oils obtained using PRICAT NI 62/15 (a: PL feed, b: mild conditions, 140 bar H_2 , 200 $^\circ\text{C}$, 4 h, c: deep hydrotreatment conditions, 100 bar H_2 , 350 $^\circ\text{C}$, 4 h).

Scheme 1. Hydrogenation of Two Representative Carbonyl-Containing Molecules and Levoglucosan to Alcohols



hydrogen consumption (limited methane formation) in combination with a high hydrodeoxygenation activity for oxygenates is desired for deep hydrotreatment. Hydrogen consumption data are summarized in Figure 2.

Hydrogen consumption levels were between 60 and 160 NL/kg feed for the tested catalysts in mild hydrotreatment conditions (Figure 2a). The highest numbers were found for the Ni-based PRICAT catalysts and particularly for PRICAT NI 62/15, whereas the one for Cu is by far lower. In mild hydrotreatment conditions, hydrogen is typically consumed for hydrogenation reactions and not for hydrodeoxygenation.^{27,29}

As such, the hydrogenation activity is the highest for the Ni-based catalysts, which is also confirmed by the elemental composition of the product oils, showing a high H/C ratio (*vide infra*). Among all Ni catalysts, PRICAT NI 62/15 showed the best performance, with a comparable hydrogen consumption as found for the reference Picula Ni-Mo.

In deep hydrotreatment conditions, by far, higher hydrogen consumption levels are recorded (190–240 NL/kg feed, Figure 2b) than for mild hydrotreatment. However, in this case, the hydrogen consumption is not a good indicator for hydrogenation/hydrodeoxygenation activity of the catalysts as

a substantial amount of hydrogen is used for methane formation (Figure 1 and Figure S3).

3.3. Properties of Organic Phases. Not only the yield of the organic phases after hydrotreatment but also the product properties of the organic phases are of utmost importance. One of the main purposes of catalytic hydrotreatment of PLs is to reduce the O/C ratio (oxygen removal), increase the H/C ratio, and improve the thermal stability of the product oil. As such, the elemental composition of all organic phases was determined, and the thermal stability was assessed using thermogravimetric analysis (TGA).

3.3.1. Elemental Composition. The elemental composition of the organic phases is provided in the form of van Krevelen plots with the H/C molar ratio on the X axis and the O/C molar ratio on the Y axis (both ratios calculated on a dry basis, Figure 3).

An overview with data for the PL feed, oil products from both mild and deep hydrotreatment conditions, and the theoretical dehydration line is provided in Figure 3a. Clear differences in elemental composition are visible for the oils obtained by mild and deep hydrotreatment experiments. The oxygen content of the deep hydrotreated PLs is considerably lower than for the mild hydrotreated ones, leading to a lower O/C ratio for the deep hydrotreated liquids. Remarkably, the H/C ratios for the mild hydrotreated liquids are higher than for the deep hydrotreated ones. This is a typical trend for catalytic hydrotreatment of PLs, rationalized by considering different types of reactions occurring in the various stages of hydrotreatment. At mild hydrotreatment, mainly hydrogenation reactions occur involving among others aldehydes/ketones, leading to higher H/C values of the product oils. In more severe conditions, water eliminating reactions are dominant, leading to a reduction in the H/C ratio. For additional details, the reader is referred to ref 9.

The elemental data for the various oils obtained after the mild hydrotreatment are shown in Figure 3b. As pointed out before, hydrogenation reactions dominate in this stage and it is preferred to obtain products with a high H/C ratio. In this respect, the PRICAT CU 50/8 performs worst and the lowest H/C ratio is obtained. The Ni-based PRICAT catalysts show higher H/C ratios than the feed, indicative of good hydrogenation activities. Among all the Ni-based catalysts, PRICAT NI 62/15 yielded the product oil with the highest H/C ratio, which is almost comparable with the benchmarked Picula Ni-Mo.

The data for the deep hydrotreatment of PLs are provided in Figure 3c. The O/C ratio for all product oils is in a very narrow bandwidth, whereas the H/C ratio differs considerably. The PRICAT NI 55/5 yielded a product oil with the highest H/C ratio. In general, the PRICAT catalysts gave product oils with higher H/C ratios compared to the reference Picula Ni-Mo. For comparison, the elemental data for a classical hydrodesulfurization Ni-Mo catalyst is also provided and showed a by far lower H/C ratio.³⁴

3.3.2. Thermal Stability. The thermal stability of the product oils was determined using TGA. Of interest is the TG residue after heating the oils to 900 °C, which is an indication of the charring tendency of the product oil. Here, a low residue is preferred. The results are plotted in Figure 4, and the TG residues are summarized in Table 6.

Considerable differences in the TG residue are detected for the oils produced by the different catalysts. In mild hydrotreatment conditions, the PRICAT CU catalyst yielded

a higher TG residue (16 wt %) compared to oils from the Ni-based catalysts (3 to 5 wt %, Table 6), and this likely is due to a lower hydrogenation activity of such Cu-based catalysts compared to the Ni ones (*vide supra*, e.g., Figure 3). On a molecular level, it is assumed that reactive aldehydes/ketones that are prone to repolymerization and charring at elevated temperatures are converted to less reactive alcohols. As such, a higher hydrogenation activity leads to products with higher stability. The best catalyst when considering a low TG residue is again the PRICAT NI 62/15 catalyst, which gave an oil with a comparable TG residue as the Picula benchmark. In deep hydrotreatment conditions, all product oils showed similar TGA curves (see Figure 4b) and no clear differences in TG residues were observed (1–2 wt %, Table 6).

When comparing mild and deep hydrotreatment, it is evident that deep hydrotreatments produce an oil with a by far lower TG residue (<1.5 wt %) than when using mild hydrotreatment conditions (>3.2 wt %). This indicates that deep hydrotreatment is essential to obtain a product with a low charring tendency, which is desired for many applications.

Based on the properties of the oil phase (elemental composition and TG results), it is concluded that PRICAT NI 62/15 shows the best performance for the mild catalytic hydrotreatment of PLs. Its performance is comparable to the reference Picula catalyst. When PRICAT catalysts are applied for a deep hydrotreatment, PRICAT NI 55/5 seems preferred, producing an oil with the lowest TG residue and highest H/C ratio.

3.4. Catalyst Recycle Experiments. Catalyst reusability was tested by carrying out catalyst recycling experiments in the batch setup using the PRICAT NI 62/15 at 200 °C. The results indicate that hydrogen consumption was reduced to about 10% after 3 successive runs (Figure S1). This implies that some deactivation occurred, for instance due to the char formation on the catalyst (Table S1).

3.5. Molecular Transformation. To gain insights into the molecular transformations occurring during mild and deep hydrotreatment, the product oils and PL feed were analyzed using GPC, GC × GC-FID, and 1D/2D-NMR, and the results are shown in Figures 5–7.

3.5.1. Molecular Weight Distributions. The molecular weight distributions of the PL feed and the product oils for both the mild and deep hydrotreatment are shown in Figure 5.

For the PL feed, a broad molecular weight distribution is observed, with a tail extending to a molar mass of at least 4000 g/mol. In addition, a clear sharp peak at lower molecular weight is observed. This peak likely arises from levoglucosan (LG), a major sugar-derived compound that is known to be present in PLs in amounts up to 10 wt %.³⁵ Its presence was confirmed by spiking a PL with pure LG.

After a mild catalytic hydrotreatment, a clear increase in the long tail part of the distribution is observed for the PRICAT CU catalysts. Actually, the tail is extended to values beyond that of the PL feed, indicating severe repolymerization of thermally labile molecules during the mild hydrotreatment with these catalysts, e.g., carbonyl and sugar molecules. This is consistent with the amounts of char formed and the TG residues (*vide supra*). For the Ni-based PRICAT catalyst and the benchmark Picula Ni-Mo, limited repolymerization occurred in mild hydrotreatment conditions, and the M_w distribution is similar to that of the PL feed. The peak associated with levoglucosan decreased while new peaks between 100 and 200 g/mol are formed, speculatively by

hydrogenolysis reactions of levoglucosan to lower molecular weight compounds (e.g., ethylene glycol,³⁶ Scheme 1).

In deep hydrotreatment conditions, the molecular weight distributions of the oil products are shifted to lower molecular weights compared to the PL feed. This is particularly evident when considering the higher molecular weight tail (Figure 5). This reduction in molecular weight is ascribed to cracking/hydrocracking reactions. The PRICAT NI and the benchmark Picula Ni-Mo catalysts yielded product oils with very similar molecular weight distributions.

3.5.2. GC × GC-FID. The various organic components present in the PL feed and product oils were evaluated by GC × GC (Figure 6) for experiments with PRICAT NI 62/15. Though very informative, it only provides information on the low-molecular-weight, GC-detectable components in the samples. In a GC × GC plot, various regions can be observed, which are representative of particular organic component groups (e.g., phenolics, acids, aldehydes, aromatics, aliphatic hydrocarbons, etc.); details about identification and classification of such components can be found in refs 37 and 38. The PL feed contains sugar molecules (mainly LG) and sugar-derived molecules like acids, aldehydes, and furanones, besides aromatic compounds like methoxyphenols and benzaldehydes from the decomposition of lignin fractions.

At mild hydrotreatment, aldehydes like glycolaldehyde and ketones (hydroxyacetone) are readily converted to the corresponding diols as clear ethylene glycol and propylene glycol peaks are observed, see Scheme 1 for details.^{36,39,40}

After deep hydrotreatment, the amounts of phenolics increase considerably and aromatics and saturated hydrocarbons are also formed. The phenolics likely arise from the hydrocracking of the pyrolytic lignin fraction in PLs,⁴¹ which are subsequently hydrodeoxygenated to aromatics and hydrocarbons. Considerable amounts of carboxylic acids are still present in the product oils, confirming that these are rather inert upon hydrotreatment with Ni-based catalysts.¹⁷

3.5.3. 1D/2D-NMR. ¹H-NMR and HSQC spectra of the PL feed and the product oil using the PRICAT NI 62/15 catalyst are shown in Figure 7. Quantification of organic functional groups based on integration of specific regions is given in Table S2. NMR techniques, in contrast to GC, provide information on the chemical composition of not only the monomers but also the oligomers in the products. Classification of the various organic groups based on NMR shifts was done using the Ingram method.⁴² The carbonyl compounds, especially ketones and aldehydes ($\delta_{\text{H}} = 8$ to 10 ppm), are readily converted upon hydrotreatment (¹H-NMR). Carbohydrates like LG ($\delta_{\text{C}} = 84$ to 110 ppm) are fully converted under mild hydrotreatment. The reactivity of carbohydrates is also confirmed by the integration results of ¹H-NMR as shown in Table S2 ($\delta_{\text{H}} = 6.4$ to 4.2 ppm). The peak area decreased from 21% to 16% after mild hydrotreatment and 4% after and deep hydrotreatment. In line with the GC data, the peak area of the aliphatic region ($\delta_{\text{H}} = 1.6$ to 0.3 ppm) increased from 10% to 20% (for mild hydrotreatment) and to 38% (for deep hydrotreatment). The -OMe groups from substituted phenolics in the pyrolytic lignin fraction of PLs are relatively stable under mild hydrogenation conditions and are only partly converted under deep hydrotreatment conditions.

4. CONCLUSIONS

In this study, 3 commercially available PRICAT catalysts have been explored for the mild hydrotreatment of PLs, and the

most active ones were also tested for deep hydrotreatment. The results were compared with the reference Picula Ni-Mo catalyst. Under mild hydrotreatment conditions, the PRICAT NI catalysts outperform the Cu one and yield a product oil with the highest H/C ratio and lowest TG residue. The performance of the Ni-based PRICAT catalysts is comparable with the benchmark Picula Ni-Mo catalyst. The more active Ni-based catalysts were further tested under deep hydrotreatment conditions. High product oil yields with the highest H/C ratio were obtained using PRICAT NI 55/5. This catalyst outperforms the benchmark Picula catalyst when considering hydrogen consumption (limited methanation activity), which is preferred when considering the techno-economic viability of the process, though the amount of char formed is considerably higher.

Based on the above findings, we can conclude that particularly, the PRICAT NI-based catalysts have the potential for the mild and deep hydrotreatment of PLs. However, slight deactivation of the PRICAT NI-based catalyst during catalytic hydrotreatment of PLs under mild conditions was observed after 3 successive runs. Further research activities should focus on catalyst stability, preferably in continuous setups at extended runtimes. These are in progress and will be reported in due course.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c02485>.

Schematic of batch setup, figures of hydrogen consumption for the catalyst recycling experiments, visual appearance of typical products after catalytic hydrotreatment and hydrogen consumption from catalytic hydrotreatment of PLs under mild and deep hydrotreatment conditions, tables of product distribution for the catalyst recycling experiments and the integrated ¹H-NMR data for PLs and product oils (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Hero Jan Heeres – Department of Chemical Engineering, Engineering and Technology Institute Groningen ENTEG, University of Groningen, 9747 Groningen, AG, the Netherlands; orcid.org/0000-0002-1249-543X; Phone: +31(0)50 363 4174; Email: h.j.heeres@rug.nl; Fax: +31(0)50 363 4479

Authors

Wang Yin – Fujian Universities Engineering Research Center of Reactive Distillation Technology, College of Chemical Engineering, Fuzhou University, Fuzhou 350116 Fujian, China; Department of Chemical Engineering, Engineering and Technology Institute Groningen ENTEG, University of Groningen, 9747 Groningen, AG, the Netherlands

Zhiwen Wang – Department of Chemical Engineering, Engineering and Technology Institute Groningen ENTEG, University of Groningen, 9747 Groningen, AG, the Netherlands

Huaizhou Yang – Department of Chemical Engineering, Engineering and Technology Institute Groningen ENTEG, University of Groningen, 9747 Groningen, AG, the Netherlands; orcid.org/0000-0001-7489-0948

Robbie H. Venderbosch – Biomass Technology Group BV,
7545 Enschede, PN, the Netherlands

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.energyfuels.2c02485>

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew. Chem., Int. Ed.* **2007**, *46*, 7164–7183.
- (2) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.
- (3) Liu, C.; Wang, H.; Karim, A. M.; Sun, J.; Wang, Y. Catalytic fast pyrolysis of lignocellulosic biomass. *Chem. Soc. Rev.* **2014**, *43*, 7594–7623.
- (4) Chen, X.; Che, Q.; Li, S.; Liu, Z.; Yang, H.; Chen, Y.; Wang, X.; Shao, J.; Chen, H. Recent developments in lignocellulosic biomass catalytic fast pyrolysis: Strategies for the optimization of bio-oil quality and yield. *Fuel Process. Technol.* **2019**, *196*, No. 106180.
- (5) Oasmaa, A.; Lehto, J.; Solantausta, Y.; Kallio, S. Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading. *Energy Fuels* **2021**, *35*, 5683–5695.
- (6) Venderbosch, R. H.; Prins, W. Fast pyrolysis technology development. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 178–208.
- (7) BTG-Bioliquids, <https://www.btg-btl.com/en>, (accessed 2021).
- (8) Elliott, D. C.; Oasmaa, A.; Preto, F.; Meier, D.; Bridgwater, A. V. Results of the IEA Round Robin on Viscosity and Stability of Fast Pyrolysis Bio-oils. *Energy Fuels* **2012**, *26*, 3769–3776.
- (9) Venderbosch, R. H.; Ardiyanti, A. R.; Wildschut, J.; Oasmaa, A.; Heeres, H. J. Stabilization of biomass-derived pyrolysis oils. *Journal of Chemical Technology & Biotechnology* **2010**, *85*, 674–686.
- (10) de Miguel Mercader, F.; Groeneveld, M. J.; Kersten, S. R. A.; Geantet, C.; Toussaint, G.; Way, N. W. J.; Schaverien, C. J.; Hogendoorn, K. J. A. Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. *Energy Environ. Sci.* **2011**, *4*, 985–997.
- (11) Eschenbacher, A.; Myrstad, T.; Bech, N.; Duus, J. Ø.; Li, C.; Jensen, P. A.; Henriksen, U. B.; Ahrenfeldt, J.; Mentzel, U. V.; Jensen, A. D. Co-processing of wood and wheat straw derived pyrolysis oils with FCC feed—Product distribution and effect of deoxygenation. *Fuel* **2020**, *260*, No. 116312.
- (12) Fogassy, G.; Thegarid, N.; Schuurman, Y.; Mirodatos, C. From biomass to bio-gasoline by FCC co-processing: effect of feed composition and catalyst structure on product quality. *Energy Environ. Sci.* **2011**, *4*, 5068–5076.
- (13) Fogassy, G.; Thegarid, N.; Schuurman, Y.; Mirodatos, C. The fate of bio-carbon in FCC co-processing products. *Green Chem.* **2012**, *14*, 1367–1371.
- (14) Fogassy, G.; Thegarid, N.; Toussaint, G.; van Veen, A. C.; Schuurman, Y.; Mirodatos, C. Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. *Appl. Catal., B* **2010**, *96*, 476–485.
- (15) Gueudré, L.; Chapon, F.; Mirodatos, C.; Schuurman, Y.; Venderbosch, R.; Jordan, E.; Wellach, S.; Gutierrez, R. M. Optimizing the bio-gasoline quantity and quality in fluid catalytic cracking co-refining. *Fuel* **2017**, *192*, 60–70.
- (16) Wang, C.; Venderbosch, R.; Fang, Y. Co-processing of crude and hydrotreated pyrolysis liquids and VGO in a pilot scale FCC riser setup. *Fuel Process. Technol.* **2018**, *181*, 157–165.
- (17) Yin, W.; Kloekhorst, A.; Venderbosch, R. H.; Bykova, M. V.; Khromova, S. A.; Yakovlev, V. A.; Heeres, H. J. Catalytic hydrotreatment of fast pyrolysis liquids in batch and continuous set-ups using a bimetallic Ni–Cu catalyst with a high metal content. *Catal. Sci. Technol.* **2016**, *6*, 5899–5915.
- (18) Zhang, M.; Hu, Y.; Wang, H.; Li, H.; Han, X.; Zeng, Y.; Xu, C. C. A review of bio-oil upgrading by catalytic hydrotreatment: Advances, challenges, and prospects. *Mol. Catal.* **2021**, *504*, No. 111438.
- (19) Elliott, D. C.; Baker, E. G.; Piskorz, J.; Scott, D. S.; Solantausta, Y. Production of liquid hydrocarbon fuels from peat. *Energy Fuels* **1988**, *2*, 234–235.
- (20) Elliott, D. C.; Oasmaa, A. Catalytic hydrotreating of black liquor oils. *Energy Fuels* **1991**, *5*, 102–109.
- (21) Ardiyanti, A. R.; Gutierrez, A.; Honkela, M. L.; Krause, A. O. I.; Heeres, H. J. Hydrotreatment of wood-based pyrolysis oil using zirconia-supported mono- and bimetallic (Pt, Pd, Rh) catalysts. *Appl. Catal., A* **2011**, *407*, 56–66.
- (22) Ardiyanti, A. R.; Khromova, S. A.; Venderbosch, R. H.; Yakovlev, V. A.; Heeres, H. J. Catalytic hydrotreatment of fast-pyrolysis oil using non-sulfided bimetallic Ni–Cu catalysts on a δ -Al₂O₃ support. *Appl. Catal., B* **2012**, *117–118*, 105–117.
- (23) Ardiyanti, A. R.; Khromova, S. A.; Venderbosch, R. H.; Yakovlev, V. A.; Melián-Cabrera, I. V.; Heeres, H. J. Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni–Cu catalysts on various supports. *Appl. Catal., A* **2012**, *449*, 121–130.
- (24) Ardiyanti, A.R., Hydrotreatment of fast pyrolysis oil: catalyst development and process-product relations. PhD Thesis, University of Groningen, 2013.
- (25) Yin, W., Catalytic hydrotreatment of pyrolysis liquids and fractions: Catalyst Development and Process Studies. PhD Thesis, University of Groningen, 2017.
- (26) Ardiyanti, A. R.; Venderbosch, R. H.; Yin, W.; Heeres, H. J. Catalytic Hydrotreatment of Fast Pyrolysis Oils Using Supported Metal Catalysts. *Catalytic Hydrogenation for Biomass Valorization* **2014**, 151–173.
- (27) Yin, W.; Venderbosch, R. H.; Alekseeva, M. V.; Figueirêdo, M. B.; Heeres, H.; Khromova, S. A.; Yakovlev, V. A.; Cannilla, C.; Bonura, G.; Frusteri, F.; Heeres, H. J. Hydrotreatment of the carbohydrate-rich fraction of pyrolysis liquids using bimetallic Ni based catalyst: Catalyst activity and product property relations. *Fuel Process. Technol.* **2018**, *169*, 258–268.
- (28) Yin, W.; Venderbosch, R. H.; He, S.; Bykova, M. V.; Khromova, S. A.; Yakovlev, V. A.; Heeres, H. J. Mono-, bi-, and tri-metallic Ni-based catalysts for the catalytic hydrotreatment of pyrolysis liquids. *Biomass Convers. Biorefin.* **2017**, *7*, 361–376.
- (29) Yin, W.; Gu, H.; Figueirêdo, M. B.; Xia, S.; Venderbosch, R. H.; Heeres, H. J. Stabilization of fast pyrolysis liquids from biomass by catalytic hydrotreatment using Raney nickel “type” catalysts. *Fuel Process. Technol.* **2021**, *219*, No. 106846.
- (30) Wildschut, J.; Melián-Cabrera, I.; Heeres, H. J. Catalyst studies on the hydrotreatment of fast pyrolysis oil. *Appl. Catal., B* **2010**, *99*, 298–306.
- (31) O'Neill, B. J.; Gürbüz, E. I.; Dumesic, J. A. Reaction kinetics studies of the conversions of formic acid and butyl formate over

carbon-supported palladium in the liquid phase. *J. Catal.* **2012**, *290*, 193–201.

(32) Huber, G. W.; Cortright, R. D.; Dumesic, J. A. Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angew. Chem.* **2004**, *43*, 1549–1551.

(33) Ma, R.; Cui, K.; Yang, L.; Ma, X.; Li, Y. Selective catalytic conversion of guaiacol to phenols over a molybdenum carbide catalyst. *Chem. Commun.* **2015**, *51*, 10299–10301.

(34) Wildschut, J.; Mahfud, F. H.; Venderbosch, R. H.; Heeres, H. J. Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts. *Ind. Eng. Chem. Res.* **2009**, *48*, 10324–10334.

(35) Bennett, N. M.; Helle, S. S.; Duff, S. J. Extraction and hydrolysis of levoglucosan from pyrolysis oil. *Bioresour. Technol.* **2009**, *100*, 6059–6063.

(36) Bindwal, A. B.; Vaidya, P. D. Kinetics of Aqueous-Phase Hydrogenation of Levoglucosan over Ru/C Catalyst. *Ind. Eng. Chem. Res.* **2013**, *52*, 17781–17789.

(37) Marsman, J. H.; Wildschut, J.; Evers, P.; de Koning, S.; Heeres, H. J. Identification and classification of components in flash pyrolysis oil and hydrodeoxygenated oils by two-dimensional gas chromatography and time-of-flight mass spectrometry. *J. Chromatogr. A* **2008**, *1188*, 17–25.

(38) Marsman, J. H.; Wildschut, J.; Mahfud, F.; Heeres, H. J. Identification of components in fast pyrolysis oil and upgraded products by comprehensive two-dimensional gas chromatography and flame ionisation detection. *J. Chromatogr. A* **2007**, *1150*, 21–27.

(39) Mahfud, F. H.; Ghijsen, F.; Heeres, H. J. Hydrogenation of fast pyrolysis oil and model compounds in a two-phase aqueous organic system using homogeneous ruthenium catalysts. *J. Mol. Catal. A: Chem.* **2007**, *264*, 227–236.

(40) Yin, W.; Tang, Z.; Venderbosch, R. H.; Zhang, Z.; Cannilla, C.; Bonura, G.; Frusteri, F.; Heeres, H. J. A One-Step Synthesis of C6 Sugar Alcohols from Levoglucosan and Disaccharides Using a Ru/CMK-3 Catalyst. *ACS Catal.* **2016**, *6*, 4411–4422.

(41) Yin, W.; Alekseeva, M. V.; Venderbosch, R. H.; Yakovlev, V. A.; Heeres, H. J. Catalytic Hydrotreatment of the Pyrolytic Sugar and Pyrolytic Lignin Fractions of Fast Pyrolysis Liquids Using Nickel Based Catalysts. *Energies* **2020**, *13*, 285.

(42) Ingram, L.; Mohan, D.; Bricka, M.; Steele, P.; Strobel, D.; Crocker, D.; Mitchell, B.; Mohammad, J.; Cantrell, K.; Pittman, C. U. Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils. *Energy Fuels* **2008**, *22*, 614–625.

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