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Research article

Stabilization of fast pyrolysis liquids from biomass by catalytic hydrotreatment using Raney nickel “type” catalysts

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ABSTRACT

The catalytic hydrotreatment of fast pyrolysis liquids (PL) from lignocellulosic biomass is a promising technology to improve the properties of PL. Mild hydrotreatment (< 250 °C) using a suitable catalyst allows the production of stabilized oils that have for instance potential for co-processing in existing oil refinery units. Here, we report a catalyst screening study to stabilize PL by a mild hydrotreatment using five Raney nickel “type” catalysts (Ra-Ni), more specifically a benchmark Ra-Ni, two types of Fe/Cr promoted, and two Mo-promoted ones. Experiments were performed at relatively mild hydrotreatment conditions (200 °C, initial 140 bar H\textsubscript{2} pressure, 4 h) in a batch autoclave. Among all the Ra-Ni catalysts, the Mo promoted (A-7063) showed the highest hydro-(deoxy)genation activity, a lower extent of repolymerization (GPC), and lower charring tendency of the product oil (TGA) compared to the promoter-free and Fe/Cr promoted Ra-Ni catalysts. Analyses of the product oils showed that the oils contain a significant amount of phenolics (7.4-15.4 wt% on oil, GC x GC-FID). These findings indicate that commercially available Raney nickel “type” catalysts, and particularly the Mo promoted ones, are attractive to be used for the mild hydrotreatment of pyrolysis liquids.

1. Introduction

Negative effects related to the use of fossil-based coal, crude oil, and natural gas like global warming by greenhouse gas emissions boosted research on the development of sustainable alternatives. Lignocellulosic biomass is the only source of renewable carbon and as such is the likely alternative for fossil-based sources [1]. However, the use of lignocellulosic biomass also has some disadvantages. The collection is known to be costly due to its scattered availability (e.g. agricultural waste, grass and forestry residues) [2], it has a lower energy density than fossil feeds due to its oxygenated nature and it is highly diverse in structure and composition [3]. As a result, cost-effective technologies are required to liquify the biomass to reduce complexity, increase energy density, and reduce the cost of transportation.

Fast pyrolysis is a commercially available technology that liquefies solid biomass to pyrolysis liquids (pyrolysis oil, bio-oil) by rapid thermal treatment of solid biomass in the absence of air [4,5]. The highest liquid yields are obtained when using small biomass particles (<2 mm) and high heating rates (> 100 °C). A variety of reactors have been developed to satisfy these requirements, examples are the rotating cone reactor developed at the Biomass Technology Group, the Netherlands, the fluidized bed reactor concept at VTT Technical Research Centre of Finland, the twin-screw auger reactor in the Karlsruhe Institute of Technology and the ablative reactor concept in Aston University, etc. [4]. Typically, liquid yields are between 60 and 75 wt%, other products are char (15–25 wt% yield) and permanent gases (10–15 wt% yield) [6]. Generally, such PL have a more uniform composition and higher energy density compared to the solid biomass feed, thus are very suitable for transportation to a central site for further conversions/upgrading. Pyrolysis is maturing, and an example of a commercialized process is the rotating cone reactor concept developed by the Biomass Technology Group in the Netherlands [4].

In the fast pyrolysis process, the lignocellulosic biomass is depolymerized to form lower molecular weight oxygenated components, such as organic acids, alcohols, aldehydes, ketones, sugar monomers and oligomers, lignin monomers and oligomers [4,7]. The presence of...
reactive oxygenated components limits the direct use of PL as a conventional (transportation) fuel. For example, PL is acidic, with a pH of around 3 that can cause corrosion of metal piping and injectors in combustion engines [8]. The low molecular weight aldehydes and ketones have a negative effect on the storage stability of PL (increase in viscosity and molecular weight) [9,10], due to ongoing repolymerization reactions, especially at elevated temperatures. Any thermal treatment such as distillation leads to significant char formation [2,11].

Upgrading of PL, for example by a catalytic hydrotreatment of the reactive oxygenated groups, is desirable, and for many applications required [12–14]. During such a catalytic hydrotreatment, the PL is treated at elevated temperatures and hydrogen pressures in the presence of a suitable catalyst to yield less reactive functional groups [14–17]. Essentially three hydrotreatment regimes can be distinguished: a low-temperature hydrotreatment (<250 °C) to stabilize the oil by hydrogenation of reactive aldehydes and ketones, an intermediate temperature region (250–300 °C) in which the produced oxygenated materials are among others dehydrated, and a third high-temperature regime (>300 °C) where the components are hydrodeoxygenated and hydrocracked.

In each regime, various reactions can occur in parallel/consecutive modes. An overview is given in Scheme 1 and shows two main reaction pathways: thermal polymerization (top route) and catalytic hydro(deoxy)genation (bottom route). The undesired thermal polymerization leads to the formation of higher molecular weight fragments, which may ultimately lead to the formation of significant amounts of char and deactivation of the catalyst. The preferred pathway involves hydrogenation of thermally labile components like aldehydes, ketones, and carbohydrates in the PL feed to more thermally stable molecules (e.g. alcohols) by a mild hydrogenation/hydrodeoxygenation step (<250 °C). Subsequent deep hydrotreatment involves reactions such as a further hydro(deoxy)genation and hydrocracking under more severe conditions (>300 °C) on a time scale of hours, giving products with strongly reduced oxygen contents and higher H/C ratios.

Various types of catalysts have been reported for catalytic hydrotreatment, and examples are hydrodesulfurization catalysts (sulfided NiMo and CoMo on γ-Al₂O₃) [18–20], noble metal-based catalysts (Ru, Pd, Pt, Rh on various support, e.g. Al₂O₃, TiO₂, active carbon, ZrO₂) [16,21–23], non-sulfided Co-Mo-B and Ni-Mo-B catalysts [24–27] and transition metal (Ni, Fe, Mo, Co, W) phosphides supported on for instance SiO₂ [28].

In the last decade, cheaper Ni-based catalysts with Ni loadings as high as 50 wt% have been investigated. Our research group was involved in the development of a family of new catalysts, referred to as Picula catalysts. These catalysts show superior performance for PL hydrotreatment compared to a more well-known Ru/C catalyst [29–31]. Over these Picula catalysts, repolymerization of the reactive components in the PL is significantly suppressed and the catalysts show good stability for around 500 h runs in continuous set-ups. These Picula catalysts are Ni loaded catalysts with a high Ni content, rather similar to existing commercially available relatively cheap Raney Nickel catalysts. As such, it is of interest to compare the performance of such catalysts with that of a representative Picula catalyst.

Raney nickel “type” catalysts (here abbreviated by Ra-Ni) are well-known hydrogenation catalysts for among others the synthesis of sorbitol from glucose [32,33]. The catalysts are composed of mainly Ni and Al, have a large specific surface area and are typically prepared from a Ni-Al alloy by leaching using a base. Ra-Ni catalysts can be promoted by other metals such as Fe, Cr, and Mo to fine-tune catalyst performance. Hydrotreatment studies with Ra-Ni catalyst using representative model components for PL have been reported [34–36]. However, the use of Ra-Ni-type catalysts has not been reported for the catalytic hydrotreatment of PL, particularly in the absence of solvents. Besides, systematic studies using various promoted Ra-Ni catalysts are also absent.

In this study, a series of five commercially available (promoted) Ra-Ni catalysts were tested for the stabilization of PL by a mild hydrotreatment. These include a standard non-promoted catalyst, two Fe/Cr promoted catalysts and two Mo promoted catalysts. All catalysts were tested in a batch autoclave at relatively mild conditions (200 °C, 140 bar initial H₂ pressure) for 4 h. This temperature is typical for a mild hydrogenation/stabilization step for pyrolysis liquids [14–17]. Both the organic product oils and the starting PL feed were analyzed in detail by various techniques (elemental analysis, GPC, TGA, and GC × GC-FID). The hydrogen consumption and the product properties, especially the elemental H/C, Mw, and TGA residue were used to evaluate the performance of the catalysts. Also, the performance of the Ra-Ni catalysts is compared with that of a benchmark Picula catalyst.

2. Experimental section

2.1. Materials

PL from pine wood was supplied by the Biomass Technology Group (BTG, Enschede, the Netherlands) and relevant properties are given in Table 1.

Hydrogen, nitrogen, and helium were obtained from Linde and where all of analytical grade (> 99.99%). A reference gas containing H₂, CH₄, ethylene, ethane, propylene, propane, CO, and CO₂ with known composition to be used for gas-phase calibration was purchased from Westfalen AG, Münster, Germany. Tetrahydrofuran (THF) and di-n-butyl ether (DBE) were obtained from Sigma-Aldrich. The commercial Ra-Ni catalysts were supplied as water-based slurries by Johnson

### Table 1

<table>
<thead>
<tr>
<th>Relevant properties of the PL used in this study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (wt%)</td>
</tr>
<tr>
<td>Element composition on a dry basis (wt%)</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O (by difference)</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>H/C, molar, dry</td>
</tr>
<tr>
<td>O/C, molar, dry</td>
</tr>
</tbody>
</table>

Scheme 1. Proposed reaction pathways during catalytic hydrotreatment of PL [2]
Matthey (J&M, UK). Relevant properties of the catalysts are given in Table 2. Detailed compositional data, when available from literature, are given Table S1 (Supporting information).

A benchmark Picula Ni-Cu catalyst was used as the reference catalyst [30,31]. The catalyst was prepared using a sol-gel method [29,37,38]. The catalyst consists of active metal species (46 wt% NiO, 5 wt% CuO, in the oxidized form) and a SiO$_2$-ZrO$_2$ support (25 wt% SiO$_2$ and 10.7 wt% ZrO$_2$). The catalyst was crushed and sieved to a fraction with 25–75 μm particles and reduced in situ for 1 h at a temperature of 350 °C before reaction.

2.2. Experimental procedures

2.2.1. Catalytic hydrotreatment of PL

Catalytic hydrotreatment reactions were carried out in a 100 mL batch autoclave (Parr, max. 350 °C). Before starting the reaction, the reactor was loaded with 1.25 g of the Raney “type” catalyst (using a 5 ml volume gravity bottle) together with 4.82 g water and subsequently with 25.0 g of PL (5 wt% catalyst concerning PL). The reactor was closed and pressurized to 140 bar hydrogen. Before the reaction, the pressure was reduced to 140 bar. For experiments with the benchmark Picula Ni-Cu catalyst, the catalyst was pre-reduced in the reactor at 350 °C under 20 bar hydrogen for 1 h. After reduction, the reactor was cooled to room temperature, 25.0 g of PL was injected into the reactor from a separate feed vessel using pressurized N$_2$ followed by flushing the reactor (3 times) with 10 bar hydrogen, then pressurized to 140 bar hydrogen pressure.

For both types of catalysts, the reactor was then heated to 200 °C at a heating rate of around 10 °C/min, while stirring at 1400 rpm and kept at this temperature for 4 h. After the reaction, the reactor was cooled to ambient temperature. The temperature and pressure in the reactor were recorded for mass balance calculations and quantitative determination of the composition of the gas phase. The gas-phase was collected using a 3 L gas bag and analyzed by GC-TCD (see Section 2.2.2 for details). The reactor after the reaction was weighted for mass balance calculations.

The liquid and solid products were transferred to a centrifuge tube (50 ml) and separated by centrifugation at 4500 rpm for 30 min. In all cases, two liquid phases were obtained: a top aqueous phase and a bottom organic (oil) phase. The aqueous and oil phase were separated and weighed. The reactor was rinsed with acetone, the suspension was filtered and the acetone was removed from the liquid by evaporation at 25 °C under a nitrogen atmosphere with a heating rate of 3 °C/min. The amount of residue minus the fresh catalyst intake. The amount of gas and char formed during the catalytic hydrotreatment was defined as the composition of the gas phase. The gas-phase was collected using a meltfit to a 120 cm × 0.25 μm film Rxi-5Sil MS column). He was used as the carrier gas (0.6 ml min$^{-1}$). A dual jet modulator was applied using carbon dioxide to trap the samples. The injector and detector temperature were set at 250 °C. The temperature profile of the oven was 40 °C for 2 min, then heated up from 40 to 90 °C at a temperature ramp of 20 °C/min and kept for 2 min. A reference gas containing H$_2$, CH$_4$, CO, CO$_2$, ethylene, ethane, propylene, and propane with known composition was used for peak identification and quantification. Before each analysis, the columns were flushed with a reference or sample gas for 30 s. The amounts of gas-phase components present in the reactor after the reaction were obtained from the pressure reading after the reactor was cooled to room temperature using the ideal gas law and the composition of the gas-phase by GC-FID.

2.2.2. Product analysis

2.2.2.1. Gas-phase analysis. The concentration of H$_2$, CH$_4$, CO, CO$_2$, and propane in the gas phase after catalytic hydrotreatment of PL was determined by a Hewlett Packard 5890 Series II GC equipped with a CP Poraplot Q Al$_2$O$_3$/Na$_2$SO$_4$ column (50 μm × 0.5 mm, film thickness 10 μm) and a CP-Molsieve 5A column (25 m × 0.53 mm, film thickness 50 μm). He was used as the carrier gas. The injector temperature was set at 150 °C and the detector at 90 °C. The following temperature profile for the oven was used: 40 °C for 2 min, then heated up from 40 to 90 °C at a temperature ramp of 20 °C/min and kept for 2 min. A reference gas containing H$_2$, CH$_4$, CO, CO$_2$, ethylene, ethane, propylene, and propane with known composition was used for peak identification and quantification. Before each analysis, the columns were flushed with a reference or sample gas for 30 s. The amounts of gas-phase components present in the reactor after the reaction were obtained from the pressure reading after the reactor was cooled to room temperature using the ideal gas law and the composition of the gas-phase by GC-FID.

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

2.2.2.3. Water content. A Karl-Fischer titration using a Metrohm 702 SM Titritron titration set-up was applied to determine the water content in the PL feed and product oils. About 0.01 g of sample was introduced to the titration vessel containing Hydranal solvent (Riedel de Haen), followed by titration with Hydranal titrant 5 (Riedel de Haen). All analyses were carried out in triplicate and the average value was reported.

2.2.2.4. Molecular weight distributions. Molecular weight distributions of the PL feed and product oils were analyzed using Gel Permeation Chromatography (GPC) with 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. THF was used as the mobile phase and standard polystyrene samples were used for calibration. 50 mg of PL/product oil was dissolved in 5 ml of THF together with 2 drops of toluene as the flow marker, followed by filtration using a syringe filter with pore size 0.2 μm before injection.

2.2.2.5. Thermal stability. Thermogravimetric Analysis (TGA) was used to evaluate the thermal stability of the PL feed and product oils. TGA analysis was carried out on a TGA 7 from Perkin-Elmer. Around 20 mg of sample was heated from 20 to 900 °C in a ceramic TGA sample holder under a nitrogen atmosphere with a heating rate of 10 °C/min. The TG residue is defined as the residual sample weight at 900 °C.

2.2.2.6. Two-dimensional gas chromatography (GC × GC). The amount and type of volatile components in the PL feed and product oils were analyzed on a GC × GC with FID detector from Interscience. The GC × GC was equipped with a cryogenic trap, and two columns (30 m × 0.25 mm i.d. and a 0.25 μm film of the RTX-1701 capillary column connected by using a meltfit to a 120 cm × 0.15 mm i.d. and a 0.15 μm film Rxi-5Sil MS column). He was used as the carrier gas (0.6 ml min$^{-1}$). A dual jet modulator was applied using carbon dioxide to trap the samples. The injector and detector temperature were set at 250 °C. The temperature profile of the oven was 40 °C for 5 min, then heating to 250 °C with a heating rate of 3 °C/min. The pressure was set at 70 kPa at 40 °C. The modulation time was 6 s. For the sample preparation, the samples were diluted 10 times with THF with 500 ppm di-n-butyl ether (DBE) as an internal standard. Details regarding calibration and quantification are provided in previous studies from our group. [39–41]

Table 2

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
<th>Particle size (μm, median)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raney Nickel A-40AA</td>
<td>Ni (Fe/Cr promoted)</td>
<td>33</td>
</tr>
<tr>
<td>Raney Nickel A-4000</td>
<td>Ni (Fe/Cr promoted)</td>
<td>33</td>
</tr>
<tr>
<td>Raney Nickel A-5000</td>
<td>Ni</td>
<td>33</td>
</tr>
<tr>
<td>Raney Nickel A-7063</td>
<td>Ni (Mo promoted)</td>
<td>33</td>
</tr>
<tr>
<td>Raney Nickel A-7KF3</td>
<td>Ni (Mo promoted)</td>
<td>39</td>
</tr>
</tbody>
</table>

* Data provided by the catalyst vendor.
The effective hydrogen to carbon ratio is defined in Eq. (1).

\[
\text{Effective hydrogen to carbon ratio } \left( \frac{H_2}{C} \right) = \frac{H - 2O}{C} \quad (1)
\]

Here, H, O, and C are the hydrogen, oxygen, and carbon contents in the product (in mole) on a dry basis.

The hydrogen consumption during the reaction was calculated using Eq. (2) [31].

\[
H_2 \text{ consumption} = \left( \frac{n_{H_2, \text{ initial}} - n_{H_2, \text{ final}}}{m_{PL, \text{ initial}}} \right) \times 22.4 (\text{NL/kg}) \quad (2)
\]

Here, the hydrogen consumption is given in NL hydrogen per kg PL feed, \( n_{H_2, \text{ initial}} \) is the initial amount of hydrogen (in moles) in the reactor, and \( n_{H_2, \text{ final}} \) is the amount of hydrogen (in moles) in the reactor after the reaction. \( m_{PL, \text{ initial}} \) is the mass of the PL fed to the reactor.

The weight average composition of the liquid phase (oil + water) was determined by considering the composition and the amount of oil and water phase present after the reaction.

### 3. Results and discussion

The five Ra-Ni and the Picula Ni-Cu catalysts were tested in a batch-set-up at typical stabilization conditions for PL hydrotreatment, viz., 200 °C, 140 bar hydrogen pressure, and a batch time of 4 h. Two liquid products were obtained after the reaction, viz. a top aqueous phase and a bottom oil phase. Besides, gas-phase components like CO2 and CH4 were formed, together with char. Satisfactory mass balance closures (> 96 wt %) and total carbon recovered in the liquid phases (> 95%) were obtained, see Table 3 for details.

#### 3.1. Product distribution

The product distributions (gas, oil, and aqueous phase, char) after the catalytic hydrotreatment of PL with the Ra-Ni and the Picula Ni-Cu catalysts are provided in Table 3. The oil yields are in the range from 27 to 34 wt% for the Ra-Ni catalysts, which is slightly lower than the 39 wt% for Picula Ni-Cu. Also, gas-phase components like CO2 and CH4 were formed. Less than 1 wt% of char was found for the Ra-Ni catalysts as well as the benchmark Picula Ni-Cu. This implies that all are active catalysts for PL hydrotreatment and that excessive repolymerization of reactive components in the PL feed leading to larger molecules and ultimately to char does not occur to a significant extent (Scheme 1). 38–50% of the carbon was recovered in the oil phase for the Ra-Ni catalysts, which is significantly lower than the 57% obtained for the Picula catalyst. As such, significant amounts of the carbon is retained in the aqueous phase in the form of more polar organic compounds (vide infra).

#### 3.2. Hydrogen consumption

The hydrogen consumption is a measure for the hydrogenation ability/activity of the catalyst when performing a mild hydrotreatment of PL. The overall hydrogen consumption for each experiment is plotted in Fig. 1. All promoted Ra-Ni catalysts show similar levels of hydrogen consumption (around 162–179 NL/kgPL feed), which is close to that of the benchmark Picula catalyst. The only exception is the promoter free catalyst. 

**Table 3** Overview of experiments for the mild catalytic hydrotreatment of PL.\(^a\),\(^b\),\(^c\),\(^d\).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A-40AA</th>
<th>A-4000</th>
<th>A-5000</th>
<th>A-7063</th>
<th>A-7KF3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic phase (wt% on PL intake)</td>
<td>29.5</td>
<td>33.4</td>
<td>33.5</td>
<td>27.3</td>
<td>27.8</td>
</tr>
<tr>
<td>Aqueous phase (wt% on PL intake)</td>
<td>68.5</td>
<td>64.8</td>
<td>63.8</td>
<td>71.7</td>
<td>70.6</td>
</tr>
<tr>
<td>Gas (wt% on PL intake)</td>
<td>0.7</td>
<td>0.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Solid (wt% on PL intake)</td>
<td>0.4</td>
<td>0.9</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Total mass balance (%)</td>
<td>99.1</td>
<td>99.6</td>
<td>98.7</td>
<td>100.0</td>
<td>99.5</td>
</tr>
<tr>
<td>Hydrogen consumption (NL/kg PL)</td>
<td>162</td>
<td>169</td>
<td>138</td>
<td>169</td>
<td>179</td>
</tr>
<tr>
<td>Water content of the organic phase (wt%)</td>
<td>11.6</td>
<td>15.6</td>
<td>12.0</td>
<td>11.8</td>
<td>11.6</td>
</tr>
<tr>
<td>Element composition of the organic phase (dry)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>67.72</td>
<td>64.41</td>
<td>68.10</td>
<td>67.21</td>
<td>67.48</td>
</tr>
<tr>
<td>H</td>
<td>8.18</td>
<td>8.34</td>
<td>8.03</td>
<td>8.48</td>
<td>8.51</td>
</tr>
<tr>
<td>O</td>
<td>24.10</td>
<td>27.26</td>
<td>28.87</td>
<td>24.31</td>
<td>24.01</td>
</tr>
<tr>
<td>Carbon in the organic phase, wt%</td>
<td>45.6</td>
<td>43.1</td>
<td>49.7</td>
<td>37.4</td>
<td>51.4</td>
</tr>
<tr>
<td>Carbon in the aqueous phase, wt%</td>
<td>53.4</td>
<td>60.5</td>
<td>46.2</td>
<td>57.3</td>
<td>57.6</td>
</tr>
<tr>
<td>Total carbon in both liquid phases (%)</td>
<td>99.0</td>
<td>103.6</td>
<td>95.8</td>
<td>95.2</td>
<td>99.0</td>
</tr>
<tr>
<td>Effective hydrogen to carbon ratio in the aqueous phase, H2/C</td>
<td>0.94</td>
<td>1.68</td>
<td>0.81</td>
<td>0.95</td>
<td>0.97</td>
</tr>
</tbody>
</table>

\(a\) Experiments were performed at 200 °C, 140 bar initial H2 pressure.

\(b\) Defined as the amount of carbon in the oil phase after reaction divided by the amount of carbon in the PL feed.

\(c\) Defined as the amount of carbon in the aqueous phase after reaction divided by the amount of carbon in the PL feed.

\(d\) average results for duplicate experiments, data for individual experiments are given in Table S2.

![Fig. 1. H2 consumption for the mild hydrotreatment of PL with different types of catalysts (200 °C, 140 bar, 4 h).](image-url)
3.3. Gas phase composition

The gas-phase compositions after the mild hydrotreatment are shown in Fig. 2. More than 97 mol% of the gas phase is unreacted hydrogen, indicating that sufficient hydrogen was available for reactions throughout the 4 h batch time. The main non-condensable gases after reaction are CH$_4$ and CO$_2$. The latter is likely formed by decarboxylation of organic acids in the PL [42] such as formic acid, whereas CH$_4$ may be formed by either reaction of e.g. the methoxy of the lignin fraction in PL or by methanation of CO$_2$/CO with H$_2$ [43]. The calculated hydrogen consumptions for the methanation reactions only are well below 10 NI/kg$_\text{oil}$. Nevertheless, the extent of methanation reactions is higher for the Ra-Ni catalysts than for the Picula one, which is not desired when considering the high costs of hydrogen.

3.4. Oil phase composition and properties

3.4.1. Van Krevelen plot

The oxygen content of the product oils is between 23.9 and 27.3 wt% and is considerably lower than for the PL feed (38.7 wt%). A substantial amount of bound oxygen is thus removed, with water as the main product. As expected, full oxygen removal is not possible under these mild hydrotreatment conditions. The elemental composition of the PL feed and the weight averaged composition of the liquid phase (oil + water) for each catalyst are given in the form of a van Krevelen plot in Fig. 3. The O/C ratio for the weight averaged composition of the liquid phase (oil + water) is in the range of 0.38–0.46. Values for the H/C ratio vary considerably from 1.54 for Picula to almost 2.06 for the A-4000 (Fe/Cr promoted). Separate plots for the oil and aqueous phases are provided in Figs. S1 and S2, respectively.

The hydrotreatment of the PL using the Raney Ni “type” catalysts follows a typical trajectory as observed for other catalysts and is given in Fig. 3. It involves initial hydrogenation resulting in a higher H/C ratio without affecting the O/C ratio, followed by the formation of water, leading to a reduction in both the H/C and O/C ratio. Chemical transformations associated with these changes are the hydrogenation of ketone/aldehydes to alcohols followed by water elimination and the formation of C-C double bonds. The latter molecules will be hydrogenated in a later stage.

3.4.2. Molecular weight distributions of the oil phases

The molecular weight distributions of the PL feed and the oil phases as determined by GPC are shown in Fig. 4 a) and b).

The molecular weight distribution of the PL feed and products shows the presence of a broad range of low and high molecular weight components. Of interest are the peaks at around 200 g/mol and the ones >1500 g/mol. The first peak is related to the presence of monomeric sugars such as levoglucosan (LG) [44]. This component is typically present in relatively high amounts in PL (up to 10 wt%) and formed by thermal degradation of the cellulose fraction in the biomass feed. The intensity of this peak is decreased upon the mild catalytic hydrotreatment, due to its conversion into smaller molecules, among others, alcohols such as ethylene glycol. For the MW range higher than 1500 g/mol, which is informative when considering the repolymerization of reactive molecules during hydrotreatment (Scheme 1), small though relevant differences were obtained for the various catalysts (Fig. 4b). The lowest tail was observed for Ra-Ni with Mo as a promoter (Ra-Ni A-7063), indicating that catalytic hydrotreatment activity of this catalyst for thermally labile compounds prone to thermal polymerization is highest.

3.4.3. Thermal Gravimetric Analysis (TGA)

One of the main purposes of a mild catalytic hydrotreatment of PL is to improve the thermal stability of the oil product. We have applied TGA for this purpose, which provides insights into the overall charring tendency of the oils, and the volatility. The TGA analysis involves heating the sample from room temperature to 900 °C at a temperature ramping of 10 °C/min under an N$_2$ atmosphere. The TG curves of both the PL feed and the product oils are shown in Fig. 5 and Fig. S3. The TG residues, defined as the residue after heating a sample to 900 °C, are shown in Table 4. The TG curves of the PL feed and upgraded oils are shown in Fig. 5 and Fig. S3.

All the product oils after catalytic hydrotreatment showed lower TG residues compared to the PL feed. This provides direct evidence that the amount of thermally labile compounds, prone to re-polymerization have
been reduced in the mild hydrotreatment process. Among the Ra-Ni catalysts tested, the Mo-promoted ones (A-7KF3 and A-7063) showed the lowest TG residues, which is a positive feature of Mo promotion.

3.4.4. Two-dimensional Gas Chromatography (GC x GC-FID)

The product oils and PL feed were analyzed by GC x GC-FID to gain insights into the chemical composition. Typical chemical groups like acids, ketones/alcohols, cyclic alkanes, linear/branched alkanes, aromatics, guaiacols, alkylphenols, and catechols can be identified and semi-quantified by this technique.

The total amount of GC detectable components in the organic phases (Fig. 6) is about 15–25 wt%. This relatively low value is due to the presence of higher molecular weight, non-GC detectable compounds in the oils, as confirmed by GPC (vide supra). The catalytic hydrotreatment led to an increase in GC detectable compounds compared to the PL feed (12 wt%), indicating the formation of low molecular weight components. Acids, especially carboxylic acids, are present in concentrations between 3 and 5 wt%. These are indeed known to be present in the PL feed and resistant to catalytic hydrotreatment, especially at mild conditions (except for formic acid [42]). The total amount of components derived from the lignin fraction in the PL such as phenolics, guaiacols, and catechols increased from 7.4 wt% in the PL feed to 15.4 wt% for Mo promoted Ra-Ni A-7063 likely due to catalytic and thermal depolymerization of the lignin fraction in the PL feed.

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>TG residue, wt%</th>
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<tr>
<td>PL feed</td>
<td>11.3</td>
</tr>
<tr>
<td>Picula Ni-Cu</td>
<td>8.9</td>
</tr>
<tr>
<td>Raney Ni A-40AA</td>
<td>6.8</td>
</tr>
<tr>
<td>Raney Ni A-4000</td>
<td>7.4</td>
</tr>
<tr>
<td>Raney Ni A-5000</td>
<td>7.1</td>
</tr>
<tr>
<td>Raney Ni A-7KF3</td>
<td>5.2</td>
</tr>
<tr>
<td>Raney Ni A-7063</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Fig. 4. Molecular weight distributions by GPC analysis: a) PL feed and product oils for the mild hydrotreatment (200 °C, 140 bar, 4 h), b) tail part of the GPC curves.

Fig. 5. TGA curves for product oils and PL feed (200 °C, 140 bar, 4 h).

Fig. 6. GC x GC-FID results for the product oils from the mild hydrotreatment of PL (200 °C, 140 bar, 4 h).
3.5. Water phase composition and valorisation

As indicated in Table 3, 40–61 wt% of the carbon from the PL feed is present in the aqueous phase (dry basis). The aqueous phase of a mild catalytic hydrotreatment is known to consist mainly of small polar organic molecules, such as unconverted organic acids from PL feed [7] as these are rather resistant to hydrogenation at mild conditions. Other components are alcohols from the hydrogenation of carbonyl compounds [45], or hydrogenolysis products like polyols from reactions involving monomeric or oligomeric sugars.

When considering a scenario that the oil phase after hydrotreatment is used for co-feeding purposes in existing refineries (e.g. in FCC-unit), valorization strategies need to be developed for the water phase. Several options can be envisaged. Small molecules in the aqueous phase can be separated by for instance distillation and used as bulk chemicals, examples are small alcohols and organic acids (e.g. acetic acid). Another possibility is water removal and the use of the remaining organics as a source for benzene, toluene xylenes (BTX) production using zeolite catalysts like HZSM-5 [46]. For this purpose, the H/C ratio of the feed is a key indicator to obtain high BTX yields and a high H/C is preferred. The H/C of the aqueous phases typically range from 0.8 to 1.7, the highest for catalyst A-4000 and A-7063 (1.68 and 0.95, respectively), which are all higher than for the other Ra-Ni catalysts (0.81 for A-5000) and benchmark Picula Ni-Cu (0.80). Further studies on the use of the aqueous phase from mild hydrotreatments of pyrolysis liquids for BTX synthesis are in progress and will be reported in due course.

3.6. Catalyst leaching and recyclability

The aqueous phase products upon catalytic hydrotreatment were analyzed by ICP to determine the extent of metal leaching during the reaction and the results are given in Table 5.

In the PL feed, negligible amounts of metals are detected. After hydrotreatment, significant amounts of Ni (31–67 ppm) are detected in the aqueous phase. The promoted catalysts showed lower Ni leaching levels than the un promoted ones, and the lowest levels were found for Mo promoted Ra-Ni catalysts. Besides, not only Ni but also the promoters tend to leach. This effect is the largest for the Fe/Cr promoted catalyst, whereas Mo leaching is by far lower. These findings imply that i) metal leaching should be taken into consideration in further studies in dedicated continuous set-up to determine the long-term stability of the catalysts and ii) Mo promotion is preferred as promoter as it shows the lowest leaching levels of Ni and the promoter.

To gain insights into catalyst stability, several catalysts recycle experiments were performed using the Mo promoted Ra-Ni A-7063 catalyst. A total of three reactions was performed, one with fresh and two with spent catalyst. After the first reaction at 200 °C for 4 h, the spent catalyst was collected and washed with acetone and water and reused in a standard experiment. Hydrogen consumption was used to evaluate the performance of the catalyst during the catalytic reusability and the results are provided in Fig. S4 and Table S4. These show a decrease in the activity of about 20% after 2 recycles, a first indication that catalyst deactivation occurs to some extent.

3.7. Comparison of catalyst performance

The primary objective of the catalytic hydrotreatment of PL under mild hydrotreatment conditions is to obtain a product oil with improved product properties and particularly improved thermal stability. Also, process-related properties of the catalysts should be considered, like metal leaching levels and hydrogen consumption. An overview of relevant properties, both quantitative and qualitative, is provided in Table 6. An important product property is the charring tendency of the product oil. This was determined using TGA, and the TGA residues are provided in Table 6. The desired, lowest values are obtained with the Mo promoted catalyst. Besides, the organic product with the lowest molecular weight, and associated with this the highest amount of volatiles (as determined by GC), was also obtained with one of the Mo promoted catalysts (A-7063). As such, from a product property point of view, the Mo-promoted Ra-Ni catalyst (A-7063) gives the best performance and is the preferred Raney Ni “type” catalyst in this study. The introduction of Mo to Ni catalysts may form NiMo solid solution and these bimetallic species may be more active than monometallic ones. It is also well possible that Mo in intermediate oxidation states have (in combination with Ni) a positive effect on activity by activation of oxygenated species from pyrolysiss liquids. Besides, the addition of Mo has a positive effect on the stability of the metal nanoparticles and that sintering rates are reduced compared to the monometallic Ni catalyst. [44] This conclusion is further supported when also considering process-related properties. For instance, catalyst leaching levels, and particularly Ni leaching, which is to be avoided as much as possible, both from a product property point of view (heavy metals are not preferred in the feed when using it for co-feeding) and catalyst considerations (leaching often leads to catalyst deactivation and thus high catalyst consumption levels with associated costs) was lowest for the Mo promoted catalysts. Thus, also when considering process-based criteria the Mo-promoted Ra-Ni catalyst (A-7063) is the preferred Raney Ni “type” catalyst in this study.

4. Conclusions

The catalytic hydrotreatment of PL was studied using five commercially available Ra-Ni catalysts under mild conditions to gain insights into the performance of such Ra-Ni catalysts and particularly the effects of promoters. Hydrogen consumption and relevant oil properties (TGA residue, GPC) were used as indicators for performance. After the mild catalytic hydrotreatment, all oils showed improved properties compared to that of the PL feed, e.g. better stability (TGA), lower molecular weight, higher H/C ratio, and lower oxygen content. Among the Ra-Ni catalysts tested, the Mo-promoted Ra-Ni catalyst (A-7063) shows a better performance than the Fe/Cr-promoted catalysts and the promoter free one concerning the oil properties (lowest TG charring tendency.

### Table 5

<table>
<thead>
<tr>
<th>Product</th>
<th>Ni (ppm)</th>
<th>Fe (ppm)</th>
<th>Cr (ppm)</th>
<th>Mo (ppm)</th>
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<tbody>
<tr>
<td>PL</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>1</td>
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<tr>
<td>Ra-Ni A-40AA</td>
<td>Fe/Cr</td>
<td>67</td>
<td>414</td>
<td>191</td>
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<tr>
<td>Ra-Ni A-4000</td>
<td>Fe/Cr</td>
<td>42</td>
<td>432</td>
<td>444</td>
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<tr>
<td>Ra-Ni A-5000</td>
<td>–</td>
<td>71</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ra-Ni A-7063</td>
<td>Mo promoted</td>
<td>32</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ra-Ni A-7KF3</td>
<td>Mo promoted</td>
<td>31</td>
<td>–</td>
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### Table 6

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<tr>
<th>Catalyst</th>
<th>A-40AA</th>
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<th>A-5000</th>
<th>A-7063</th>
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<td>Active metal Ni</td>
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<tr>
<td>Promoters Fe/Cr</td>
<td>–</td>
<td>–</td>
<td>Fe/Cr</td>
<td>–</td>
<td>Mo</td>
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<tr>
<td>Product properties</td>
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</tr>
<tr>
<td>TG residue, wt% 6.8</td>
<td>7.4</td>
<td>7.1</td>
<td>5.2</td>
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<td></td>
</tr>
<tr>
<td>Volatiles, wt% by GC</td>
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<td>20.2</td>
<td>15.7</td>
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<td>23.2</td>
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<tr>
<td>GPC tail Highest Medium Medium Lowest Medium</td>
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<tr>
<td>Process related properties</td>
<td></td>
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<tr>
<td>Ni leaching levels Medium Medium Highest Lowest Lowest</td>
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<tr>
<td>Hydrogen consumption, NL/kg</td>
<td>163</td>
<td>164</td>
<td>127</td>
<td>163</td>
<td>175</td>
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</table>

W. Yin et al.

Fuel Processing Technology 219 (2021) 106846
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2021.106846.

References


