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Hydrotreatment of the carbohydrate-rich fraction of pyrolysis liquids using bimetallic Ni based catalyst: Catalyst activity and product property relations

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Research article

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1. Introduction

Lignocellulosic biomass has been identified as a renewable resource for the production of transportation fuels and biobased chemicals [1,2]. However, biomass logistics are complex and expensive and as such there is a strong incentive to develop cost effective technologies for the densification liquefaction of biomass. Fast pyrolysis is such a promising technology as it converts lignocellulosic biomass into a vapor phase which is subsequently condensed to obtain a pyrolysis liquid at relatively mild temperatures (450–600 °C) [3,4]. Liquid yields of 70 to 80% on dry biomass input have been reported. However, the pyrolysis liquids are rather acidic (pH usually around 3) [5]. The presence of acids and other reactive oxygenated functional groups renders the liquids relatively polar, and non-miscible with hydrocarbons. Furthermore, thermal stability is limited due to repolymerization of reactive organic compounds [5]. In addition, the energy density is typically < 50% of that of conventional oils due to the presence of water (15–30%) and oxygenates (typical oxygen contents are between 35 and 40%) [6].

Catalytic hydrotreatment has shown to be an attractive technology to obtain stabilized pyrolysis liquids with a tunable oxygen content [5,7]. Various metal-support combinations have been applied either using pyrolysis liquids as such or in combination with a solvent. Early studies on the hydrotreatment of pyrolysis liquids involved the use of conventional hydrodesulfurization catalysts, e.g. sulfided NiMo and CoMo on γ-Al2O3, and allowing for for the production of fully deoxygenated products [8]. However, these catalysts have some drawbacks such as (i) the requirement of high temperatures (up to 400 °C), (ii) significant deactivation under the harsh conditions and (iii) requirement of the presence of S for good performance. Noble metal catalysts were also tested extensively (Ru, Pd, Pt, Rh on various supports, e.g. Al2O3, TiO2, active carbon, ZrO2 etc.) [9,10]. Among these, Ru/C was found to be superior to the classical hydrotreating catalysts with respect to oil yield (up to 60 wt%), though deep deoxygenation in a single step proved not possible [10].

In previous studies on the catalytic hydrotreatment of pyrolysis liquids using a Ru/C catalyst [5], various parallel and consecutive reactions were proposed to explain the product portfolio after the hydrotreatment reaction (Scheme 1). At relatively low temperatures, the desired hydro-(deo)xygenation and undesired thermal, non-catalyzed polymerization reactions occur in parallel. The latter route ultimately
leads to char, thus lowering the carbon efficiency of the process and causing operational issues.

It is generally assumed that the sugar fraction of pyrolysis liquids, which is known to contain among others acetol, glycolaldehyde, furfural, furanone, levoglucosan and oligomeric (dehydrated) carbohydrates, is prone to thermal polymerization reactions leading to char (top route in Scheme 1) [5]. Efficient hydrogenation of this sugar fraction into more stable components, e.g. aldehydes and ketones to alcohols and sugars to sugar alcohols, is thus expected to reduce char formation. Experimental studies on related processes have indeed confirmed this statement. For instance, Vispute and et al. [11] reported bio- aromatics production from the sugar fraction of pyrolysis liquids using zeolite catalysts. Coke formation was considerably reduced (from 32.3 down to 12.6%) and aromatics yields increased (from 8.2 up to 21.6%) by first applying a low temperature hydrogenation step of the water soluble phase of the pyrolysis liquids using Ru/C or Pt/C catalysts. Vispute and et al. [12] also reported alkane production from the aqueous phase processing of pyrolysis liquids and showed that prior hydrogenation of the water soluble phase of the pyrolysis liquids at 175 °C using a Ru/C catalyst considerably increased the selectivity to alkanes from 42 to 85%.

Recently, a new series of non-noble metal based catalysts was introduced by our groups for the hydrodreatment of pyrolysis liquids [13]. These catalysts are Ni-based, prepared by as sol-gel method and promoted by among others Cu or Pd, and show clear advantages compared to Ru/C such as (i) low methane formation rates, limiting the consumption of (expensive) hydrogen and (ii) reduced rates of char formation [13]. Ni based catalysts for the catalytic hydrodreatment of pyrolysis liquids have also been reported by other groups [14–17].

As mentioned earlier, primarily the sugar fraction is assumed to be responsible for repolymerization reactions leading to char, which makes it obvious that this fraction should be treated responsible for repolymerization reactions leading to char, which makes it obvious that this fraction should be treated

Relevant properties of the pyrolytic sugars used in this study.

<table>
<thead>
<tr>
<th>Code</th>
<th>Metal loading, wt%</th>
<th>Support, wt%</th>
<th>Reduction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>48</td>
<td></td>
<td>15.5</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>46</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Ni-Pd</td>
<td>57</td>
<td>8.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Ni-Pd-Cu</td>
<td>54</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Ni-Mo</td>
<td>41</td>
<td>7.4</td>
<td>13.3</td>
</tr>
<tr>
<td>Ni-Mo-Cu</td>
<td>38</td>
<td>3.8</td>
<td>10.8</td>
</tr>
</tbody>
</table>

* In oxidized form.
The catalyst was then activated by applying 20–30 bar H₂ at a temperature of 350–400 °C (see Table 2) for 1 h, after which the reactor was cooled to room temperature and 25.0 g of PS was injected to the reactor from a feed vessel using pressurized nitrogen gas. The reactor was flushed 3 times with 10 bar of hydrogen to remove any remaining air/oxygen, and was subsequently pressurized with hydrogen to 120 bar at room temperature. Finally, the reactor content was heated up to 180 °C with a heating rate of 10 °C/min. The reactor was kept at 180 °C for 4 h while stirring at 1400 rpm and subsequently cooled to ambient temperature. The pressure in the reactor was determined and the gas phase was sampled using a 3 L gas bag. The liquid and solid product (mainly spent catalyst) were collected after reaction and transferred to a centrifuge tube. Both phases were separated by centrifugation (4500 rpm, 30 min) and collected and weighted. The reactor was thoroughly rinsed with acetone. The acetone was evaporated (in air at room temperature), and the resulting product was weighted and added to the liquid phase for mass balance calculation. The suspension was combined with the solid residue in the centrifuge tube, filtered over a paper filter, washed with acetone and water, further dried at 100 °C until constant weight. The amount of char formed is defined as the amount of solid residue minus the original catalyst intake. The amount of gas phase components after reaction was determined by the pressure difference in the reactor before and after reaction at room temperature using the ideal gas law in combination with the measured composition of the gas phase by GC. It is assumed that the volume of the gas hold-up in the reactor before and after reaction is equal. For non-catalytic runs, the pyrolytic sugar was heated in the reactor to 180 °C for 4 h under 120 bar of N₂ gas and samples of the liquid and solid phase after reaction were collected using the same methodology as for the catalytic runs.

2.3.2. Analysis of gas- and liquid phase

2.3.2.1. GC-TCD. The composition of the gas phase after reaction was determined by GC-TCD. A Hewlett Packard 5890 Series II GC equipped with a CP Poraplot Q Al₂O₃/Na₂SO₄ column (50 m × 0.5 mm, film thickness 10 μm) and a CP-Molsieve 5 Å column (25 m × 0.53 mm, film thickness 50 μm) was used. The injector temperature was set at 200 °C, the detector temperature at 90 °C. The oven temperature was kept at 40 °C for 2 min, then heated up to 90 °C at 20 °C/min and kept at this temperature for 2 min. Helium was used as the carrier gas. The columns were flushed for 30 s with reference and sample gas before starting the measurement. A reference gas containing H₂, CH₄, CO, CO₂, ethylene, ether, propylene and propane with known composition was used for peak identification and quantification.

2.3.2.2. Determination of the composition of the pyrolytic sugar. The composition and particularly the amounts of monomeric and oligomeric sugars were determined using a hydrolysis method [22]. A glass pressure tube was filled with 100 mL of a 500 mM sulphuric acid (98%) solution in water and 1.0 g of pyrolytic sugar. The tube was closed and placed in an oven at the preset temperature (80 and 120 °C) for 24 h. After reaction, the content was cooled to room temperature, the solution was filtered and analyzed using HPLC. The HPLC was equipped with a Hewlett Packard 1050 pump, a Bio-Rad organic acid column (Aminex HPX-87H) and a differential refractometer. The mobile phase consisted of an aqueous solution of sulfuric acid (5 mmol/L) using a flow rate of 0.55 cm²/min. The column was operated at 60 °C. Quantification of the various products was performed using calibration curves obtained from standard solutions of known concentrations. The amounts of levoglucosan and glycolaldehyde in the pyrolytic sugar fraction were quantified without the hydrolysis step by direct injection of the diluted pyrolytic sugars solution.

2.3.2.3. Calculation of the hydrogen consumption in a batch reaction. The H₂ consumption for each batch experiment was calculated according to a literature method [23,24]. It is based on the initial pressure, temperature and composition of the gas phase before and after the reaction. In these calculations, it is assumed that the volume of the gas phase in the reactor is constant and that the ideal gas law is applicable. The initial number of moles of H₂ in the reactor is given by:

\[ n_{H_2, initial} = \frac{V_{gas, cap} P_{initial}}{R T_{initial}} \]  

where \( n_{H_2, initial} \) is the initial amount of hydrogen (in moles) in the reactor, \( V_{gas, cap} \) is the volume of the reactor that is not occupied by the liquid, \( P_{initial} \) is initial pressure in the reactor (in room temperature), \( R \) is gas constant, and \( T_{initial} \) is the initial temperature in the reactor (room temperature).

After reaction, the reactor was cooled to room temperature and the pressure was recorded. In combination with the known composition of the gas phase (GC-TCD), the amount of hydrogen at the end of the reaction is given by:

\[ n_{H_2, final} = \frac{Y_{H_2, final} V_{gas, cap} P_{final}}{R T_{final}} \]  

where \( n_{H_2, final} \) is the amount of hydrogen uptake (in moles) in the reactor after the reaction, \( Y_{H_2, final} \) is the mole fraction of the hydrogen in the gas cap after reaction (as measured by GC-TCD), \( V_{gas, cap} \) is the volume of the reactor that is not occupied by the liquid, \( P_{final} \) is the pressure in the reactor after the reaction (measured in room temperature), \( R \) is gas constant, \( T_{final} \) is the final temperature in the reactor (room temperature).

The hydrogen uptake per kg feed was calculated using Eq. (3).

\[ H_2 \text{ consumption} = \frac{(n_{H_2, initial} - n_{H_2, final}) \cdot \frac{P_{298K}}{P_{final}}}{m_{PS, initial}} \]  

where \( H_2 \text{ consumption} \) is the hydrogen uptake (in NL per kg dry feed), \( n_{H_2, initial} \) is the initial amount of hydrogen (in moles) in the reactor, \( n_{H_2, final} \) is the amount of hydrogen uptake (in moles) in the reactor after the reaction, \( R \) is gas constant, \( m_{PS, initial} \) is the mass of the pyrolytic sugar fraction fed to the reactor.

2.3.2.4. Elemental analysis. The elemental composition of the pyrolytic sugar feed and the product oils were analyzed using a EuroVector EA3400 Series CHNS-O analyzer with acetonitrile as the reference. The oxygen content was determined by difference. All analyses were carried out at least in duplicate and the average value is reported.

2.3.2.5. Water content. The water content of the pyrolytic sugar feeds and the product oils were determined using a Karl-Fischer (Metrohm 702 SM Titriunit) titration. About 0.01 g of sample was introduced to an isolated glass chamber containing Hydralan solvent (Riedel de Haen) by a 1 mL syringe. The titration was carried out using Hydralan titrant 5 (Riedel de Haen). Mill-Q water was assumed as water content 100% used to calibrate the results of titration. All analyses were carried out at least in duplicate and the average value is reported.

2.3.2.6. Gel permeation chromatography (GPC). GPC analyses of the organic products were performed using an Agilent HPLC 1100 system equipped with a refractive index detector. Three columns in series of mixed type E (length 300 mm, i.d. 7.5 mm) were used. Polystyrene was used as a calibration standard. All analyses were carried out at least in duplicate and the average value is reported.

2.3.2.7. Thermogravimetric analysis (TGA). TGA analysis of the pyrolytic sugar feeds, the product oils and spent catalysts were determined using a TGA 7 from Perkin-Elmer. The samples were heated in a nitrogen atmosphere with a heating rate 10 °C/min and a temperature range between 20 and 900 °C.

2.4.1. Nitrogen physisorption analyses

Nitrogen physisorption analyses (−196.2 °C) were carried out using a Micromeritics ASAP 2420 device. The samples were degassed in vacuum at 350 °C for 10 h. The surface area was calculated using the standard BET method (SBET). The single point pore volume (VT) was estimated from the amount of gas adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distributions (PSD) were estimated from the amount of gas adsorbed at a relative pressure of 0.01 in the adsorption branch and 0.4 in the desorption branch.

2.4.2. CO chemisorption

The metallic surface area of the catalyst in reduced state was determined by CO pulse chemisorption measurements using a Chemisorb analyzer (Modern laboratory equipment, Novosibirsk, Russia). 50 mg of fresh catalyst was placed inside an U-shaped quartz reactor and heated to the preset temperature (350 °C for Ni-Cu, Ni-Pd, Ni-Pd-Cu catalysts and 400 °C for Ni, Ni-Mo, and Ni-Mo-Cu catalysts, heating rate 40 °C/min) under a flow of H2 (30 mL/min). When the final temperature was reached, the reactor was purged by an inert gas (He) followed by cooling to RT. Subsequently, pulses of CO were fed to the reactor (100 µL) until the amount of CO in the outlet was constant according to thermal conductivity detector (TCD). Thereafter the amount of chemisorbed CO was estimated.

2.4.3. Transmission electron microscopy (TEM)

A Philips CM12 instrument equipped with a high-resolution camera was used to acquire and elaborate TEM images. Powdered samples were dispersed in 2-propanol under ultrasound irradiation and the resulting suspension was placed drop-wise on a holey carbon-coated support grid.

2.4.4. Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX)

The morphology of the samples was investigated by scanning electron microscopy (SEM-EDX) using a Philips XL-30-FEG SEM at an accelerating voltage of 5 kV. Prior to analyses, the samples were treated with Au using a gold sputter coater device. EDX analysis was carried out by using samples without a pretreatment.

3. Results and discussion

3.1. Pyrolytic sugar (PS) analysis

The PS used in this study was prepared by the addition of water to a typical PL obtained from pine wood using a fast pyrolysis process. This results in the precipitation of the pyrolytic lignin fraction, which was separated, leaving an aqueous PS fraction. The PS feeds were analyzed in detail using various analytical techniques (elemental analysis (EA), GPC, HPLC and GC–MS). The elemental composition is given in Table 3, an overview of HPLC and GC–MS data is given in Table 3.

<table>
<thead>
<tr>
<th>Sample preparation</th>
<th>Component in PS</th>
<th>Analysis method</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Levoglucosan</td>
<td>HPLC</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>Glycolaldehyde</td>
<td>HPLC</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>Acids</td>
<td>GC–MS</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Ketones</td>
<td>GC–MS</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Phenolics</td>
<td>GC–MS</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>Karl-Fisher titration</td>
<td>14.5</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Total</td>
<td>HPLC</td>
<td>45.6</td>
</tr>
<tr>
<td></td>
<td>Glucose</td>
<td>HPLC</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>Mannose/xylose</td>
<td>HPLC</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>Arabinose</td>
<td>HPLC</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Total sugars</td>
<td></td>
<td>33.4</td>
</tr>
</tbody>
</table>

*Hydrolysis data are for an experiment at 80 °C (see experimental section for details).

When summing up the total of GC-HPLC detectable species, it is clear that a considerable amount of the PS fraction is not detectable by GC and HPLC (up to 55 wt%, see Table 3) and likely consists of higher molecular weight components. This was indeed confirmed by GPC measurements, see Fig. 2 for details.

The PS feed shows a relatively broad distribution with a sharp peak at lower molecular weights. The latter peak is likely associated with the presence of LG. This was confirmed by the addition of LG to a product sample followed by GPC analysis, resulting in an increase in the area of this particular peak. The higher molecular weight fraction likely consists of oligo-(anhydro)sugars.

To gain insight in the composition and the amount of hydrolysable sugars, the PS fraction was hydrolysed using dilute sulfuric acid at 80 and 120 °C for 24 h. At 80 °C, 25.2 wt% of glucose, 7.8 wt% of mannose/xylose and 0.4 wt% of arabinose were detected in the hydrolysate as shown in Table 3. The glucose is formed both from the hydrolysis of LG as well as from the oligomeric sugars. Thus, part of the PS oligomers is hydrolysable to monomeric sugars (glucose, mannose, xylose, arabinose). A hydrolysis experiment at 120 °C for 24 h gave very similar results, see Table S1 (Supporting information).

The total amounts of monomeric sugars in the PS fraction as detected after hydrolysis (80 °C) by HPLC is 33.4 wt%. This value is significantly lower than the total amounts measured by GPC.

Fig. 1. Representative GC–MS spectrum of the PS feed.
CO2 is formed by decarboxylation reactions of small organic acids [27], mass balance closures are very satisfactory and above 95% for all experiments. Solids formation is limited (0–1.2 wt%), implying that thermal repolymerization does not occur to a considerable extent.

### 3.2. Catalysts screening experiments in a batch set-up

Catalytic screening experiments were performed in a batch set-up at 180 °C for 4 h. All catalysts, except the monometallic Ni catalyst, yielded a single liquid phase product (94 to 99 wt% on PS intake) with a reddish brown colour for Ni-Cu, Ni-Pd, Ni-Pd-Cu catalysts and a dark brown colour for the Ni-Mo-Cu and Ni-Mo catalysts. An experiment with the monometallic Ni catalyst yielded two liquid phases, a water-rich top phase, an organic bottom phase and a sticky, viscous layer on the reactor wall. The amounts of gas, liquid and solid phase for each experiment are summarized in Table 4.

Minor amounts of gas phase components (0.6 to 1.4 wt% on PS intake) are formed, the major one being CO2 (1.9–3.4 mol%). Likely, CO2 is formed by decarboxylation reactions of small organic acids [27], which were shown to be present in the PS fraction (around 2.5 wt%, see Table 3). Methane and higher alkanes were not observed, indicating that the hydrogen is consumed solely for liquid phase reactions. Total mass balance closures are very satisfactory and above 95% for all experiments.

### 3.3. Catalyst activity

Since CO2 is the sole product in the gas phase and methane and higher alkanes are absent (Table 4), all the hydrogen consumed is used for hydrogenation reactions. As such, the experimentally measured hydrogen uptake during a reaction is a good measure for catalyst activity and the results are given in Fig. 3. Lowest activity was found for the monometallic Ni catalyst (81 NL/kgfeed) whereas the bimetallic Ni-Mo catalyst is the most active (167 NL/kgfeed). Thus, a clear promoting effect of the second metal is observed. The addition of Cu to the monometallic Ni catalyst lead to higher hydrogenation activity [28,29], whereas the addition of Pd (in both Ni-Pd and Ni-Pd-Cu) gave a further improvement. Thus, Pd seems to be a better promoter in these reactions than Cu, which is in agreement with results obtained for pyrolysis liquids [13].

Promotion by Mo gave the best results and the highest hydrogenation activity was found for a bimetallic Ni-Mo catalyst. Thus, Mo is a better promoter for these Ni-based catalysts than Cu. Comparison with Pd is not well possible as considerably lower amounts of Pd were used in the catalyst formulation compared to Mo (Table 2).

### 3.4. Product analysis

All the liquid product phases were analyzed by elemental analysis and the data are provided in a van Krevelen plot given in Fig. 4. For reference, the data for the PS feed, the theoretical dehydration line and the results for a non-catalytic experiment are displayed as well. The latter was performed with PS and nitrogen in the absence of a catalyst. This led to the formation of large amounts of solids and a very viscous black organic phase (less than 5 wt%). In this case, polymerization of reactive molecules associated with water formation and the formation of char/humin type materials is occurring to a significant extent (Scheme 1) [30].

The van Krevelen plot gives valuable insights in the reaction pathways occurring during the catalytic hydrotreatment, specifically on hydrogenation and reactions involving the formation of water (e.g. condensation, polymerization and alcohol dehydrations) [5]. The elemental composition of the product oils is a clear function of the type of catalyst used. The O/C ratio varies between 0.40 and 0.51, whereas the H/C ratio spans a much larger range and is between 1.36 and 1.84.

---

**Table 4** Overview of results for the catalytic hydrotreatment of pyrolytic sugars.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni</th>
<th>Ni-Cu</th>
<th>Ni-Pd</th>
<th>Ni-Pd-Cu</th>
<th>Ni-Mo-Cu</th>
<th>Ni-Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid phase (wt% on PS intake)</td>
<td>99.1</td>
<td>95.5</td>
<td>94.2</td>
<td>95.9</td>
<td>96.8</td>
<td>99.2</td>
</tr>
<tr>
<td>Solid (wt% on PS intake)</td>
<td>0.05</td>
<td>0.03</td>
<td>0.00</td>
<td>0.04</td>
<td>0.43</td>
<td>1.21</td>
</tr>
<tr>
<td>Gas phase (wt% on PS intake)</td>
<td>1.4</td>
<td>1.3</td>
<td>1.2</td>
<td>1.2</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Carbon dioxide (mol%)</td>
<td>3.4</td>
<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen (mol%)</td>
<td>96.6</td>
<td>96.9</td>
<td>96.9</td>
<td>96.9</td>
<td>98.1</td>
<td>97.9</td>
</tr>
<tr>
<td>Formation of a separate water phase</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Water content in liquid phase (wt%)</td>
<td>26.1</td>
<td>24.2</td>
<td>22.7</td>
<td>21.0</td>
<td>21.1</td>
<td>20.1</td>
</tr>
<tr>
<td>Amount of water formed (wt% on dry PS intake)</td>
<td>13.6</td>
<td>11.4</td>
<td>9.6</td>
<td>7.7</td>
<td>7.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Mass balance closure</td>
<td>101</td>
<td>97</td>
<td>95</td>
<td>97</td>
<td>98</td>
<td>101</td>
</tr>
<tr>
<td>Hydrogen uptake (NL/kg PS)</td>
<td>81</td>
<td>105</td>
<td>118</td>
<td>124</td>
<td>148</td>
<td>167</td>
</tr>
</tbody>
</table>

*Reaction conditions: 5 wt% catalyst on PS intake, 120 bar H2 (room temperature), 180 °C, 4 h.*

*Two liquid phases.*

*Average value for the two liquid products.*
Products with a higher H/C ratio are associated with a high hydrogenation activity of the catalysts. This was confirmed by plotting the hydrogen consumption versus the H/C ratio for all product oils (Fig. 5). An almost linear relationship is observed, with higher H₂ consumptions yielding products with higher H/C molar ratios. Thus, the H/C ratio of the product is indeed a good quantitative measure for catalytic activity.

For the monometallic Ni catalyst, the hydrogen uptake and the H/C and O/C molar ratio are the lowest within the series. Surprisingly, the elemental ratios (H/C and O/C) are even lower than for the PS feed. However, the oxygen content is considerably lower. These findings indicate that dehydration is not the main reaction occurring and that hydrogenation reactions leading to higher H/C ratios, also play a major role.

The statement that the non-catalytic thermal repolymerization reactions particularly lead to the formation of water is supported by considering the water production during the hydrotreatment reaction (Table 4) versus the activity of the catalysts (Fig. 6).

Indeed, for the most active catalysts, the lowest amount of water is formed, implying that repolymerization reactions leading to water do not occur to a significant extent for these catalysts. It supports the hypothesis that these catalysts are very active for the hydrogenation of reactive compounds to stabilized compounds that are less prone to polymerization at relatively low temperature.

To determine the extent of polymerization during reaction, the molecular weight distributions of the organic products were analyzed by GPC and the results are given in Fig. 7. After the catalytic hydrotreatment reactions, the molecular weight of the products are slightly higher than for the starting PS feed, indicative for the occurrence of polymerization reactions during the catalytic hydrotreatment. As postulated before, this is likely due to thermal reactions involving the carbonyl groups of the various sugars and smaller aldehydes (glycolaldehyde, Table 3) and ketones present in the PS feed (30). When considering the low molecular weight part of the distribution, the peak of LG (about 250 g/mol) is reduced considerably and a new peak at around 150–200 g/mol is formed. The latter is likely ethylene glycol (EG), which was confirmed by spiking the sample with pure EG. The latter may be formed by hydrolysis of LG (31).

A small but clear difference in the molecular weight distribution is found for the product oils obtained from the various catalysts (Fig. 7 top). The molecular weight increase is smallest for the Ni-Mo catalyst and highest for the Ni-Cu catalyst. For the monometallic Ni catalyst, the increase in molecular weight is more difficult to determine as two liquid phases are formed. However, the molecular weight of the organic phase is the highest of all, indicative for the occurrence of a high extent of polymerization reactions (Fig. S1, Supporting information).

The molecular weight increase is anticipated to be a function of the rate of polymerization versus hydrogenation, suggesting that a catalyst with the highest hydrogenation activity will give the smallest increase in molecular weight (Scheme 1). This hypothesis is indeed confirmed by plotting the activity of the catalyst, expressed in terms of H₂ uptake, versus the molecular weight of the product oil (Fig. 8). A clear trend is visible, with the most active catalyst (Ni-Mo) giving a product with the lowest molecular weight.

Based on these results, the Mo promoted catalyst is the best catalyst with H/C ratios similar or higher than the PS feed. However, the oxygen content is considerably lower. These findings indicate that dehydration is not the main reaction occurring and that hydrogenation reactions leading to higher H/C ratios, also play a major role.
for the hydrotreatment of the pyrolytic sugars at the prevailing relatively mild reaction condition. It shows the highest hydrogen uptake, the highest H/C value of the product oil and the least increase in the amount of higher molecular weight components.

The products were also analyzed by TGA to determine the residue after heating a sample to 900 °C. This residue (TG residue) is an indicator for the charring tendency of the liquid [13] (and as such related to the micro carbon residue test (MCRT) value conventionally used for crude oil feeds [32]). Products with a lower TG residue are preferred. The TG residues for the various products are plotted in Fig. 9; the TGA curves of the PS feed and a typical product using the Ni-Mo catalysts are shown in Fig. S2 (Supporting information). The TG residue of the products decreased from > 12 wt% for the original PS to values between 6 and 10 wt% for the product oils. For a non-catalytic run, the main product was a solid and only 10 wt% of a liquid phase was obtained. The TG residue of the solid phase was as high as 25 wt%, see Fig. S2 (Supporting information). The Ni catalyst with Mo as the promoter gave a product with the lowest TG residue. The TG residue of the products also correlates nicely with the activity of the catalysts in terms of H2 uptake. As such, it implies that a higher hydrogenation activity leads to products with a lower charring tendency.

These findings can be rationalized considering that in particular the aldehydes and ketones are responsible for polymerization reactions and the formation of char. During the hydrotreatment process, aldehydes and ketones are converted to alcohols [33] (Scheme 2), examples are the conversion of glucose and LG to sugar alcohols such as hexitols [34,35] and diols [36,37]. These alcohols have a lower charring tendency than the aldehydes/ketones present in the original PS feed.

The reactivity of carbonyl compounds were confirmed by GC-MS measurements as shown in Fig. 10.

The original PS feed contains significant amount of carbonyl-containing molecules, e.g. aldehydes (formaldehyde, acetaldehyde, glycolaldehyde, etc.) and ketones (acetol, 2(5H)-furanone) as shown in Fig. 1 (vide supra). After hydrogenation at 180 °C for 4 h, aldehydes and ketones are absent in the product. Hydrogenation of carbonyl-containing molecules was further confirmed by 1H-13C NMR (Fig. 11). After
hydrogenation at 180 °C for 4 h, the carbonyl compounds are fully converted, in agreement with the GC–MS results.

It is of interest to notice that the conversion of LG is far from quantitative and considerable amounts of LG are detected in the product. As such, the hydrolysis of LG to glucose and the subsequent hydrogenation of glucose to among others sorbitol is relatively slow on the timescale of the reaction under the prevailing reaction conditions with the Ni-Mo catalyst.

3.5. Catalysts characterization

Detailed catalyst characterization studies for the fresh catalysts used in this study are given in Ref. [38]. Here, we report additional measurements (N₂ physisorption data and CO chemisorption data) for the most active (Ni-Mo/SiO₂-Al₂O₃) and the least active catalyst (Ni/SiO₂-Al₂O₃). In addition, the spent catalysts after reaction were also analyzed to gain insights in structural changes induced by the hydrotreatment reaction.

### 3.5.1. Characterization of the fresh catalysts

XRD and TPR studies [38] revealed that the oxidized NiMo catalyst contains isolated highly dispersed Mo oxides, as well as highly dispersed Mo oxides in intimate contact with NiO. Upon reduction at 400 °C, only part of the Ni is reduced and the highly dispersed Mo oxides in intimate contact with NiO likely form a NiMo solid solution. These bimetallic species may be more active than monometallic ones and may explain the experimentally observed higher activity of the NiMo catalyst compared to the monometallic one. However, 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. Evidence for the latter has been reported for the

### Table 5

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET} m² g⁻¹</th>
<th>μmol CO g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>16.3</td>
<td>416</td>
</tr>
<tr>
<td>NiMo</td>
<td>13.2</td>
<td>337</td>
</tr>
</tbody>
</table>

Samples were pre-treated at 400 °C prior to the measurement, the details are given in Section 2.4.

Fig. 10. Representative GC-MS spectrum of the hydrogenated PS using Ni-Mo catalyst.

Fig. 11. Heteronuclear Single Quantum Coherence (HSQC) spectra of PS and hydrogenated PS using Ni-Mo: PS (green) and hydrogenated PS (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

![Image]

In Retention Time, min

13 14 15 16 17

18 19 20 21 22 23

Fig. 11. Heteronuclear Single Quantum Coherence (HSQC) spectra of PS and hydrogenated PS using Ni-Mo: PS (green) and hydrogenated PS (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
hydrodeoxygenation of esters using Mo supported Ni catalysts [39].

The N₂ adsorption-desorption isotherms of fresh Ni/SiO₂-Al₂O₃ and Ni-Mo/SiO₂-Al₂O₃ catalysts are provided in Fig. S3 (Supporting information). The BET surface area of fresh Ni/SiO₂-Al₂O₃ was 266 m²·g⁻¹ whereas a slightly lower value for the Ni-Mo catalyst was observed (219 m²·g⁻¹). These values are somewhat higher than reported in the literature for related catalysts (about 100–180 m²·g⁻¹) [7,19,20,40]. These differences are likely due to the fact that the
The spent catalysts were analyzed using TEM and SEM-EDAX. Clear agglomeration of metal nanoparticles was observed for the monometallic Ni catalyst after the catalytic hydrogenation as shown in Fig. 12e. This is likely due to the high Ni loading on the catalyst (48%). Agglomeration is by far less for the bimetallic catalyst (Fig. 12f and g). As such, it is well possible that 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. It also suggests that the Mo promoted catalyst is likely a more stable catalyst, though this effect was by far lower for the bimetallic Ni-Mo catalyst. As such, the presence of carbonaceous deposits on the Ni-Mo catalyst is likely a more stable catalyst, though this effect is particularly evident for the monometallic catalyst occurring during the hydrogenation reaction. These findings may affect catalyst activity considerably. Studies in continuous set-ups are in progress to determine the catalyst stability for prolonged runtimes.

4. Conclusions

The catalytic hydrotreatment of the PS fraction of pyrolysis liquids was studied at relatively low temperature (180 °C) using monometallic Ni and bimetallic Ni-Mo based catalysts characterized by a high amount of Ni. Catalyst screening experiments revealed that Mo addition to the nickel based catalyst gives the most active catalysts. Product analysis reveals that hydrogenation occurs to a significant extent and that thermal re-polymerization is reduced considerably for this catalyst. As such, these findings support the statement that active hydrogenation catalysts at low hydrotreatment temperatures (< 200 °C) are required to avoid excessive polymerization of mainly small aldehydes, ketones and other low molecular weight C5 and C6 sugars, ultimately leading to char.

Catalyst characterization studies revealed that the NiMo catalyst contains small metal nanoparticles with a certain amount of a NiMo solid solution, which could be the reason for the high activity of this catalyst. Alternatively, the Ni nanoparticles in combination with MoO4+ species may also have a positive effect on catalyst activity as the latter are known to be able to activate oxygenated molecules. Metal agglomeration was shown to be a possible source for catalyst deactivation. This was particularly evident for the monometallic Ni catalyst, whereas this effect was by far lower for the bimetallic Ni-Mo catalyst. As such, the presence of Mo appears to prevent Ni sintering. In addition, some coke deposition on the catalyst surface was detected by TEM and SEM-EDAX. Further studies in a continuous set-up to assess catalyst stability in detail are in progress and will be reported in due course.
The results of this study will be valuable input for the development of efficient catalytic hydrotreatment technologies for pyrolysis liquids involving a mild stabilization step followed by a deep hydrotreatment to obtain product oils with considerably reduced oxygen contents to be used as a co-feed in FCC units or as a blending component in biofuel. It appears that the Ni-Mo/SiO2-Al2O3 catalyst reported here is a very promising catalyst for the 1st mild hydrotreatment step to obtain a stabilized product in high carbon efficiencies to be used as input for the second deep hydrotreatment step.

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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.2017.10.006.

References


