Hydrotreatment of pyrolysis liquids derived from second-generation bioethanol production residues over NiMo and CoMo catalysts

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Keywords:
Lignin-rich digested stillage
Pyrolysis liquids
Hydrotreatment
Sulphided catalysts
Biobased chemicals

ABSTRACT

Lignin-rich digested stillage from second-generation bioethanol production is a unique biomass-derived feedstock, not only because it contains high amounts of lignin but also due to its residual amounts of cellulose and hemicellulose. In this study, catalytic hydrotreatment experiments were conducted on pyrolysis liquids obtained from the lignin-rich feedstock using sulphided NiMo/Al2O3 and CoMo/Al2O3 catalysts. The aim was to obtain a high conversion of the initial pyrolysis feed into a hydrotreated oil with a high phenolics and aromatics fractions. Experiments were carried out in a stirred batch reactor at 350 °C and 10 MPa of H2 (initial pressure). Product oils were obtained in about 60–65% w/w, the remainder being an aqueous phase (12–14% w/w), solids (7–8% w/w) and gas phase components (all on initial pyrolysis oil feed basis). The product oils were characterised in detail using various techniques (elemental composition, GCxGC-FID, GPC, and 2D HSQC NMR). The oxygen content was reduced from 23% w/w in the pyrolysis oils to 7.5–11.5% in the hydrotreated oils, indicative of the occurrence of hydrodeoxygenation reactions.

1. Introduction

The use of fossil resources for energy generation, transportation fuels and chemicals is under debate, particularly because of high CO2 emissions. Alternative resources are required, [1,2] and biomass is considered as an attractive alternative for biofuels and biobased chemicals, particularly because it is currently the only viable source of sustainable carbon [3,4]. Of all biomass sources, lignocellulosic (woody) biomass has been studied intensively, due to its abundance, availability, wide distribution, and non-direct competition with edible feedstocks.

Liquefaction of lignocellulosic biomass is considered to be of high importance as it facilitates transport and logistics [5]. One of the possible approaches to produce liquid products from lignocellulosic biomass is the conversion to bioethanol. Second-generation bioethanol processes are currently being commercialised (e.g., by Poet, Abengoa [6,7]). However, inevitably a solid residue is co-produced, known as stillage. This residue contains not only the original lignin, which is not converted in the process but also residual cellulose and hemicellulose fragments [8]. Anaerobic digestion has been applied as a means to convert the stillage to biogas, but significant quantities of a lignin-rich solid residue, known as digested stillage, remains [9,10].

As such, there is a high incentive to valorise the digested stillage. An attractive technology for this purpose is fast pyrolysis, which is typically carried out at elevated temperature (400–550 °C) in the absence of oxygen, resulting in depolymerisation/volatilisation of the biomass feedstock. From lignocellulosic biomass, the resulting vapour is rapidly condensed to give a pyrolysis liquid in yields up to 70% w/w [11–13]. Techno-economical evaluations of fast pyrolysis technology have shown it to be an economically feasible process, [14–18] and a number of some companies have semi-commercial pyrolysis units in operation (e.g., BTG’s Empyro [19,20]).

It is well established that the pyrolysis of (technical) lignins and lignin-rich feeds, such as the digested stillage from second generation bioethanol processes, is more difficult than of lignocellulosic biomass. Pyrolysis liquid yields are considerably lower than for woody biomass.
(approximately 20–50% w/w on dry basis), and operational issues are reported [21]. For instance feeding issues related to the low melting/softening temperature of lignin lead to blockage of the feeding system. However, considerable progress has been made in recent years by using advanced feeding systems [22]. We have recently explored the conversion of a lignin-rich digested stillage by fast-pyrolysis technology using a modified fluidised bed reactor in combination with staged condensation. A phase-separated liquid product was obtained in 28% w/w (as received feedstock basis), which consists of an organic phase (18% w/w) and an aqueous phase (10% w/w). The first was shown to have a higher energy density (27.2 MJ kg$^{-1}$) than the initial feedstock (20.6 MJ kg$^{-1}$) and the produced chars (24 MJ kg$^{-1}$).

The application of pyrolysis liquids is limited due to their relatively low thermal stability, high oxygen and water content, high viscosity and immiscibility with hydrocarbons [23,24]. A wide range of technologies have been employed to improve the product properties of pyrolysis liquids; examples include (reactive) esterification [25] and catalytic hydrotreatments [26–28]. The latter involves treatment of the pyrolysis liquid with hydrogen in combination with a suitable solid catalyst at elevated temperatures and pressures [25,26,29]. Typical reaction conditions for deep hydrotreatment are 10–20 MPa of hydrogen pressure and temperatures around 300–400 °C [29,30]. During the process, several reaction pathways occur; examples are hydrogenation, hydrogenolysis, hydrodeoxygenation, decarboxylation, decarboxylation, cracking/hydrocracking, and polymerisation reactions [30].

The type of catalyst determines the amount of oxygen removed, as well as the yields and the physical and chemical properties of the hydrotreated product oils [30,31]. Sulfided NiMo and CoMo catalysts on alumina are considered to be attractive ones as they are commercially available and have shown good performance regarding deoxygenation [32,33]. In addition, NiMo and CoMo catalysts are sulfur tolerant and actually require sulfur for high activity [30,34].

The catalytic hydrotreatment of lignin-derived pyrolysis liquids has been studied less often, and in less detail than that of pyrolysis liquids from lignocellulosic biomass. So far, the main emphasis has been on the catalytic hydrodeoxygenation of lignin model components such as anisole and guaiacol, while minor attention has been paid to real lignin-derived pyrolysis liquids. Recently, the catalytic hydrotreatment of lignin oils derived from the fast pyrolysis of various technical and organosolv lignins has been reported by de Wild et al. (2017). The best results were obtained using a phosphided NiMo catalyst on a carbon support; which provided a liquid product enriched in alkylphenols.

The focus of this study is catalytic hydrotreatment of a pyrolysis liquid obtained from the fast pyrolysis of a lignin-rich digested stillage using commercially available NiMo and CoMo catalysts supported on alumina. The primary objective was to obtain high yields of hydrotreated oils containing high amounts of low molecular weight compounds, (e.g., phenolics and aromatics), which are useful biobased chemicals. Aromatics and particularly benzene, toluene, and xylenes are currently produced from fossil resources in millions of tons per year and are important feeds for the production of a wide range of polymers (e.g., polystyrene, polyesters, polyamines, polyurethanes). Phenol and alkylated phenols are used for instance for the preparation of various resins (e.g., phenol-formaldehyde) and adhesives. The experiments were carried out in a batch reactor set-up, and the resulting product oils were analysed using a range of analytical techniques (GCxGC-FID, GPC and HSQC-NMR) to reveal more details of the molecular composition of the hydrotreated oils. Finally, a reaction network on molecular level is proposed based on the experimental data.

2. Materials and methods

2.1. Materials

The initial lignin-rich digested stillage was obtained from laboratory scale experiments at the Center for Microbial Ecology and Technology (CMET), Ghent University, Belgium (Fig. 1) from poplar wood using a two-step process involving bioethanol synthesis and subsequent biogas production from the resulting stillage. The dried digest digested stillage was used as the feed for a fast-pyrolysis experiment conducted at the Department of Green Chemistry and Technology, Ghent University Belgium.

Relevant properties of the lignin-rich digested stillage and the catalytic hydrotreatment feed are given in Table 1. The material contains significant amounts of carbon, oxygen and some nitrogen. The latter is likely from residual microorganism in the feed which contains nitrogen in the form of proteins. The acid insoluble lignin content (based on TAPPI T222 om-02 method) is 63.2% w/w (as received feedstock basis) indicating that the stillage is rich in lignin and confirming that the lignin fraction is hardly converted during the saccharification/fermentation and subsequent anaerobic digestion.

The pyrolysis liquids used in the study were obtained by fast pyrolysis of the lignin-rich digested stillage. A mechanically stirred N2 fluidized bed of sand particles at 480 °C was used as the pyrolysis reactor. Details of the setup are described in a previous catalytic fast-pyrolysis study from our group [36]. The liquid product from the first condenser (operated at 80 °C) was collected and shown to consist of two...
separate phases, an organic and a water phase. The organic phase was used as the feed for the hydrotreatment studies (Table 1).

NiMo (KF 848) and CoMo (KF 752) on alumina support from EuroCat were used as the catalysts. High purity hydrogen gas (> 99.99 mol%) was obtained from Hoekloos (The Netherlands).

### 2.2. Analytical techniques

#### 2.2.1. Elemental analyses and energy content of the feed and product oils

The elemental composition (CHN) of the pyrolysis liquid and hydrotreated-oils were determined using a FLASH 2000 organic elemental analyser (Thermo Fisher Scientific, Waltham, USA) equipped with a thermal conductivity detector (TCD). High purity helium (Alphagaz 1) from Air Liquide was used as a carrier and reference gas. High purity oxygen (Alphagaz 1) also from Air Liquide was used as the combustion gas. The oxygen content was calculated by difference.

The energy content of the pyrolysis liquids and hydrotreated oils was calculated using the Milne equation (eq. (1)) [37]. Input elemental data are mass percentage based.

\[
HHV (MJ \, kg^{-1}) = 0.341 \, C + 1.322 \, H - 0.12 \, (O + N) + 0.0686 \, S - 0.0153 \, Ash
\]  

#### 2.2.2. Gas phase product analyses

The composition of the produced gases was determined off-line using a GC (Hewlett Packard 5890 Series II) equipped with a thermal conductivity detector (GC-TCD) according to a method described in Ref. [29]. A Porablot Q Al2O3/Na2SO4 column and a molecular sieve (5 Å) column were used for separation. The injector temperature and the detector temperature were pre-set at 150 °C and 90 °C. The oven temperature was kept at 40 °C for 2 min, then heated to 90 °C at a rate of 20 °C min⁻¹ and kept at this temperature for 2 min. A reference gas supplied by Westfalen Gassen Nederland B.B. (55.19 mol% H₂, 19.70 mol% CH₄, 3.00 mol% CO, 18.10 mol% CO₂, 0.51 mol% ethylene, 1.49 mol% ethane, 0.51 mol% propylene and 1.50 mol% propane) was used for identification and calibrated quantification.

#### 2.2.3. Analysis of hydrotreatment feed and product oils

Two-dimensional gas chromatography with flame ionisation detection (GCxGC-FID) and gel permeation chromatography (GPC) analyses were performed following previously reported protocols [30,38]. The sample was analysed on a GCxGC-FID (JEOL) equipped with a cryo-detector temperature were pre-set at 150 °C and 90 °C. The oven temperature and the detector temperature were pre-set at 150 °C and 90 °C. The oven temperature was kept at 40 °C for 2 min, then heated to 90 °C at a rate of 20 °C min⁻¹ and kept at this temperature for 2 min. A reference gas supplied by Westfalen Gassen Nederland B.B. (55.19 mol% H₂, 19.70 mol% CH₄, 3.00 mol% CO, 18.10 mol% CO₂, 0.51 mol% ethylene, 1.49 mol% ethane, 0.51 mol% propylene and 1.50 mol% propane) was used for identification and calibrated quantification.

The pyrolysis liquids and product oils were also analysed by two-dimensional (2D) H–¹³C heteronuclear single-quantum correlation NMR (2D HSQC-NMR) using methods described by Lancefield et al. (2007) [39]. The resulting spectrum is two-dimensional (2D) with one axis for proton (¹H) and the other for a heteronucleus, in this case ¹³C. The spectrum contains a peak for each unique proton attached to a carbon atom and as such provides additional information on molecular composition compared to 1D NMR techniques. Either a Bruker Ascend 700 MHz equipped with a CPP TCI probe or a 500 MHz spectrometer with a CPP BBO probe were used. The pyrolysis liquids and product oils were dissolved in DMSO-d₆ (10 wt%). The HSQC-NMR spectra (1024 points for ¹H or 256 points for ¹³C) were recorded using a 90° pulse angle, a 1.5 s relaxation delay, and 0.08 s acquisition time for a total of 48 scans.

### 2.4. Experimental setup

The catalytic hydrotreatment reactions were carried out in a stainless steel batch reactor (100 ml, Parr Instruments Co.) equipped with a Rushton-type turbine using a procedure given in Refs. [26,39]. The stirring speed was set at 1000 rpm for all experiments. The autoclave has a maximum operating temperature of 400 °C and pressure of 35 MPa. Temperature and pressure were monitored on-line and logged on a computer. A schematic representation of the set-up is given in Fig. 2.

The reactor was filled with 15 g of a pyrolysate liquid, 0.75 g of catalyst and 25 μl of DMDMS (Sigma-Aldrich). The pyrolysate liquid to catalyst ratio was selected based on previous research in batch set-ups on the catalytic hydrotreatment of pyrolysis liquids from various biomass sources in our group [26,29,34]. Initially, the reactor was flushed with hydrogen several times to remove excess air and then pressurised using hydrogen at room temperature for further leak testing. Leak testing was done by pressurising the reactor at 15 MPa. Subsequently, the pressure was reduced purposely to achieve an initial pressure of 10 MPa. Stirring was started at 1000 rpm, and the reactor was heated to 350 °C at a heating rate of approximately 8 °C min⁻¹. The reaction time was set at t = 0 h when the predetermined temperature was reached. Reactions were performed in batch mode without addition of the consumed hydrogen gas. The pressure and temperature values were
recorded during the reactions, and the profiles were recorded and displayed using a data logger. After 4 h of reaction time, the reactor was cooled to room temperature at a rate of about 10–15 °C min$^{-1}$.

For the blank experiment, the reactor was loaded with the pyrolysis liquid feed and no catalyst, and using nitrogen instead of a hydrogen atmosphere. All experiments, except the blank experiment, were done in duplicate and the average values (including standard deviations) are given.

2.5. Products separation and quantification

Four main product phases were formed after the catalytic hydrotreatment reaction, viz. two liquid phases (an organic product oil and a water phase), solid residue (including the catalyst) and gas phase components. An overview of the procedure to separate the various products for mass balance calculations and product characterisation is given in Fig. 3.

After the hydrotreatment reaction, the reactor was depressurized, and the gas phase was collected in a 3L Tedlar gas bag, for its further analysis using GC-TCD analysis. The liquid and solid products were taken from the reactor and transferred to a 15 ml centrifuge tube (Sigma-Aldrich) and then centrifuged at 4500 rpm for 15 min. The hydrotreated liquid phase consists of an organic phase (lighter-than-water) and an aqueous phase. The liquid phases were separated and weighed for mass balance calculations. The solids in the centrifuge tube were washed with dichloromethane (DCM, Sigma-Aldrich) and then filtered using a filter paper with known weight and left to dry overnight.

The reactor was washed with DCM to remove residual oil and solids. The resulting dispersion was filtered using a filter paper with known weight and dried overnight to collect the solids. The two DCM washing liquids were combined and the DCM was removed by evaporation. The remaining organic fraction was weighted and added to the organic phase obtained after reaction. The measured weights of the organic
phase, aqueous phase, and the combined solid products were used for product yield calculations (% w/w). The gas yield was calculated from mass balance closures. Product yields and mass balances are calculated on a pyrolysis feed intake basis, as specified in Eqs. (2) and (3).

\[
\text{Product yield (\\% w/w)} = \frac{\text{Mass of product(s)}}{\text{Mass of pyrolysis feed}} \times 100 \tag{2}
\]

\[
\text{Mass balance (\\% w/w)} = \sum \left(\frac{\text{Mass of product(s)}}{\text{Mass of pyrolysis feed}}\right) \times 100 \tag{3}
\]

3. Results and discussion

3.1. Characterisation of the pyrolysis liquid used for the hydrotreatment experiments

Relevant properties of the pyrolysis liquid used as the feed for the catalytic hydrotreatment reactions in this investigation are given in Table 1. The elemental composition shows that the oil contains about 23% w/w of oxygen and 4.5% w/w of nitrogen. The HHV value was calculated using the Milne equation (eq. (1)) and found to be about 27.2 MJ kg\(^{-1}\). The pyrolysis liquid feed contain up to 20% w/w of low molecular weight compounds belonging to various groups (aromatics, alkylphenolics, ketons, esters), and a high proportion of higher molecular weight, non-GC detectable compounds, such as sugar oligomers and lignin fragments, as shown by GPC analysis (vide infra). The presence of nitrogen in the pyrolysis liquid feed is due to the presence of N-containing aromatics, for example, substituted indoles.

3.2. Catalytic hydrotreatment experiments

Catalytic hydrotreatment experiments with the pyrolysis liquids derived from the lignin-rich digested stillage were performed in a batch set-up at 350 °C, and 10 MPa of H\(_2\) (initial pressure), and 4 h reaction time. The conditions were selected based on previous studies on the catalytic hydrotreatment of various lignins [29]. Reactions were carried out in duplicate using CoMo and NiMo catalysts supported on alumina. In addition, a blank reaction was performed in the absence of hydrogen and catalysts.

As previously specified in the experimental section, the liquid phase consisted of two layers, a dark brown organic top phase and a clear aqueous bottom phase regardless of the type of catalyst used. These two layers could be separated easily using centrifugation and decantation. The main product is the organic phase, with yields between 60 and 65% w/w for the catalytic runs (Table 2). This yield is on the high side when compared with typical yields obtained for the hydrotreatment of pyrolysis oils from lignocellulosic biomass, and even commercial technical lignins using a sulfided catalyst [40]. For instance, Wildschut et al. (2009) reported the use of such catalysts for the hydrotreatment of wood-derived pyrolysis oils in batch set-ups at similar conditions and oil yields of 25% w/w (CoMo) and 30% w/w (NiMo) were given. However, a better comparison is the use of literature data for the hydrotreatment of typical lignin-derived pyrolysis oils in batch set-ups, as recently reported by de Wild et al. (2017). Here, the oil yield was 81% w/w using a CoMo on alumina catalyst, which is higher than found in

| Catalyst | Organic | Aqueous | Solid | Gas (by difference) |
|----------|---------|---------|-------|---------------------|
| NiMo catalyst | 60.4 ± 1.8 | 14.3 ± 0.3 | 6.9 ± 0.6 | 18.3 ± 2.6 |
| CoMo catalyst | 64.7 ± 1.3 | 11.9 ± 0.7 | 7.7 ± 1.5 | 15.7 ± 0.6 |
| Blank reaction | 41.1 | 9.8 | 36.9 | 12.2 |

* Product yields are based on initial pyrolysis feed.
this study, possibly due to the differences in reaction temperature (400 °C instead of the 350 °C used here) and the feed (a pure lignin-derived pyrolysis oil versus an oil from a more complex feed with also sugar derived molecules).

The yields of the aqueous phases are between 11.9% and 14.3% w/w, indicating the occurrence of hydrodeoxygenation reactions with the concomitant formation of water. These yields are by far lower than found after the hydrotreatment of typical pyrolysis liquids derived from wood (> 30%) [43]. The main cause for this difference is the water content of the feed. The feed used in this study only contains very low amounts of water whereas typical pyrolysis liquids from wood contain typically between 15 and 35% of water. Solid formation was limited and about 6.9–7.7% w/w for both catalysts. These values are slightly lower than found for this type of catalysts when processing wood-derived pyrolysis liquids (7.5–10% w/w) and higher than for an organosolv lignin-derived pyrolysis liquid oil (2.7% w/w, CoMo) [30,35].

The blank reaction resulted in the formation of high amounts of solids (36.9% w/w). Apparently, polymerisation reactions ultimately leading to solids occur to a significant extent in the absence of a catalyst. The formation of an aqueous phase indicates that dehydration reactions are taking place, in line with non-catalytic experiments for wood derived pyrolysis liquids (high-pressure thermal treatment process) [41].

Analysis of the gas phase by GC-TCD showed the presence of residual hydrogen, indicating that the catalytic reactions were not performed under hydrogen starvation conditions (Table 3). The main gas phase components were hydrocarbons in the form of methane, ethane and propane, whereas minor amounts of CO and CO2 were present. The sum of all gas phase components identified was less than 100 mol% (between 87 mol% and 93 mol%), indicating the formation of additional gas phase components higher than C3, e.g. butanes, which were not detected by the analyses method. Furthermore, additional small peaks were detected in each chromatogram which could not be identified and quantified. The formation of hydrocarbons and particularly methane may be explained by demethoxylation or hydrogenolysis reactions of the O-Me units, gasification reactions of reactive lignin fragments as well as gas phase reactions between initially formed CO/CO2 and hydrogen [42]. When comparing both catalysts, only minor differences in gas phase compositions were observed.

3.3. Characterisation of the product oils after catalytic hydrotreatment

3.3.1. Elemental composition and energy content of the product oils

Table 4 summarises the elemental composition of the product oils from the catalytic runs. Compared to the pyrolysis liquid feed, the oxygen content of the product oils is about halved, whereas the carbon and hydrogen contents are considerably higher. This is also clearly illustrated in a van Krevelen plot (Fig. 4), showing the molar H/C and O/C ratios of the feed and the product oils. The product oil obtained using the NiMo catalyst shows a lower oxygen content than that from the CoMo catalyst, showing that NiMo is more effective for deoxygenation reactions.

This is also clearly illustrated in a van Krevelen plot (Fig. 4), showing the molar H/C and O/C ratios of the feed and the product oils. The product oil obtained using the NiMo catalyst shows a lower oxygen content than that from the CoMo catalyst, showing that NiMo is more effective for deoxygenation reactions.

Apparently, full hydrodeoxygenation is not yet attained under the prevailing reaction conditions. These findings are in line with results reported by Wildschut et al. (2009) for the hydrotreatment of a pyrolysis liquid derived from woody biomass using supported CoMo and NiMo catalysts at similar conditions in a batch set up, attaining oxygen contents between 7.5 and 10.5% w/w in the hydrotreated oils. When deep hydrodeoxygenation to oxygen-free product is targeted, a two-stage hydrotreatment process with a second stage at higher process
Fig. 7. 2D HSQC NMR analysis of pyrolysis liquid feed and product-oils.
severity (higher temperature, longer times) is required [43–45].

Considerable amounts of nitrogen are present in the product oils (3.9–4.3 wt%, see Table 4). Actually, the amounts are only slightly lower than for the feed used for the hydrotreatment experiments (4.5 wt%, see Table 1). These findings imply that the nitrogen-containing compounds in the feed (e.g. substituted indoles, likely originating from residual proteins in the digested stillage) are rather recalcitrant to the catalytic hydrotreatment. This is in line with literature data on catalytic hydrodenitration, showing that aromatic nitrogen-containing molecules are not very reactive [46].

The reduction in oxygen content coupled with an increase in carbon and hydrogen content also results in a higher energy density of the product oils (up to 38.8 MJ kg$^{-1}$).

The molecular weight distributions of the products were determined using GPC (Fig. 5) and compared with the feed and the oil derived from the blank reaction (without catalyst, under 10 MPa of N$_2$ pressure). It shows that the molecular weight of the product oils after the catalytic runs are reduced considerably compared to the hydrotreatment feed. As such, catalytic hydrocracking reactions occur to a significant extent.

### 3.3.2. GCxGC-FID analysis

GCxGC analysis has shown to be a valuable tool to characterize complex bioliquids and to obtain quantitative information on the molecular composition [47]. Fig. 6 shows the GCxGC-FID chromatograms of the original hydrotreatment feed and the product oils. Clearly, the product composition has changed after catalytic hydrotreatment and it (visually) appears that more alkylphenolics, aromatics and hydrocarbons are present in the product oils.

The amounts of the various component classes were determined, and the results are given in Table 5. The total amounts of volatile, GC detectable components of the product oils from the catalytic runs is considerably higher (42% w/w hydrotreated oils basis for the CoMo catalyst and 50% w/w hydrotreated oils basis for NiMo catalyst) than for the hydrotreatment feed (17% w/w pyrolysis organic phase basis). These findings are in line with the GPC results and show the occurrence of hydrocracking and hydro(deoxy)genation reactions leading to the formation of low molecular weight components.

The chemical composition changes dramatically upon the catalytic hydrotreatment procedure. The amounts of the oxygenated compounds in the form of ketones, acids, esters and alcohols are reduced considerably. Most of the guaiacols present in pyrolysis liquid feed are also converted, likely by demethoxylation and methane formation, as seen experimentally. In addition, large amounts of alkylphenolics are formed and these are actually the major component class in the product oils. These findings are in line with the results obtained for the catalytic hydrotreatment of a lignin-rich pyrolysis liquid obtained from Kraft lignin using a CoMo catalyst (alkylphenolics up to 22% w/w on hydrotreated oils basis [35]). In addition, the amounts of hydrocarbon compounds (e.g. alkanes, cyclohexanes, aromatics, and naphthalenes) also increased considerably, likely by subsequent hydrodeoxygenation reactions of alkylphenolics (vide infra).

### 3.3.3. 2D HSQC NMR analysis

The use of GC methods for analysis of complex bio-liquids with a
large number of components belonging to different product classes and with a large spread in molecular weight is hampered by the fact that only the low molecular weight, volatile fraction is detectable and quantifiable. NMR analysis, and particularly 2D-NMR provides insight on all component classes present in the sample. The NMR spectra for the pyrolysis liquid feed and the product oils obtained using both catalysts are given in Fig. 7.

The NMR spectrum for the pyrolysis liquid feed show signals in three discrete regions, viz. the aromatics/alkylphenolics/naphthalene, the oxygenated-aliphatic and the aliphatic region. The NMR spectra of the product oils after the catalytic hydrotreatment using both catalysts differ considerably from the feed. The only clear resonances present in the product oils are from the aromatic/alkylphenolics/naphthalenes and aliphatic compounds, in line with GC data. A clear reduction in the amount of –O–Me groups is observed after the hydrotreatment as evident from a reduction in the intensity of resonances in the oxygenated aliphatics C-H’s region. This finding is in line with the GCxGC data, showing only minor amounts of (substituted) guaiacols. The combined GC and NMR data suggest that not only the level of methoxy removal from the low molecular weight components as detected by GC is high, but that this is also true for the oligomer fraction in the product oils that is not GC detectable. In addition, the NMR data also imply that the chemical composition of the product oils for both the CoMo and NiMo catalysts is similar.

3.4. Comparison of catalytic performance of the NiMo and CoMo catalysts

Both the NiMo and CoMo catalyst on alumina are active for the hydrotreatment of the pyrolysis liquids obtained from digested stillage and give product oils in yields larger than 60% w/w hydrotreated oils basis, which are significantlydeoxygenated and depolymerised. An overview of relevant product yields and product composition data for both catalysts is given in Table 6.

The NiMo catalysed hydrotreatment reaction gave a slightly lower product oil yield than the CoMo catalysed one. However, the quality of the product oil in terms of oxygen content, heating value and amounts of low molecular weight components (total GC detectable compounds and GPC data) is higher, see Table 6 for details. In addition, when aiming for high yields of valuable low molecular weight aromatics and alkylphenolics, the yields based on pyrolysis liquid feed are slightly higher for the NiMo catalyst (14.3% w/w, versus 12.4% w/w for CoMo).

3.5. Reaction network for the catalytic hydrotreatment reaction

Based on all results reported here and literature data, a simplified reaction network is given in Fig. 8 for the catalytic hydrotreatment process of a lignin-rich pyrolysis liquid like digested stillage.

The hydrotreatment feed contains three main component classes, viz. lignin monomers and oligomers, some sugar derived molecules (levoglucosan, glycolaldehyde) and nitrogen-containing heterocycles, in line with all analytical data. In the figure, only a limited number of representative compounds are given. The lignin oligomers are prone to depolymerisation and in combination with demethoxylation by hydrogenolysis reactions result in the formation of alkylphenolics. The latter are also reactive under the prevailing reaction conditions and may be converted to either aromatics or directly to (cyclic) alkanes. The ratio between both pathways is determined by the tendency of the catalyst to either hydrogenate aromatic C-C bonds or hydrodeoxygenate the alkylphenolics. Given the fact that the low molecular weight alkylphenolics are dominant in the GC detectable fraction, it is clear that the rate of these subsequent reactions to aromatics/alkanes is low under the prevailing reaction conditions. Some of the intermediates (oligomers, monomers) are relatively unstable and may repolymerise to highly condensed aromatic structures, ultimately leading to solids. The sugar-derived molecules are all converted during the hydrotreatment process (2D-NMR). Levoglucosan is possibly initially hydrolysed to glucose, which is known to be converted under reductive conditions to a number of C6 alcohols/hydrocarbons as well as lower carbon number components (by retro-aldol reactions, giving diols and triols). Analysis by GC-MS show that the nitrogen-containing heterocycles in the feed like indoles are converted to (substituted) pyrroles. However, nitrogen removal by hydronitrification is known to be rather difficult for such aromatic heterocyclic compounds, supported by the limited difference of the amount of N in the feed and product oils.

4. Conclusions

Catalytic hydrotreatment of pyrolysis liquids obtained from the fast pyrolysis of a lignin-rich digested stillage yielded significant amounts of upgraded product oils (60–64% w/w, initial pyrolysis oils feed basis) and limited amounts of char. Deoxygenation, as well as depolymerisation, was shown to occur to a significant extent and as such the quality of the oil in terms of oxygen content, amounts of monomeric components and heating value has improved considerably compared the pyrolysis liquid feed. The product oil contains up to 50% w/w (hydrotreated oil basis) of low molecular weight compounds (GCxGC), particularly in the form of alkylphenolics. These may, after further work-up by for example distillation and/or solvent extraction, be used as green alternatives for fossil-derived phenol derivatives. The catalytic performance for both the sulphided NiMo and CoMo catalysts were rather similar, the main difference being the oil yield (slightly higher for CoMo) and the deoxygenation level (slightly higher for NiMo).

The results indicate that a lignin-rich solid residue from a second-generation bioethanol/an anaerobic digestion process has potential to be converted to a liquid energy carrier using a sequential fast pyrolysis - hydrotreatment process leading to a product oil with a higher energy content than the original pyrolysis liquid and the digested stillage. Typically the amount of digested stillage is about 30% w/w (feedstock basis) on biomass intake after the fermentation/anaerobic digestion processes. When considering a fast pyrolysis liquid yield of 18% w/w based on digested stillage in the fast pyrolysis step and a 60% w/w yield for the product oil based on fast pyrolysis liquid after hydrotreatment as shown here, this means that approximately 11% w/w of the digested stillage is converted to a product oil with potentially higher value. This is expected to have a positive effect on the techno-economic viability of second generation bioethanol processes by giving value to a solid waste product. However, more detailed techno-economic evaluations for the whole value chain will be required to substantiate this statement.

Acknowledgements

The authors would like to acknowledge Léon Rohrbach from the University of Groningen for help with the GC-TCD, GPC, and GCxGC-FID analyses; H.H. van de Bovenkamp, Fenna Heins, and Monique Bernardes Figueirêdo from University of Groningen, for technical and practical assistance. The Multidisciplinary Research Platform “Ghent Bio-economy” is acknowledged for providing access to the lignin feedstock. The LOTUS Programme of the European Union is acknowledged for providing a doctoral scholarship to Neil Priharto.

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