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Published in:
Fuel processing technology

DOI:
[10.1016/j.fuproc.2021.107160](https://doi.org/10.1016/j.fuproc.2021.107160)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2022

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Yang, H., de Wild, P., Lahive, C. W., Wang, Z., Deuss, P. J., & Heeres, H. J. (2022). Experimental studies on a combined pyrolysis/staged condensation/hydrotreatment approach to obtain biofuels and biobased chemicals. *Fuel processing technology*, 228, [107160]. <https://doi.org/10.1016/j.fuproc.2021.107160>

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Experimental studies on a combined pyrolysis/staged condensation/hydrotreatment approach to obtain biofuels and biobased chemicals

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ARTICLE INFO

Keywords:

Fast pyrolysis
Staged condensation
Catalytic hydrotreatment
Biofuels
Biobased alkylphenols

ABSTRACT

Fast pyrolysis is an efficient technology to convert lignocellulosic biomass to a liquid product. However, the high contents of oxygenated compounds and water hinder the direct utilization of pyrolysis oils. Here, we report an upgrading concept to obtain liquid products with improved product properties and enriched in valuable low molecular weight chemicals and particularly alkylphenols. It entails two steps, viz. i) pyrolysis with in-situ staged condensation at multiple kg scale followed by ii) a catalytic hydrotreatment of selected fractions using a Ru/C catalyst. Of all pyrolysis oil fractions after staged condensation, the product collected in a condenser equipped with an electrostatic precipitator (ESP) at 120 °C was identified as the most attractive for hydrotreatment when considering product yields and composition. The best hydrotreatment results (Ru/C, 350 °C, 100 bar H₂, 4 h) were achieved using beechwood and walnut shells as feedstock, resulting in a high oil yield (about 64 wt% based on pyrolysis oil fraction intake) with a higher heating value of about 37 MJ/kg and enriched in alkylphenols (about 16 wt%). Overall, it was shown that the type of biomass (beech sawdust, walnut granulates, and pine/spruce sawdust) has a limited impact on liquid and alkylphenols yields which implies feedstock flexibility of this integrated concept.

1. Introduction

The use of renewable carbon resources such as biomass for transportation fuels and chemicals is in high demand due to environmental concerns related to the use of fossil fuels. Among various biomass resources, lignocellulosic biomass is a promising resource to produce biofuels, biobased chemicals, and materials because of its abundance, availability, and non-direct competition with edible feedstocks [1].

Fast pyrolysis is considered an effective and economical way to convert biomass into liquid products facilitating transport and logistics [2,3]. The product, pyrolysis oil or pyrolysis liquid [4] is a single-phase, brown, viscous liquid containing water and a large number of oxygenated chemicals [5,6]. Typically upgrading is required to extend its application range.

Catalytic hydrotreatment is an attractive technology to upgrade pyrolysis oil and its fractions [3,7]. It is a process where pyrolysis oil is reacted with hydrogen and a catalyst at elevated temperature and pressure leading to a product with improved product properties. A

network of consecutive and competing reactions including repolymerization, decarbonylation/decarboxylation, hydrodeoxygenation, hydrogenation, and (hydro)cracking [4] has been proposed to explain the molecular transformations occurring during hydrotreatment. Repolymerization of pyrolysis oil during processing mainly involves the sugar fraction of the oil and occurs at the initial stage of the hydrotreatment process, which ultimately leads to the unfavorable formation of char [8]. An active hydrogenation catalyst is needed to stabilize pyrolysis oils to minimize these unfavorable repolymerization reactions. Ru/C has proven to be an excellent catalyst for the stabilization of pyrolysis oils [8,9]. It can also be applied for deep hydrodeoxygenation of pyrolysis oil at elevated temperatures (e.g. 350 °C) [10,11] as well as hydrotreatment of technical lignin or lignin pyrolysis oil to obtain alkylphenols [12,13]. As a result, Ru/C was selected as a benchmark catalyst in this study.

In this investigation, the emphasis is not on the catalytic hydrotreatment of pyrolysis oils as such but the hydrotreatment of selected fractions of pyrolysis oil to improve liquid yields and to enhance the yields of interesting biobased chemicals in general and alkylphenols in

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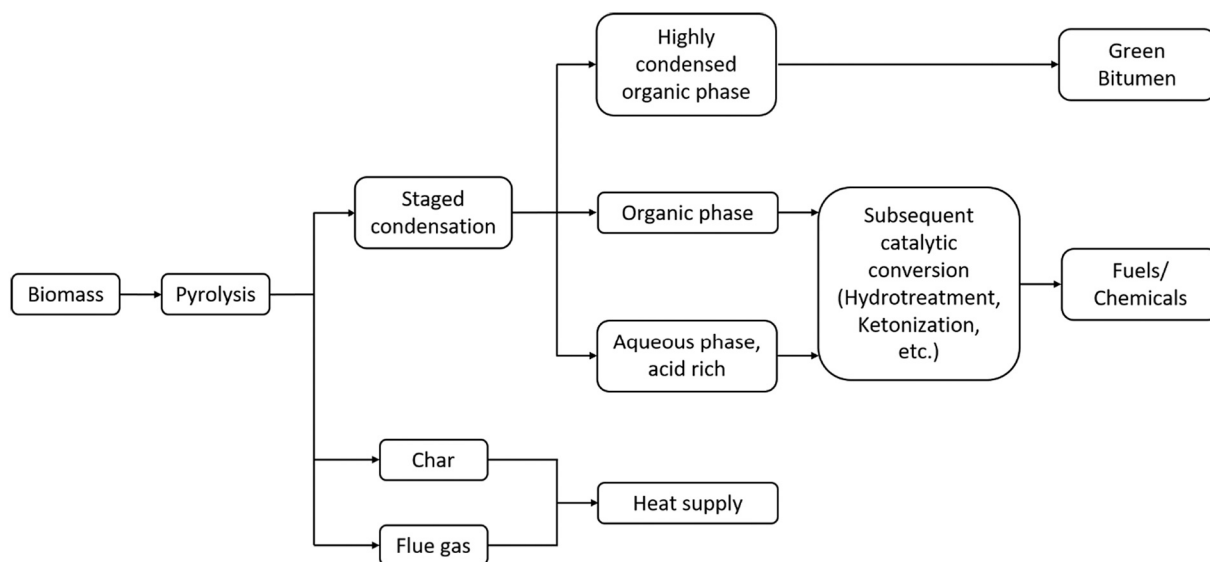
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<https://doi.org/10.1016/j.fuproc.2021.107160>

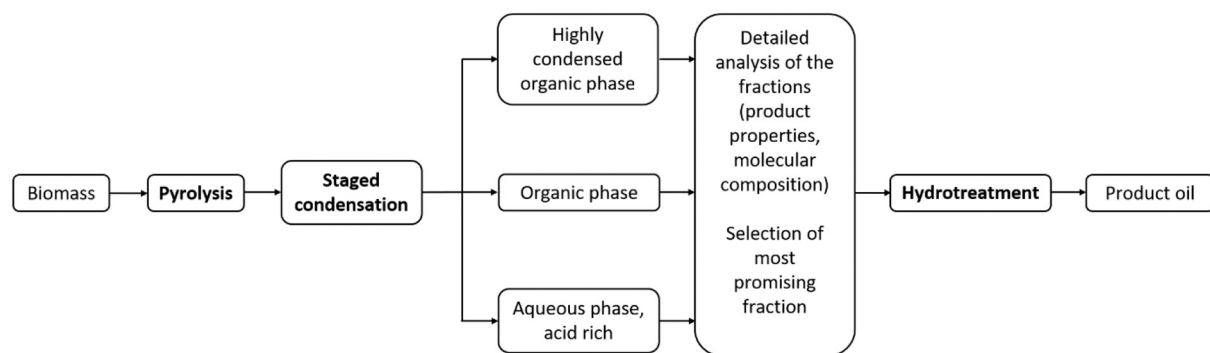
Received 12 October 2021; Received in revised form 28 December 2021; Accepted 31 December 2021

Available online 17 January 2022

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Scheme 1. Overview of the concept of combined fast pyrolysis, staged condensation and catalytic upgrading.



Scheme 2. Integrated approach of fast pyrolysis, staged condensation and catalytic hydrotreatment used in this study.

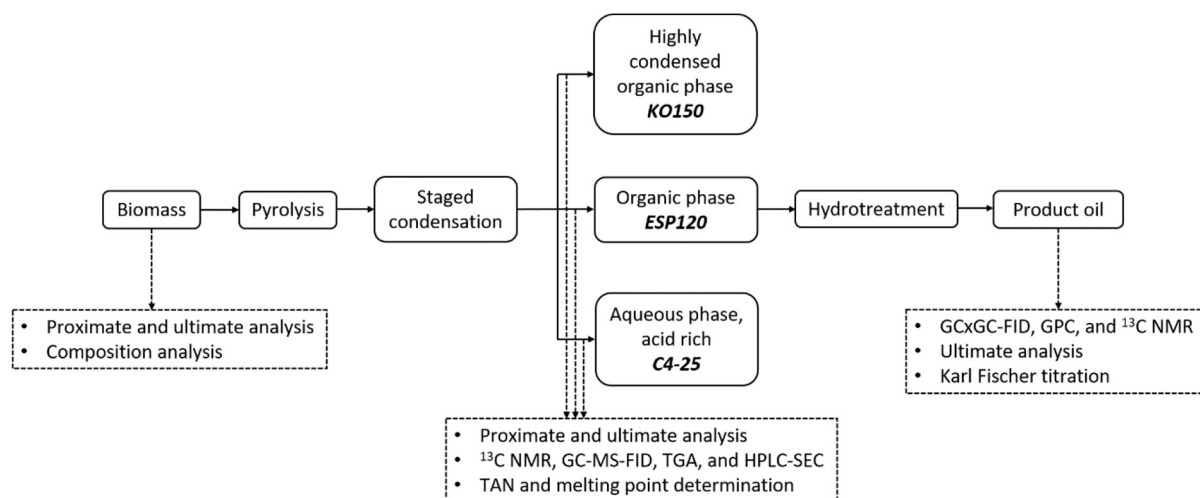
particular. Fractionation of pyrolysis oil has been investigated in detail in the last decade and is mainly aimed to obtain oil fractions with improved product properties, such as lower water content, lower acidity, and higher heating values [14]. The fractionation can be conducted via either *ex-situ* or *in-situ* methods. The *ex-situ* approach includes molecular distillation and precipitation of the pyrolytic lignin fraction by adding water [15,16]. The *in-situ* approach aims to separate the hot pyrolysis vapors with electrostatic precipitators or cyclonic condensers at different temperatures [14]. Therefore, the chemical composition and product properties (viscosity, heating value, water content, and acidity) of the fractions heavily depend on the condensation setup [17,18]. These unique properties lead to different potential applications of each fraction, see Scheme 1 for details [19].

Aqueous phase fractions are rich in organic acid (carboxylic acid), which may be upgraded by ketonization to remove the acid functionality and to increase the carbon chain length [20]. The organic acids can also be used to pretreat the biomass feed and to remove alkali and alkaline earth metals (AAEMs), which has been shown to lead to higher pyrolysis oil yields and particularly the pyrolytic sugar fraction [21]. Highly condensed oil fractions can be used as bitumen modifiers to improve the physical properties, road performance, and water resistance of asphalt [22]. Less condensed fractions with lignin-derived oligomers [18] have the potential to be upgraded to valuable chemicals (e.g. alkylphenols) via catalytic hydrotreatment. However, previous studies about upgrading these fractions by hydrotreatment focused on producing transportation fuels [9,23,24]. As far as we know, studies aiming at the

optimization of biobased chemicals in general and alkylphenols in particular by catalytic hydrotreatment of organic fractions of pyrolysis oils have not been reported.

In this paper, a two-step approach *viz.* i) pyrolysis with *in-situ* staged condensation followed by ii) a catalytic hydrotreatment of a selected fraction using a Ru/C catalyst was studied to obtain a product oil with improved product properties and preferably enriched in valuable biobased chemicals in general and biobased alkylphenols in particular (Scheme 2). The latter are interesting building blocks for a wide range of chemicals (e.g. phenol, or as a monomer for resin production), which are currently produced from petrochemical resources. There is a strong incentive to green up phenols production, for instance by using lignocellulosic biomass [25].

Three types of lignocellulose biomass were used as feedstock (beech sawdust, walnut granulates, and softwood sawdust) in this study. These were selected as they are i) abundantly available and ii) have different lignin contents, which is known to be the main precursor for monomeric alkylphenols when using catalytic thermochemical technologies. In the first part of this paper, pyrolysis/staged condensation including detailed determination of the properties and molecular composition of the different pyrolysis oil fractions will be discussed. Subsequently, the most suitable fraction was selected for catalytic hydrotreatment studies to obtain liquids with improved properties. The product yields, heating value, and amounts of biobased chemicals in general and alkylphenols in particular in the liquid product oils were determined. With this information, the preferred biomass source, the most interesting staged



Scheme 3. Schematic representation of the experimental procedure, abbreviations used for the various pyrolysis oil fractions, and the analytical techniques used for characterization of the different fractions.

condensation fraction, and hydrotreatment conditions to obtain the highest yield of liquid product and alkylphenols were evaluated. The combination of in-situ pyrolysis oil fractionation and hydrotreatment to obtain products enriched in valuable biobased chemicals (alkylphenols), the rational identification of the most suitable pyrolysis oil fraction for the purpose of obtaining biobased chemicals based on extensive analyses of the various fractions using dedicated analytical techniques, and the selection of the most promising biomass sources by testing a variety of feedstocks for the integrated concept are novel elements of the research reported in this paper.

2. Experimental section

2.1. Chemicals and feed

Three biomass feeds were used in this project: (1) deciduous (beech) sawdust, (2) coniferous (spruce and pine) sawdust, of which the lignin content is relatively high, and (3) granulated walnut shells as an example of a lignin-rich agricultural residue. The deciduous and coniferous sawdusts are commercial products that are available from the Rettenmaier company. The deciduous sawdust is produced from beechwood and marketed under the trade name “Räuchergold™”. The average particle diameter is 0.75 mm. The coniferous sawdust (coded LignoCel 9 - Mixed Conifers, spruce, and pine) is a fairly coarse and fibrous sawdust with a particle size of approx. 0.8–1.1 mm. The walnut shell granulate is also a commercial product marketed by the Kuhmichel company in Holten as a mild abrasive. The material was supplied as granules with an average diameter of 0.8–1.0 mm. The feedstocks were analyzed by standard chemical analysis methods.

All the chemicals used in this study were of analytical grade and were used without further purification. Ru/C with 5 wt% Ru loading was acquired from Sigma-Aldrich. Sulfuric acid (95–97%, Boom B.V.), xylose ($\geq 99\%$, Sigma-Aldrich), mannose ($\geq 99\%$, Sigma-Aldrich), and galactose ($\geq 99\%$, Sigma-Aldrich) were used for composition analysis of the biomass feedstock. Dimethyl sulfoxide- d_6 (DMSO- d_6 , 99.5 atom%) for ^{13}C NMR was obtained from Sigma-Aldrich. Potassium hydroxide ($\geq 85\%$, Sigma-Aldrich) was used for acidity assessment. Isopropanol ($\geq 99.5\%$, Sigma-Aldrich) was used as the solvent to dilute the pyrolysis oil fractions. Deuterated ethylbenzene, phenol, and resorcinol were obtained from Sigma-Aldrich and used as internal standard; dichloromethane (DCM) and acetone from Boom B.V. were used as a solvent for the extraction of organic fractions after hydrotreatment. Tetrahydrofuran (THF, Boom B.V.) and di-*n*-butylether (DBE, 99.3%, Sigma-Aldrich) were used for the quantification of main components in hydrotreated

oils. High purity (>99.99 mol%) nitrogen, helium, and hydrogen were purchased from Linde. The reference gas for quantification of the gas-phase compound was supplied by Westfalen Gassen Nederland B.V.

2.2. Analytical techniques

All analytic techniques used in this study are summarized in Scheme 3 and they are described in detail in the following sections.

2.2.1. Carbohydrate analysis of the feedstocks

The carbohydrate composition analysis was conducted according to an NREL method [26]. 0.3 g sample was hydrolyzed by 72% sulfuric acid at 30 °C for 1 h and further diluted to 4% at 121 °C for another 1 h. The monosaccharide content was determined by HPLC (1200 Agilent Technologies) with a refractive index detector (RID). An Aminex column HPX-87H (Bio-Rad) was used and operated at 50 °C with 5 mM sulfuric acid as the eluent at a flow rate of 0.6 mL min $^{-1}$. Xylose, mannose, and galactose are eluted at the same retention time and as such integrated as a single peak.

2.2.2. Characterization of pyrolysis oil fractions

For all three feedstocks, the organic pyrolysis oil fractions KO150, ESP120, and C4-25 (see Scheme 3 for coding) were extensively analyzed using state-of-the-art physical and chemical analysis methods detailed below.

2.2.3. Ultimate analysis of pyrolysis oil fractions

Ultimate analyses (C, H, N, O, S, HHV, ash elements) were conducted according to standard (ASTM) methods. A EuroVector EA3400 Series CHNS-O analyzer was used to determine the C, H, N, and S content. The amount of oxygen was determined by the difference. All analyses were carried out in duplicate and the average value is reported. The higher heating value (HHV) of all samples including pyrolysis oil fractions and hydrotreated oils was evaluated by the Milne equation as shown in Eq. (1) [27]. Elemental data used in the equation are mass-based.

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

2.2.4. Acidity assessment for the pyrolysis oil fractions

A rough approximation of the acidity of the pyrolysis oil fractions was obtained by measuring the amount of potassium hydroxide needed to neutralize the carboxylic acids (acetic acid, formic acid, and levulinic acid, as analyzed via GC-MS-FID) in 1 mg of a pyrolysis oil fraction.

2.2.5. GC-MS-FID analysis of the pyrolysis oil samples

GC-MS-FID analyses of the pyrolysis oil samples were conducted using an Agilent 7890A GC equipped with an Agilent 5975C MS detector. After a cold-trap collection at $-150\text{ }^{\circ}\text{C}$ (a concentration step, before the actual injection and separation on the GC column to enhance resolution), the pyrolysis products were thermally desorbed and injected on a capillary column (Zebtron ZB-WAXplus, $30\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$). The injection temperature was set at $250\text{ }^{\circ}\text{C}$ and a split ratio of 40 was applied. Helium was used as the carrier gas at a constant flow mode of 1 mL min^{-1} . The following GC oven program was used: $50\text{ }^{\circ}\text{C}$ isotherm for 5 min, and then heated up to $245\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$. This GC-MS-FID method was developed in-house (ECN - TNO) for the analysis of isopropanol (IPA) dissolved polar compounds from the thermal conversion of biomass. The calibration standard is an IPA solution with a collection of around 60 compounds that are regularly encountered in biomass-derived samples (volatile compounds, various ketones, and aldehydes, various phenols, other aromatics such as poly-aromatic hydrocarbons (PAH) and organic acids). Via the analysis of a range of calibration standard solutions in IPA, a calibration curve is prepared to determine the amounts of the identifiable compounds in the pyrolysis oil fractions. The concentration range of the calibration curve is typically $5\text{--}250\text{ }\mu\text{g/mL}$. An internal standard was used ($50\text{ }\mu\text{L}$), which consisted of a mixture of deuterated ethylbenzene, deuterated phenol and deuterated resorcinol (about $1000\text{--}2000\text{ }\mu\text{g/mL}$) in IPA. The GC-MS method is only suitable to determine amounts of individual known compounds. Peaks, originating from unknown species cannot be determined accurately by MS detection. To enable an estimation of the amounts of unknown compounds, samples were analyzed by GC-FID as well. The GC-FID method is identical to the GC/MS method to ensure as much as possible identical peak retention times. First, the GC-MS standard solution was used to establish the retention times of the identifiable species. Then, the cumulative peak area of all known compounds was calculated. Finally, the amount of unknown species is calculated according to Eq. (2):

$$\text{unknowns}_{\text{total}} = (100\% - \%\text{knowns}_{\text{total}}) \times (\text{knowns}_{\text{total}}) / (\%\text{knowns}_{\text{total}}) \quad (2)$$

Higher molecular weight components with low volatility are not measured by the GC-MS-FID method. They are designated as oligomeric species and their yield is estimated as the difference between the total sample weight and the cumulative weight of all the quantified species (knowns and unknowns), including the water.

2.2.6. HPLC-SEC and GPC analysis of the pyrolysis oil samples

The molar mass distribution of the pyrolysis oil samples (50 mg dissolved in 50 mL of a 0.5 M NaOH solution) was determined using size exclusion chromatography (SEC). Analyses were performed using commercially available PSS MCX columns ($5\text{ }\mu\text{m}$ particle size, $500\text{ }\text{\AA}$ porosity designed for polymers between 100 and $35,000\text{ Da}$) equipped with a UV detector (280 nm , Agilent). The temperature of the column was set at $40\text{ }^{\circ}\text{C}$. The flow rate of the mobile phase (aqueous NaOH) was set at 1 mL min^{-1} . Sodium poly(styrene sulfonate) samples with known molecular weight distributions were used for calibration. The molecular weight distributions of the pyrolysis oil fractions (KO150, ESP120, and ESP100) and hydrotreated pyrolysis oils were also determined using gel permeation chromatography (GPC) analyses using an Agilent HPLC 1100 system equipped with three MIXED-E columns (length 300 mm , i. d. 7.5 mm) in series, and a GBC LC 1240 refractive index detector (RID). Polystyrene standards with different molecular weights were used for calibration. All samples were diluted by THF with a concentration of about 10 mg mL^{-1} and two drops of toluene were added as a flow marker.

2.2.7. TGA of the pyrolysis oil samples

TGA is a versatile method that was deployed to assess the thermal behavior of the pyrolysis oil samples as a function of temperature. TGA offers a quick method to determine parameters such as moisture,

volatiles, ash, fixed carbon contents (proximate analysis) and micro carbon residue (MCR) in the samples. In addition, TGA was deployed to assess the thermal stability of pyrolysis oil samples at a fixed (maximum) temperature to assess their potential for applications that would require a thermal treatment such as for bitumen or shipping fuels. A small amount ($10\text{--}50\text{ mg}$) of material is placed in a crucible, located in a sensitive thermal (micro) balance, and heated under an inert atmosphere according to a programmed temperature ramp at a slow rate (e.g. $10\text{ }^{\circ}\text{C min}^{-1}$). Upon increasing the temperature, the sample will start losing weight, first from the release of moisture, later as a consequence of thermal devolatilization of degradation fragments. This continues until a stable level is reached. The remaining solid residue is a measure of char. By changing the atmosphere from inert to air, the residual carbonaceous char can be combusted. The small amount left in the crucible after this combustion step is indicative of the amount of (inorganic) mineral matter (ash). The pyrolysis oil samples were measured using the Mettler TGA/DSC 3+ with the following temperature program: heat up from room temperature to $105\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 , 10 min at $105\text{ }^{\circ}\text{C}$ under N_2 , further heating from $105\text{ }^{\circ}\text{C}$ to $900\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 , $900\text{ }^{\circ}\text{C}$ for 10 min , change the atmosphere to air to the combust char to determine the ash content. In the thermal stability test, the sample was heated to $180\text{ }^{\circ}\text{C}$ using the temperature ramp as given above. The weight loss at isothermal ($180\text{ }^{\circ}\text{C}$) conditions was then measured.

2.2.8. NMR analysis of the pyrolysis oil and hydrotreated pyrolysis oil samples

^{13}C NMR was recorded with a Bruker 600 MHz spectrometer. Quantitative ^{13}C NMR was acquired using 0.5 g oil dissolved in 0.8 g $\text{DMSO-}d_6$ with 0.1 g of chloroform as internal standard, employing an inverse-gated decoupling sequence, with a relaxation delay of 5 s and 1024 scans. The obtained data was managed by MestReNova software. As the KO150 fractions proved to be only sparingly soluble in any tested solvents including $\text{DMSO-}d_6$, the ^{13}C NMR spectra showed only peaks corresponding to those of levoglucosan present (Fig. S3). So quantitative ^{13}C NMR analysis was only conducted for ESP120 fraction and their hydrotreated pyrolysis oil samples.

2.2.9. GC-TCD analysis of the gas phase samples

The composition of the gas phase after hydrotreatment was determined using gas chromatography (Hewlett Packard 5890 Series II) with a thermal conductivity detector (TCD). A Porablot Q $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ column and a molecular sieve column (5 \AA) were connected in series for separation. A reference gas with the following composition: 54.40% H_2 , 20.70% CH_4 , 2.99% CO , 17.90% CO_2 , 0.51% ethylene, 1.50% ethane, 0.51% propylene, and 1.49% propane was used for identification and quantification of produced gas products.

2.2.10. GCxGC-FID analysis of the pyrolysis oil and hydrotreated pyrolysis oil samples

Two-dimensional gas chromatography analyses were performed on the organic liquid products, using a Trace GCxGC Interscience equipment equipped with a cryogenic trap system, two capillary columns: an RTX-1701 capillary column ($30\text{ m} \times 0.25\text{ mm i.d.}$ and $0.25\text{ }\mu\text{m}$ film thickness) connected to a Rxi-5Sil MS column ($120\text{ cm} \times 0.15\text{ mm i.d.}$ and $0.15\text{ }\mu\text{m}$ film thickness), and a flame ionization detector (FID). A dual jet modulator was applied to trap the samples by CO_2 with a modulation time of 6 s . Helium was used as the carrier gas with a flow rate of 0.8 mL min^{-1} . The injector temperature and FID temperature were set at $280\text{ }^{\circ}\text{C}$. The oven temperature was kept at $40\text{ }^{\circ}\text{C}$ for 5 min and then heated to $250\text{ }^{\circ}\text{C}$ with a rate of $3\text{ }^{\circ}\text{C min}^{-1}$. The pressure was set at 0.7 bar at $40\text{ }^{\circ}\text{C}$. The identification and quantification of the main component groups (e.g., alkanes, aromatics, and alkylphenols) in the hydrotreated oils were performed following reported protocols from our group, using an average relative response factor (RRF) per component group with DBE as an internal standard [28,29]. All samples were

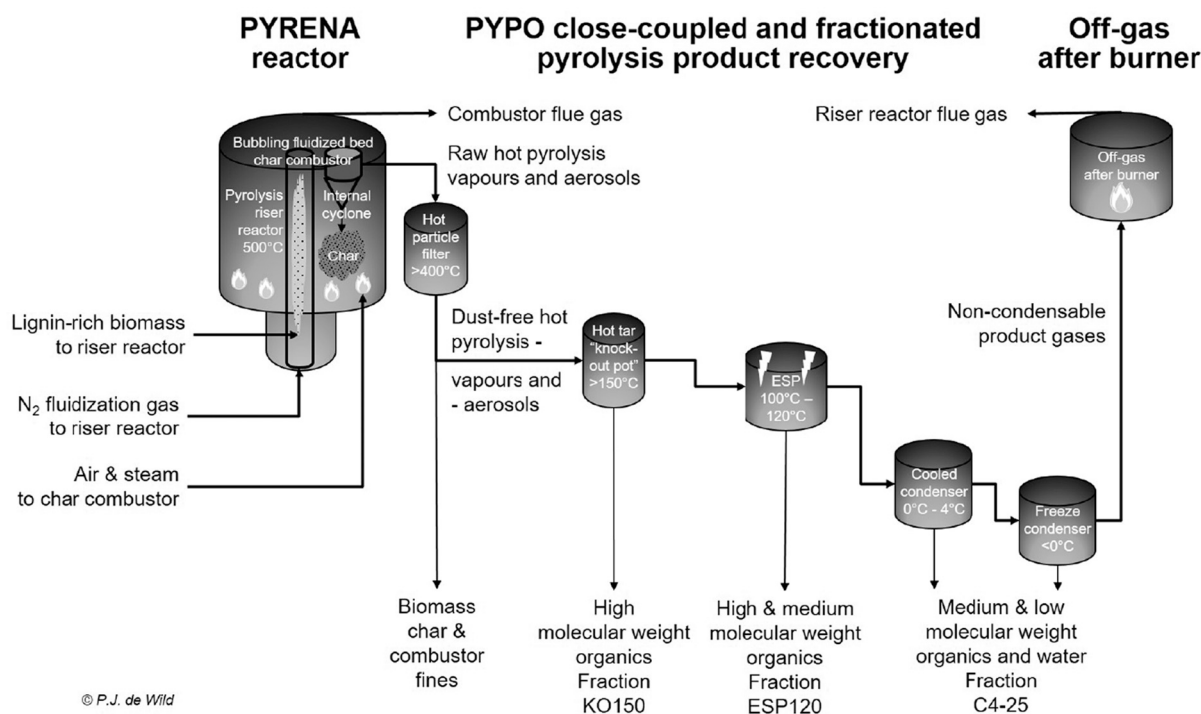


Fig. 1. PYRENA-PYRO set-up used for the pyrolysis experiments.

diluted about 25 times by a solution with 500 ppm DBE in THF.

2.2.11. Water content

The water content was determined by Karl Fischer titration using a Metrohm 702 SM Titrino potentiometric titrator. The titrations were carried out using the HYDRANAL™ 5 as the titer and HYDRANAL™ as the solvent (supplied by Honeywell). All analyses were performed at least in duplicate and the average value is reported.

2.2.12. Melting point and thermal behavior of the highly condensed organic fractions (KO150)

An M-560 (BUCHI) device was used to determine the melting temperature for the highly condensed organic fractions (KO150). All samples were loaded into glass capillaries and heated to 200 °C with a heating rate of 2 °C min⁻¹. The melting process was observed through a magnifying lens. The thermal behavior of the highly condensed pyrolysis oil fractions was determined using a TGA 4000 from PerkinElmer. The samples were heated in an N₂ flow (30.0 mL min⁻¹) from 50 to 900 °C with a heating rate of 10 °C min⁻¹.

2.3. Biomass pyrolysis and fractional condensation

2.3.1. Biomass pyrolysis

The PYRENA reactor (PYRolysis for RENawble Aromatics) was used for the pyrolysis experiments. It consists of a stainless steel fluidized bed reactor vessel with a sand bed (typically silica sand particles with an average diameter of 0.25 mm), which features an integrated riser reactor, provided with a cyclone at the top end for returning sand and char to the surrounding fluidized sand bed combustion vessel. The maximum biomass feed intake of the PYRENA is 5 kg/h. With a typical solid feed flow rate of 2–3 kg/h, a riser fluidization flow rate of approx. 20 NL/min N₂ is used, resulting in a gas phase residence time of less than one second. The pyrolysis temperature in the riser is typically around 500 °C. The heat required for the pyrolysis is obtained via electrical heating of the fluidized sand bed vessel (at start-up) and via the combustion of char in the surrounding fluidized bed. Fig. 1 presents a simplified scheme of the experimental set-up. The biomass is fed via a

conventional screw feeder configuration, consisting of a feed bunker with calibrated dosing screw to a reactor screw that feeds the biomass to the lower part of the riser reactor. At the inlet of the riser, the biomass is subsequently fluidized together with hot sand from the fluidized bed vessel with an inert gas (for example nitrogen) that enters the riser at the bottom. Pyrolysis then takes place in the riser.

2.3.2. Fractional collection of pyrolysis products

The gaseous pyrolysis products formed are discharged to the PYRO (PYrolysis Production Obtention) collection set-up for a fractional (staged) condensation of various pyrolysis product fractions at different temperatures. The overarching idea behind this stepwise condensation is to obtain a separation between high molecular weight organic material, low molecular weight organic material, and water. After condensation, the resulting non-condensable gases are incinerated in an afterburner. Non-condensable pyrolysis gas and flue gas from the combustion of char is measured online with NDIR (non-dispersive infra-red) and a micro-GC for CO, CO₂, CH₄, and light hydrocarbons. At the end of an experiment, the mass balance is calculated based on the weight of the fractions collected and the amount of gas and char formed. The amount of char is calculated via the online measured concentration of the CO₂ that originates from the combustion of the char in the fluidized bed combustion vessel.

The most important parts of the PYRO setup are i) a high temperature (150 °C tar “knock-out pot”, fraction KO150), ii) a temperature-controlled electrostatic filter (120 °C, ESP (electrostatic precipitator), fraction ESP120), iii) a low temperature (0 °C–4 °C) condenser with external and internal cooling, iv) a deep cooled (approx. –25 °C) condenser. For further analysis, the contents of the 0 °C–4 °C condenser and the –25 °C condenser were combined in one jar (fraction C4-25). The KO150 fractions from beech, walnut, and lignocel are denoted as B150, W150, and L150, respectively. The ESP120 fractions from different biomass are named as B120, W120, and L120, respectively.

2.4. Catalytic hydrotreatment of pyrolysis oil fractions

The solvent-free catalytic hydrotreatment of pyrolysis oil fractions

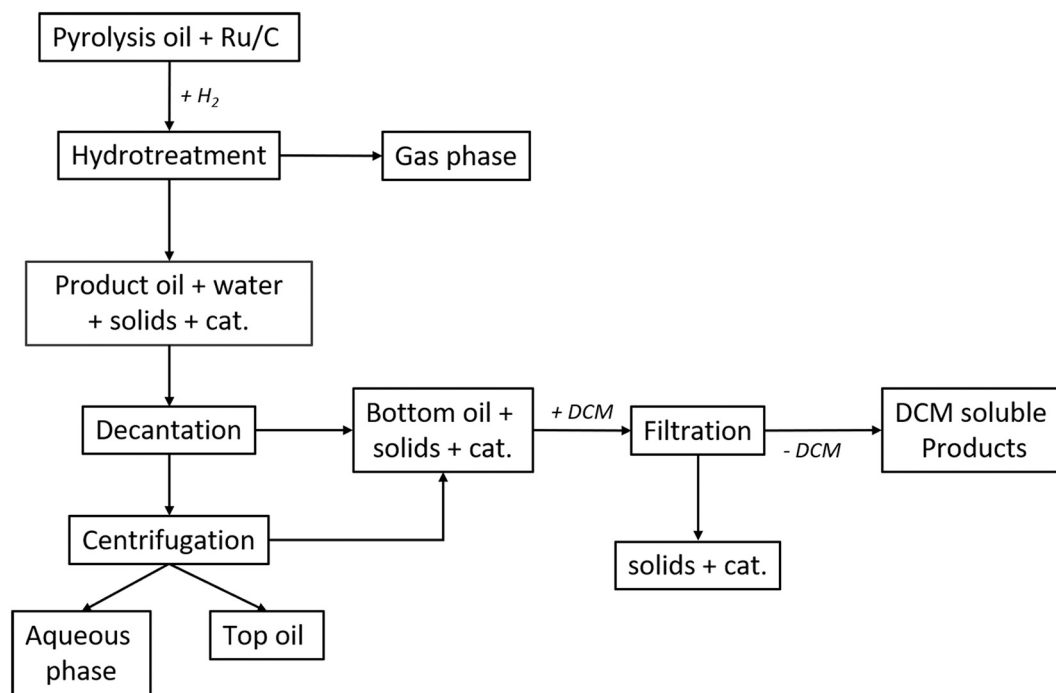


Fig. 2. Schematic representation of the hydrotreatment workup procedure for fractions ESP120.

was carried out in a stainless steel batch reactor (100 mL, Parr Instruments Co.) with a Rushton-type turbine, using a procedure given in a previous publication from our group [30]. The reproducibility was tested and shown to be good (Supporting information, Fig. S1). 15 g of the pyrolysis oil fraction and 0.75 g of catalyst were charged to the reactor. After loading the reactor, it was flushed several times with H_2 and then pressurized to 175 bar with H_2 at room temperature for a leak test. Subsequently, the H_2 pressure decreased to 100 bar and the stirring rate was set to 600 rpm. The reactor was heated to 200 °C with a heating rate of about 6 °C min^{-1} for the stabilization step, and time zero was set when the predetermined temperature (200 °C) was reached. The stirring rate was increased to 1000 rpm at the time zero. After the desired reaction time of 2 h, it was heated up to 350 °C for hydrocracking/hydrodeoxygenation and the reaction time was 2 h. The reactor was cooled to room temperature after the reaction at an approximate rate of 10 °C min^{-1} . The pressure and temperature at room temperature were recorded for calculating H_2 consumption and quantification of gaseous products. An overview of the hydrotreatment workup procedure is given in Fig. 2.

Five main products were collected after the reaction, viz. a top oil, a DCM soluble product, solid residue, an aqueous phase, and gas-phase components (Fig. 2). The gas phase after the reaction was collected by a 3 L Tedlar gas bag after cooling to room temperature. The liquid products were separated by decantation and transferred to a 15 mL centrifuge tube, followed by centrifuging at 4500 rpm for 30 min. Three layers were present in the tube after centrifugation, a top oil (light organic fraction), aqueous phase, and bottom oil (heavy organic fraction). The bottom oil and solid residues in the reactor were combined and washed with DCM, then filtered and dried to obtain the spent catalyst as well as coke formed during the reaction.

Product yields and mass balance closures were calculated on a pyrolysis oil (fraction) intake basis, as shown in Eqs. (3) and (4).

$$Product\ yield\ (wt\%) = \frac{Product\ weight\ (g)}{pyrolysis\ oil\ intake\ (g)} \times 100 \quad (3)$$

$$Mass\ balance\ closure\ (wt\%) = \frac{\sum(Product\ weight\ (g))}{pyrolysis\ oil\ intake\ (g)} \times 100 \quad (4)$$

Table 1

Carbohydrates and lignin content in the biomass feedstock used in this study^a.

| Biomass | Acid insoluble lignin (wt%) ^b | Acid soluble lignin (wt %) ^b | Cellulose (wt%) ^b | Hemicellulose (wt%) ^b |
|-------------------------------|--|---|------------------------------|----------------------------------|
| Beech sawdust | 23.10 | 6.39 | 35.79 | 21.72 |
| Walnut shell granulate | 28.31 | 4.83 | 26.18 | 23.81 |
| Softwood sawdust (lignocel 9) | 25.63 | 2.19 | 41.99 | 21.11 |

^a Determined according to an NREL method [26].

^b Compositions are on an as-received (a.r.) basis.

3. Results and discussion

3.1. Feedstock

Three different biomass feedstocks were tested, two woody biomasses (beech hardwood and coniferous softwood lignocel 9) and a lignin-rich feed in the form of walnut shells. The two woody biomass are representative of abundantly available European forestry biomass types that contain an appreciable amount of lignin. Walnut shell was selected as a typical agro-food residue with high lignin content. Relevant compositional data for the three biomass resources are presented in Table 1, whereas more details (proximate and ultimate analysis) are provided in Table S1.

3.2. Biomass pyrolysis

3.2.1. Pyrolysis experiments

Pyrolysis experiments were carried out in the PYRENA pyrolysis reactor with a biomass intake of 2–3 kg/h and operated at 500 °C. The vapor phase after pyrolysis is transferred to the PYPO section for staged condensation to obtain various pyrolysis product fractions at different temperatures. The overarching idea behind this stepwise condensation

Table 2
Pyrolysis yield data for the three biomass sources used in this study.

| Biomass source | Walnut | Softwood sawdust | Beech sawdust |
|--|--------|------------------|---------------|
| Total amount of biomass fed to pyrolyzer (g) | 44,370 | 30,450 | 39,150 |
| Total liquid yield (wt% on intake) | 62.9 | 60.0 | 64.8 |
| Yield of fractions (wt% on intake) | | | |
| KO150 | 2.4 | 3.4 | 3.0 |
| ESP120 | 12.9 | 14.3 | 14.3 |
| C4-25 | 47.5 | 42.3 | 47.5 |

is to obtain a separation between high molecular weight organic material, low molecular weight organic material, and water. These fractions can then be separately upgraded using dedicated methodologies to get maximum feedstock utilization efficiency and value extraction.

The yields for the individual fractions after staged condensation (KO150, ESP120, and C4-25, Fig. 1) are presented in Table 2. The highest yield is obtained for the aqueous fraction C4-25 (42.3% to 47.5%). Yields for the organic fractions are considerably lower, viz. between 12.9% to 14.3% for ESP120 and between 2.4% to 3.4% for the KO150 fraction. The total pyrolysis liquid yields are between 60% and 64.8% based on the intake of biomass (a.r.), which are typical values for fast pyrolysis processes [31,32].

3.2.2. Characterization of the individual fractions

The individual fractions after staged condensation for each biomass source were characterized in detail using a range of analytical techniques. These include techniques to obtain information on relevant product properties (stability, acidity, heating value) and molecular

Table 3
Characterization of the pyrolysis oil fractions obtained from fractional condensation.

| Staged condensation fraction | | Walnut | | | Softwood sawdust | | | Beech sawdust | | | |
|--------------------------------|--------------------------------------|------------------|---------------------|-----------|-------------------|------------|-----------|---------------|------------|-----------|------|
| | | KO 150 | ESP 120 | C 4-25 | KO 150 | ESP 120 | C 4-25 | KO 150 | ESP 120 | C 4-25 | |
| High molecular weight material | wt% on intake | 2.4 | 10.2 | 1.4 | 3.4 | 11.1 | 0.8 | 2.9 | 10.0 | 0.0 | |
| Monomers | | 0.01 | 2.7 | 27.2 | 0.06 | 3.2 | 29.7 | 0.05 | 4.3 | 33.6 | |
| Water | | 0.02 | 0.1 | 18.9 | 0.02 | 0.2 | 11.9 | 0.02 | 0.2 | 13.9 | |
| Elemental composition | O | wt% in sample a. | 23.0 | 29.8 | 42.7 | 29.2 | 34.0 | 52.8 | 26.0 | 32.8 | 46.6 |
| | C | r. ^a | 71.0 | 63.6 | 29.9 | 64.7 | 59.5 | 26.8 | 68.1 | 60.3 | 30.9 |
| | N | | 0.4 | 0.3 | 0.0 | 0.2 | 0.1 | 0.0 | 0.4 | 0.3 | 0.1 |
| | H | | 5.1 | 6.1 | 8.5 | 5.6 | 6.1 | 8.5 | 5.4 | 6.1 | 8.5 |
| | S | ppm | 116 | 50 | n.d. ^b | 54 | 80 | 47 | 78 | 51 | n.d. |
| Cal. value | HHV | MJ/kg | 28.1 | 26.1 | 20.1 | 25.9 | 24.3 | 15.9 | 27.2 | 24.7 | 18.8 |
| TGA | Moisture at 105 °C | wt% in sample | 0.9 | 1.1 | n.d. | 0.5 | 1.4 | n.d. | 0.7 | 1.3 | n.d. |
| | MCR at 500 °C | | 60 | 27.2 | n.d. | 48.8 | 27.5 | n.d. | 50 | 24.8 | n.d. |
| | Volatiles | | 40 | 72.8 | n.d. | 51.2 | 72.5 | n.d. | 50 | 75.2 | n.d. |
| | Fixed carbon | | 59.4 | 27.1 | n.d. | 48.5 | 27.4 | n.d. | 49.9 | 24.4 | n.d. |
| | Ash 500 °C - air | | 0.5 | 0.1 | n.d. | 0.3 | 0.1 | n.d. | 0.1 | 0.3 | n.d. |
| | Wt loss at 180 °C | | 1.4 | 19.5 | n.d. | 2.8 | 20.1 | n.d. | 1.9 | 19.4 | n.d. |
| Acidity | TAN based on carboxylic acid content | mg KOH/g sample | 0.0 | 2.5 | 90.0 | 0.0 | 1.4 | 47.0 | 0.0 | 3.8 | 93.6 |
| GC-MS-FID | Oligomers | wt% in sample | 99.5 | 79.1 | 2.9 | 98.2 | 77.9 | 1.8 | 98.2 | 69.9 | 0.0 |
| | Monomers | | 0.5 | 20.9 | 57.3 | 1.8 | 22.1 | 70.1 | 1.8 | 30.1 | 70.8 |
| | C2-C4 oxygenates | | 0.0 | 0.3 | 13.8 | 0.0 | 1.0 | 18.3 | 0.0 | 0.9 | 15.4 |
| | Methanol | | b.d.l. ^c | b.d.l. | 1.5 | b.d.l. | b.d.l. | 0.9 | b.d.l. | b.d.l. | 1.5 |
| | Furans | | 0.0 | 0.2 | 1.3 | 0.0 | 0.8 | 1.4 | 0.0 | 0.5 | 1.7 |
| | Carboxylic acids | | 0.0 | 0.3 | 9.4 | 0.0 | 0.2 | 4.6 | 0.0 | 0.5 | 9.7 |
| | Guaiacols | | 0.0 | 1.0 | 1.3 | 0.0 | 1.4 | 2.0 | 0.0 | 1.0 | 1.0 |
| | Syringols | | 0.0 | 1.5 | 1.3 | 0.0 | 0.0 | 0.0 | 0.2 | 2.0 | 1.1 |
| | Alkyl phenols | | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 |
| | Catechols | | 0.0 | 0.7 | 0.6 | 0.0 | 0.3 | 0.2 | 0.0 | 0.6 | 0.4 |
| | Other phenols | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Levoglucosan | | 0.4 | 3.6 | 0.2 | 1.4 | 7.5 | 0.1 | 1.3 | 7.0 | 0.2 |
| | Unknowns | | b.d.l. | 13.2 | 27.6 | 0.4 | 11.0 | 42.6 | 0.4 | 17.8 | 39.8 |
| SEC | Average Mwt | Dalton | 4177 | 1053 | 539 | 6477 | 1009 | 418 | 5325 | 1015 | 438 |
| | Polydispersity | PD | 4.9 | 2.1 | 1.7 | 6.6 | 2 | 1.5 | 6 | 2.1 | 1.5 |

^a On an as received (a.r.) basis.

^b Not Detectable (n.d.).

^c Below Detection Limit (b.d.l.).

composition (GC, NMR, SEC). An overview of the data is given in Table 3.

For subsequent catalytic hydrotreatment, the preferred fraction is formed in significant amounts (relevant for overall carbon yield) and has i) a low water content (low dilution level), ii) a low acidity (to reduce issues with catalyst degradation), iii) a high carbon content (to achieve potentially high C yields), iv) a high content of aromatic fragments (to obtain high amounts of alkylphenols and v) preferably a low molecular weight, and vi) high thermal stability (to reduce charring when heating up and upon hydrotreatment).

Based on these requirements, the ESP120 fraction of all three biomass types has the highest potential for subsequent hydrotreatment (Table 3). The water content is relatively low (< 0.2 wt%), the acidity is below 3.8 mg KOH/g sample (c.f. > 47 for the aqueous C4-25 phase) and the C content is between 60 and 64 wt%. In addition, GC-MS analyses in combination with SEC show that the molecular weight of the fraction is relatively low and by far lower than the KO150 fraction. As such, this fraction was selected for further hydrotreatment studies.

The molecular composition of the ESP120 fractions was studied in more detail using ¹³C NMR and GC-MS-FID. This is relevant information to gain insights into the chemical transformations occurring during the subsequent hydrotreatment step. The ¹³C NMR spectrum of the beech ESP120 fraction is shown in Fig. 3, along with the NMR chemical shift assignment ranges, adapted from the work of Ben and Ragauskas [33]. Quantitative information regarding the relative contents of relevant chemical functionalities (carbonyl, aromatic, aliphatics, methoxy), and levoglucosan is summarized in Table 4, more detailed information is given in Table S2.

The ¹³C NMR data indicate the presence of substantial amounts of C

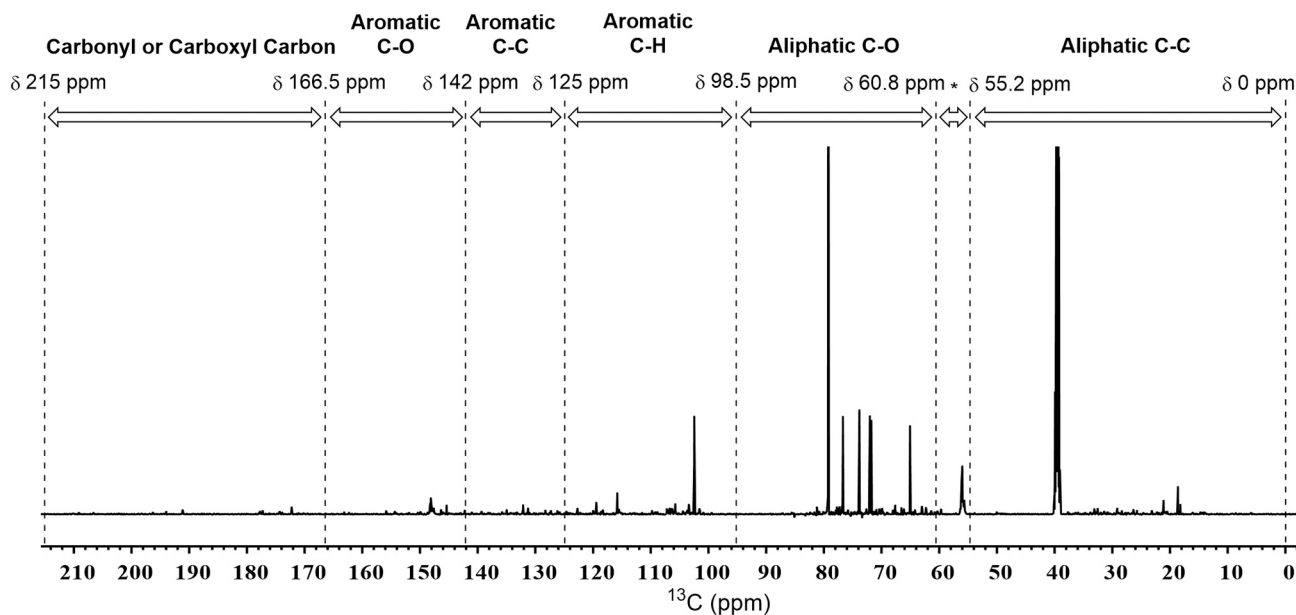


Fig. 3. Quantitative ^{13}C NMR spectra (DMSO- d_6) for Beech ESP120 fraction with relevant ranges of chemical units. *methoxy groups δ 60.8–55.2 ppm. [33].

Table 4

Concentrations and relative contents of carbonyl, aromatic, aliphatics, methoxy and levoglucosan as determined by ^{13}C NMR in the Beech ESP 120 pyrolysis fraction.

| | Total [Carbonyl] mmol $\text{g}_{\text{sample}}^{-1}$ | Total [Arom] mmol $\text{g}_{\text{sample}}^{-1}$ | Total [Aliph] mmol $\text{g}_{\text{sample}}^{-1}$ | Total [MeO] mmol $\text{g}_{\text{sample}}^{-1}$ | Total [Levo] mmol $\text{g}_{\text{sample}}^{-1}$ | Carbonyl (%) | Arom (%) | Aliph (%) | MeO (%) | Levo (%) |
|--------------------|--|--|---|---|--|-----------------|-------------|--------------|------------|-------------|
| Beech ESP120 | 0.32 | 3.77 | 3.25 | 3.63 | 0.54 | 2.8 | 32.8 | 28.2 | 31.5 | 4.7 |
| Walnut ESP120 | 0.25 | 4.67 | 3.20 | 3.63 | 0.29 | 2.1 | 38.8 | 26.6 | 30.1 | 2.4 |
| Lignocel ESP120 | 0.32 | 4.04 | 4.46 | 2.12 | 0.60 | 2.8 | 35.0 | 38.6 | 18.3 | 5.2 |

atoms in particularly the aliphatic C-O range. These include resonances from methoxy groups and carbon atoms present in sugars like levoglucosan. ^{13}C NMR spectra of all ESP120 fractions are provided in Fig. S4 and show a strong resemblance, despite differences in the chemical composition of the feedstocks used for pyrolysis. However, small differences are noted, e.g. in the amounts of levoglucosan and methoxy groups (Table S2). The walnut ESP120 fraction shows the lowest levoglucosan concentration. This is most likely due to the lowest amount of cellulose (26 wt%) in the feed, which is the precursor for levoglucosan upon fast pyrolysis [34]. The ESP120 fractions from the two hardwoods (beech and walnut) contain higher amounts of methoxy groups than that from softwood sawdust (spruce/pine, LignoCel 9). This is consistent with the differences in relative contents of S-G-H aromatic units in biomass sources, with hardwood having higher amounts of S units with two methoxy groups [35].

GC-FID-MS analyses of the ESP120 fractions show only a limited

Table 5

Product yields (wt% on pyrolysis oil intake) and mass balance for catalytic hydrotreatment experiments of the ESP120 fractions.

| ESP 120 feed | Top oil (wt%) | DCM solubles (wt%) | Aqueous phase (wt%) | Gas (wt%) | Solid residue (wt%) | Mass balance (wt%) |
|-----------------|----------------------------|----------------------------|---------------------------|---------------------------|---------------------------|----------------------------|
| Beech | 48.2 | 15.5 | 18.9 | 7.4 | 3.6 | 93.6 |
| Walnut | 47.6 (2.4) ^a | 18.9 (0.7) ^a | 15.7 (0.1) ^a | 8.8 (2.4) ^a | 2.2 (0.1) ^a | 93.2 (0.5) ^a |
| Spruce/ pine | 43.8 | 16.4 | 19.8 | 9.7 | 2.2 | 91.9 |

^a Number in parentheses is the standard deviation.

amount of GC-detectable compounds (< 30%, see Table 3), indicating the presence of substantial amounts of oligomeric components.

Although the ESP 120 fractions were selected for further hydro-treatment, the other two fractions (KO150, C4–25) also have the potential for further valorization. The KO150 fractions have a relatively high molecular weight (> 4100 Da, no GC detectable), though they contain the highest amount of carbon and thus the highest HHV's. In addition, the relatively small weight loss at 180 °C indicates good thermal stability of the KO150 fractions. Potential applications are in the field of bitumen and asphalt [22]. The aqueous phase (C4–25) contains considerable amounts of organic acids and other small oxygenates. Some of the organic acids (e.g. propionic acid) are valuable chemicals. In addition, this fraction may serve as a feed for reforming to obtain syngas (a.o. with hydrogen e.g. for hydrotreatment) [36] or may be used as a feed for ketonization to obtain intermediate long-chain ketones). These ketones can be used as reactants for aldol condensation, followed by hydrodeoxygenation, to produce biobased fuel (additives) [20].

3.3. Catalytic hydrotreatment of the ESP120 fractions

The catalytic hydrotreatment with Ru/C was conducted in a batch reactor setup using a combination of a mild and deep hydrotreatment strategy [37]. The mild hydrotreatment of the ESP120 fractions of the three biomass sources was performed at 200 °C for 2 h, directly followed by a deep hydrotreatment at 350 °C for 2 h without intermediate isolation of the mild hydrotreated oil. The latter temperature was selected based on literature data regarding the hydrotreatment of pyrolysis oil (fractions) [30]. Similar hydrotreatment experiments were also conducted for the KO150 fractions see Supporting Information for

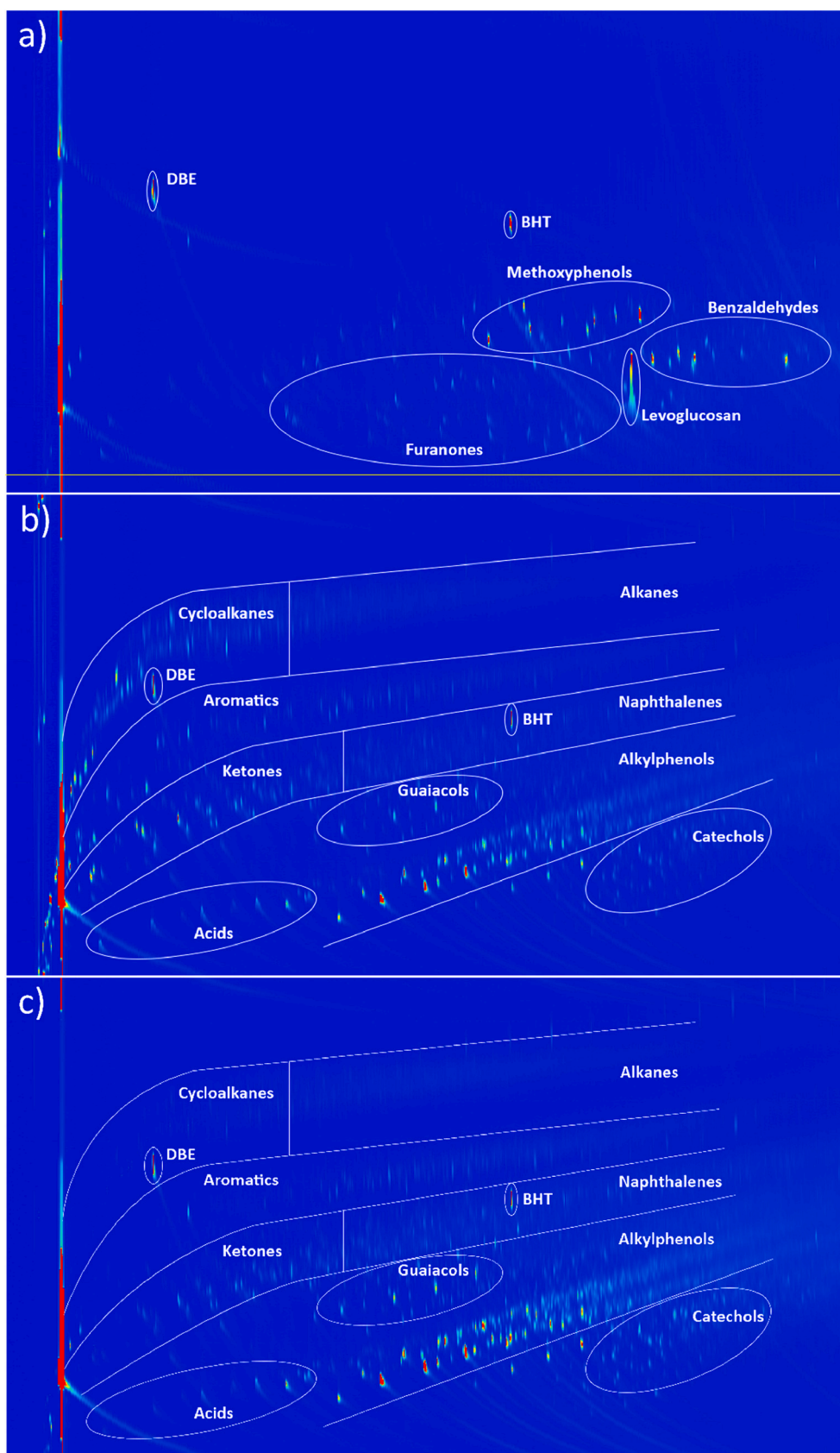


Fig. 4. GCxGC-FID chromatograms of a) Beech120 (B120), b) top oil and c) the DCM soluble fraction of hydrotreated pyrolysis oil from B120.

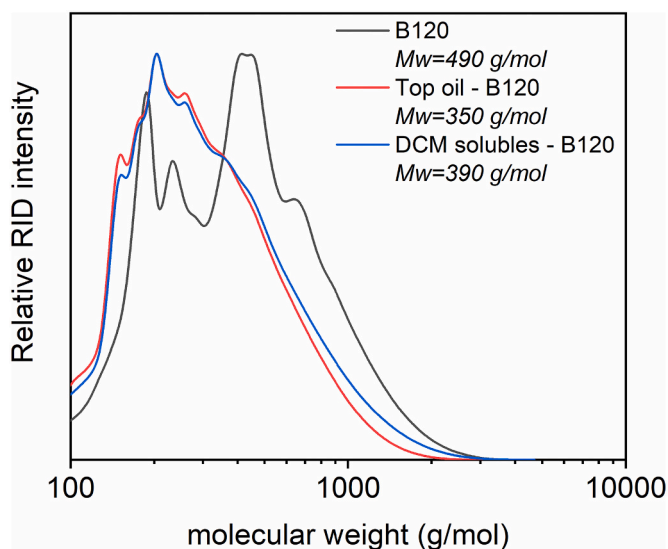


Fig. 5. Molecular weight distributions of the feed (Beech, B120), top oil, and DCM soluble fraction of hydrotreated pyrolysis oil determined by GPC.

details (Figs. S2, S8 & S9 and Tables S6, S7 & S8). The total monomer yields were significantly lower compared to those for the ESP120 fraction (40% lower), demonstrating that this fraction has less potential for upgrading by catalytic hydrotreatment when aiming for low molecular weight biobased chemicals.

Typically, the hydrotreatment led to the formation of two liquid phases after reaction, (top oil and aqueous phase), a solid residue with some oil absorbed on it, which can be recovered by a wash with dichloromethane (DCM solubles) and the formation of gas-phase components. The product yields after hydrotreatment are shown in Table 5. The organic fraction (sum of the top oil and DCM solubles) accounts for 60–67 wt% based on pyrolysis oil intake (Table 5). This yield of 60–67 wt% is comparable with that obtained from the hydrotreatment of pyrolysis oil derived from the lignin-rich digested stillage but is typically higher than for hydrotreatment of pyrolysis oils obtained from lignocellulose biomass [30]. This higher oil yield may be attributed to the lower water content and higher organic content of the feeds used in this study. Mass balance closure was very satisfactorily, with values of >91 wt%. The amount of solids is below 3.6 wt%, which is typical for hydrotreatment using Ru/C as the catalyst [10]. The gas-phase mainly consists of H₂ (58.9–71.2 mol%), CH₄ (12.5–19.4 mol%), and CO₂ (8.2–11.0 mol%) (Table S4). A large amount of remaining H₂ after reactions indicates that the experiments were not run at hydrogen starvation conditions. CH₄ formation is proposed to originate from hydrogenolysis of methoxy groups in lignin-derived compounds and gas-phase reaction between CO/CO₂ and H₂ to CH₄ [12]. CO₂ formation is likely from decarboxylation reactions of organic acids present in the pyrolysis oil fraction [10].

3.3.1. Analyses of the hydrotreated product oils

The liquid products (top oil and DCM solubles) obtained after hydrotreatment of the low molecular weight organic phase for all three biomass sources were analyzed using elemental analyses, GPC, GCxGC-FID, and NMR.

Two-dimensional gas chromatography (GCxGC-FID) was used for qualitative and quantitative analysis of the product oils after hydrotreatment. Typical chromatographs of pyrolysis oil fraction (Beech 120) and its hydrotreated oils (top oil and DCM soluble fractions) are shown in Fig. 4. It clearly shows the changes in oil composition before and after hydrotreatment. These changes in composition when hydrotreating pyrolysis oils are well established [4]. Reactive oxygenates are hydrodeoxygenated to hydrocarbons while methoxygroups from various

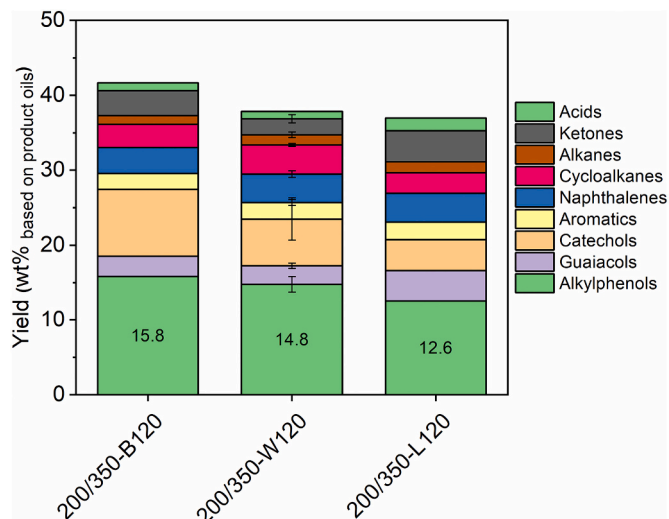


Fig. 6. Yield (wt% on the sum of the top oil and DCM solubles) for the hydrotreated pyrolysis oil fractions from different biomass sources by GCxGC-FID. B120, W120, and L120 stand for ESP120 fractions from beech, walnut, and lignocel, respectively.

phenolics are removed giving alkylphenols as the main product (Fig. 6). The number of identified compound species (mainly monomers) increases considerably for the hydrotreated pyrolysis oil because of depolymerization reactions occurring during hydrotreatment. Depolymerization was confirmed by a reduction of the average molecular weight of the product oils, see Fig. 5 for details. Qualitatively, a significant increase in the amounts of cycloalkanes and alkylphenols is visible, and to a lesser extent, in aromatics, ketones, catechols, alkanes, naphthalenes, and acids. The peak assigned to levoglucosan disappears after hydrotreatment.

Quantification results of the amounts of the main product classes by GCxGC-FID are shown in Fig. 6. The total amounts of identified GC detectables in the hydrotreated oils vary from 37 to 42 wt% based on product oil. Oxygenated aromatic compounds including alkylphenols, guaiacols, and catechols are the major chemical groups for all feeds. Of these, alkylphenols are the dominant ones (13–16 wt% based on product oils). This yield is comparable to that obtained by hydrotreatment of pyrolysis oil derived from a lignin-rich digested stillage over CoMo/Al₂O₃ (around 19 wt%) [30].

The type of biomass feedstock has some impact on the yields of monomers in general and alkylphenols in particular. The hydrotreated pyrolysis oil derived from beech sawdust and walnut have similar compositions and contain more monomers and alkylphenols (~3 wt%) than that from softwood sawdust (pine/spruce). As such, the higher lignin content of the walnut shells and the corresponding higher amounts of aromatic units in the ESP120 fraction do not result in a significantly higher yield of alkylphenols in the product oils after

Table 6

GCxGC-FID quantification of the top oil and the DCM soluble fractions of hydrotreated oil from B120 (wt% on the corresponding organic fraction).

| Chemical groups | Top oil | DCM solubles |
|--------------------------|---------|--------------|
| Alkylphenols | 14.8 | 19.0 |
| Guaiacols | 2.7 | 2.9 |
| Catechols | 8.1 | 11.6 |
| Aromatics | 2.2 | 1.8 |
| Naphthalenes | 3.1 | 4.5 |
| Cycloalkanes | 4.1 | 0.2 |
| Alkanes | 1.1 | 1.3 |
| Ketones | 3.8 | 1.7 |
| Acids | 1.2 | 0.6 |
| Total volatile compounds | 41.1 | 43.6 |

Table 7

Concentrations and relative contents of the Beech ESP120 pyrolysis fraction (B120) and the hydrotreated oil fractions (B120 DCM and B120 Top oil) showing the carbonyl, aromatic, aliphatics, methoxy, and levoglucosan content as determined by ^{13}C NMR.

| | Total [Carbonyl] mmol g _{Sample} ⁻¹ | Total [Arom] mmol g _{Sample} ⁻¹ | Total [Aliph] mmol g _{Sample} ⁻¹ | Total [MeO] mmol g _{Sample} ⁻¹ | Total [Levo] mmol g _{Sample} ⁻¹ | Carbonyl (%) | Arom (%) | Aliph (%) | MeO (%) | Levo (%) |
|--------------------------|--|--|---|---|--|-----------------|-------------|--------------|------------|-------------|
| Beech ESP120 | 0.32 | 3.77 | 3.25 | 3.63 | 0.54 | 2.8 | 32.8 | 28.2 | 31.5 | 4.7 |
| Beech120 top oil | 0.37 | 5.37 | 15.48 | 0.46 | 0.00 | 1.7 | 24.8 | 71.4 | 2.1 | 0.0 |
| Beech120 DCM solubles | 0.16 | 5.83 | 13.20 | 0.34 | 0.01 | 0.8 | 29.8 | 67.6 | 1.8 | 0.0 |

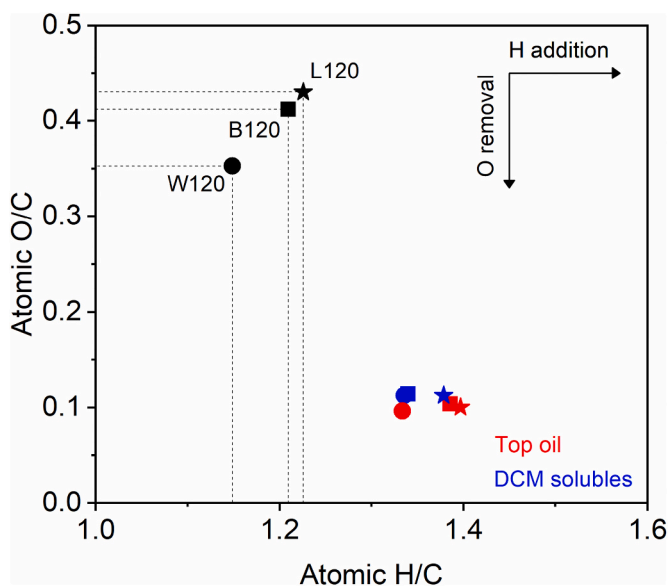


Fig. 7. Van Krevelen plot for ESP120 fractions, and their corresponding top oil as well as DCM soluble fractions (on a dry basis). B120 (■), W120 (●), and L120 (★) stand for ESP120 fractions from beech, walnut, and lignocel, respectively.

hydrotreatment. Possible explanations are differences in the condensation level of the lignin in the three feeds, with the lignin in walnut shell being the most recalcitrant for depolymerization or a higher rate of repolymerization of reactive intermediates during hydrotreatment [38].

The difference in composition between the top oil and the DCM solubles from B120 hydrotreatment of the beech ESP fraction, obtained by washing the residue after the reaction (Fig. 2), was investigated and the data are given in Table 6. The top oil appears to have higher amounts of cycloalkanes, ketones, and acids than the DCM soluble fraction. The amount of alkylphenols, however, is considerably higher in the DCM soluble fraction. This may be due to preferential adsorption of alkylphenols to char and spent catalyst, which implies that the oil recovery from the solid residue is essential to increase the alkylphenol yield. The molecular weight distribution of both fractions is very similar (Fig. 5), indicating that molecular weight differences are not relevant.

The difference in composition between the top oil and the DCM soluble fraction from beech ESP120 is also evident from ^{13}C NMR data, see Table 7 for details. More carbonyl and aliphatic carbons are present in the top oil, which is in line with the GCxGC-FID data, showing higher amounts of ketones and cycloalkanes in the top oil. Besides, a significant decrease in the amount of methoxy groups is observed, indicating that demethoxylation occurs to a significant extent during hydrotreatment.

The elemental composition of the feeds and the product oils was determined for all ESP120 fractions (Table S5) and the results are provided in a van Krevelen plot in Fig. 7. The elemental compositions of the ESP120 fractions from the three biomass sources (walnut, beech, and spruce/pine) differ considerably with C contents between 59 and 64 wt%. Upon hydrotreatment, the oxygen content is reduced, leading to

lower O/C ratios in the van Krevelen plot (Fig. 7). The H/C ratio of the hydrotreated products is also considerably higher than the feeds, indicating that hydrogenation reactions occurred to a significant extent. The spread in the composition of the product oils is considerably lower than that of the feed, indicating that hydrotreatment leads to product oils with rather similar chemical compositions.

The hydrotreatment of the ESP120 fraction for the three biomasses also led to a considerable increase in the heating value. For example, the higher heating value (HHV) of staged condensation fraction W120 (26.1 MJ/kg) increased to 38.0 MJ/kg for the top oil after hydrotreatment. As such, these product oils do not only contain interesting biobased chemicals like alkylphenols but also have potential as energy carriers, and as co-feeds for refinery processes.

4. Discussion

Based on the liquid product yields after hydrotreatment in combination with the elemental composition, the carbon yield was calculated to be about 80% (78–82%), corresponding with a mass yield between 60 and 67 wt%. Best results regarding carbon yields were obtained for beech sawdust (B120). As such, hydrotreatment is an effective technique to decrease the oxygen content and to increase the C and H content of pyrolysis oil fractions obtained by pyrolysis with fractional condensation. The amount of alkylphenols was close to 16 wt%, in the product oil. This value is considerably higher than in the product oil from a typical pyrolysis oil hydrotreatment. For instance, a value of 9 wt% was recently reported when using a Mo-promoted Raney Ni as a catalyst [39]. As such, the use of selected low molecular weight organic fractions from a pyrolysis process with staged condensation is indeed a good approach to obtain product oils with high heating values and considerable amounts of alkylphenols.

The overall carbon balance for the pyrolysis/fractional condensation-hydrotreatment concept for beech wood is given in Fig. 8. Data for the other two sources are given in the supporting information (Fig. S10 and Fig. S11). The yield of high-value alkylphenols [40] is about 1.6–2.2% based on biomass input.

In this paper, we have demonstrated a valorization strategy for the low molecular weight organic liquid. However, to obtain high carbon yields for the overall concept, efficient technology needs to be developed for the aqueous phase. As reported in the introduction, catalytic technology has been reported for the fraction, like ketonization and the use as a fermentation feed though more efforts are needed regarding optimization and scale-up.

The approach used in this study involves the separation of the pyrolysis oil using fractional condensation in the pyrolysis step (in-situ approach). It is of interest to compare this approach with an ex-situ approach, involving separation of the pyrolysis oil after condensation. One of the simplest ways to do so is a phase separation of the lignin fraction and the sugar fraction by water addition. We have recently shown that catalytic hydrotreatment of the obtained pyrolytic lignin fraction is also feasible [12,29], and a product oil with an alkylphenol content as high as 27 wt% was obtained [12]. However, direct comparison of both approaches needs further studies, also considering the efficiencies (yields) for upgrading techniques for the aqueous phase fraction.

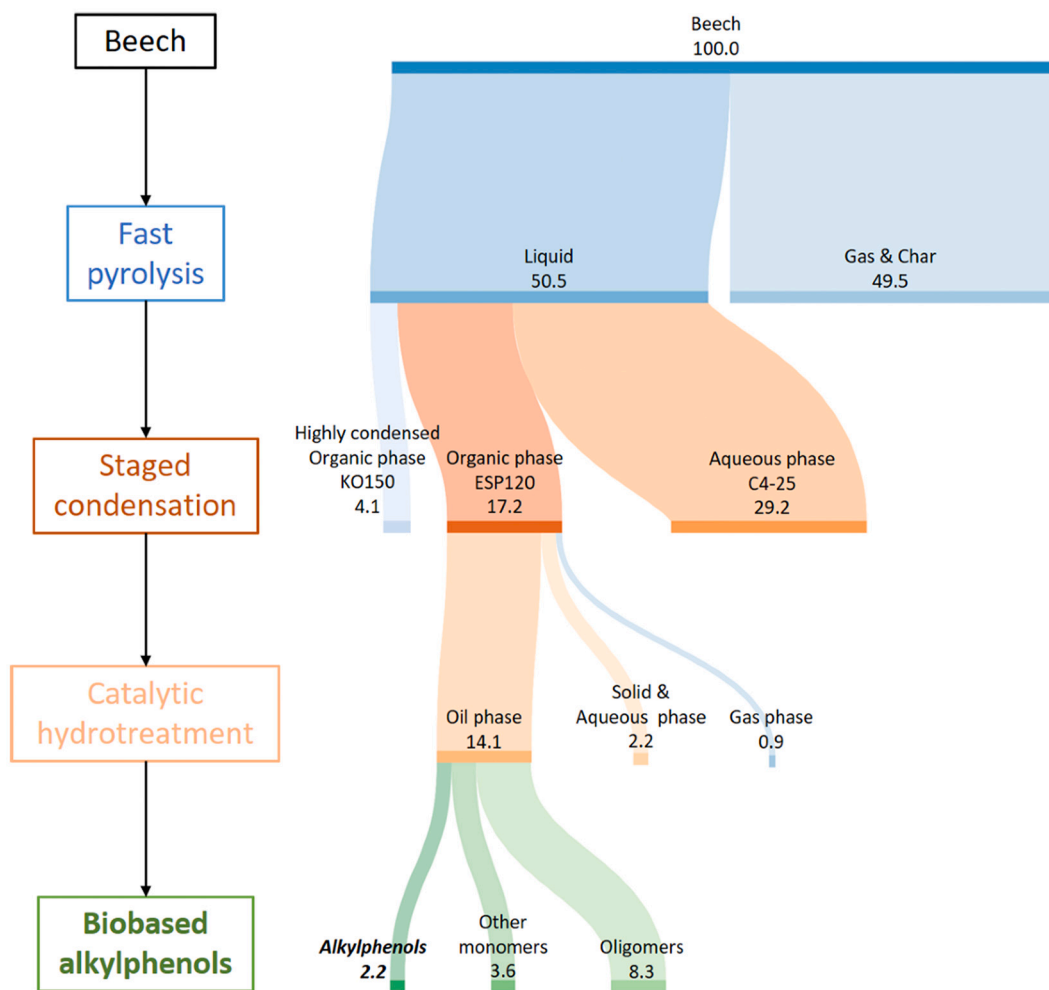


Fig. 8. Carbon yields for the fast pyrolysis-staged condensation-catalytic hydrotreatment concept, using beech sawdust as feedstock. (data for alkylphenols, other monomers, and oligomers are calculated based on weight yield, assuming a similar elemental composition).

5. Conclusions

We have explored an integrated process consisting of fast pyrolysis combined with staged condensation and a catalytic hydrotreatment of a selected fraction. We have shown that particularly the low molecular weight organic fraction after staged condensation is suitable for catalytic hydrotreatment. When using Ru/C for the hydrotreatment, a liquid product in high carbon yields (> 80C%) with an HHV > 36 MJ/kg and enriched in valuable biobased chemicals, particularly alkylphenols, was obtained. The research illustrates that the initial separation of pyrolysis liquids followed by tailored catalytic conversions of selected fractions is more attractive when considering yields and flexibility than conversion of the pyrolysis liquids as a whole.

It was shown that the type of biomass (beech sawdust, walnut granulates, and pine/spruce sawdust) has a limited impact on liquid and alkylphenols yields which implies feedstock flexibility of this integrated concept. However, this claim only holds for biomasses low in ash (< 0.5 wt%). Biomass sources with higher ash contents may provide pyrolysis oil fractions with higher ash contents and these may have a negative effect on catalyst performance, and particularly stability in the hydrotreatment step.

Further exploratory research will be required to develop efficient separation technology for the isolation of the alkylphenols from the hydrotreated fractions. Possible options are liquid-liquid extractions using tailored extraction solvents. In addition, hydrotreatment experiments in continuous set-ups will be required with longer times on stream

to assess catalyst stability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

H.Y. and Z.W. acknowledge the China Scholarship Council for funding their Ph.D. studies (grant number 201706160156 and 201706300138, respectively). Financial support from the Dutch Ministry of Economic Affairs and Climate for this project is gratefully acknowledged (TKI-BBEI project “CALIBRA”, reference TEBE117014). Wang Yin, Leon Rohrbach, Erwin Wilbers, Marcel de Vries, and Hans van der Velde, all from the University of Groningen, are acknowledged for technical and analytical support. We also thank Ben van Egmond and Ron van der Laan from TNO for technical and analytical support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2021.107160>.

