Reductive catalytic fractionation of black locust bark†

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Tree bark is a major waste stream from the wood processing industries, and thus an alluring feedstock for biorefineries. This contribution explores a catalytic biorefining strategy for black locust (*Robinia pseudoacacia*) bark. In this *Reductive Catalytic Fractionation* (RCF) strategy, bark is processed in methanol at elevated temperatures (200–250 °C) in the presence of a heterogeneous hydrogenation catalyst (*e.g.* Ru/C) and pressurized hydrogen. This enables the (partial) extraction and solvolytic depolymerization of lignin, suberin and hemicellulose which are present in bark. The formed lignin intermediates are effectively stabilized *via* catalytic hydrogenation, thereby avoiding repolymerization reactions and thus enabling the formation of a highly depolymerized lignin fraction. RCF of black locust bark results in a solid phase (mainly cellulose and residual lignin) and a process liquor. The soluble products were further separated *via* liquid/liquid extraction into an aqueous phase, containing glycerol and carbohydrate derivatives, and an organic phase, containing phenolic mono-, di- and oligomers as well as suberin-derived, long-chain aliphatic monomers (mainly α,ω-dimethyl esters and ω-OH methyl esters, next to alkanols and methyl esters). A comparison with black locust wood (hardwood) was made, highlighting the presence of suberin and the more condensed lignin structure in bark. Furthermore, this contribution examines the effect of various process parameters (*e.g.* temperature, reaction time, catalyst type and loading) on the extraction and depolymerization of lignin and suberin polymers. Finally, a heptane extraction was executed on the bark oil (*i.e.* dried organic phase) as a proof-of-concept separation of the suberin-derived aliphatics on one hand and the lignin phenolics on the other.

Introduction

Plant biomass is widely regarded as a promising resource of renewable chemicals and materials.[2,3] Within the context of green chemistry,[4] the biorefinery has received considerable attention.[5–7] In such a refinery, biomass is fractionated into different product streams, amenable to further valorization.[8,9] The product slate of a biorefinery is mainly determined by the biorefinery technology and the feedstock type, which are strongly intertwined.

Tree bark is an interesting resource since it is a waste in wood processing industries such as pulp and paper industry, and timber production. Currently, it is mainly burned or used as soil coverage in horticulture. Bark is a cheap, abundant, and readily available form of biomass and thus an appealing feedstock for a biorefinery.[10–12]

Bark is the non-technical term for tissue external to the vascular cambium. In older trees it consists mainly of rhytidome (*i.e.* outer bark) and secondary phloem (*i.e.* inner bark). The rhytidome protects the tree against pathogens and weather influences, while the phloem enables the transport of sap throughout the tree.[13,14] The structure and chemical composition of bark is very complex. It varies strongly between species, but also between different parts of the tree (*e.g.*, inner *vs.* outer bark, branches *vs.* stems) and between growing conditions, age, *etc*.[15] In general, bark is composed of carbohydrate polymers (cellulose, hemicellulose, and pectins), phenolic polymers (lignin and condensed tannins), aliphatic polymers (suberin), extractives, and inorganics.[15–17]

Bark generally has a higher content of inorganics, extractives and lignin compared to wood, in contrast to the carbohydrate content, which is lower for bark.[15] The lignin fraction in bark is characterized by a lower methoxyl-content than wood lignin.[15,16,18] For instance, the bark of cork oak and willow has a much lower S/G ratio and therefore contains more condensed lignin structures than the corresponding wood.[19,20]

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In addition, certain barks contain suberin, which is not present in wood.[21] Suberin is a polyester composed of long-chain (C_{16}–C_{26}) aliphatics (α,ω-diacids, ω-OH acids, acids and alcohols) and glycerol. This polyester is covalently linked to lignin *via* hydroxycinnamic acids (mainly ferulic acid). These ferulates are linked to suberin's aliphatic hydroxyl groups *via* ester bonds and to lignin (or lignin-like polyaromatics) *via* ether and C–C bonds.[22,23]

For wood, and lignocellulose in general, a wide variety of biorefinery schemes have been proposed. In many processes, the goal is to remove the lignin to obtain a high value carbohydrate fraction such as in Kraft, organosolv, and sulphite pulping.[8,24,25] Bark is often not suitable for these processes because of its lower carbohydrate content and less crystalline cellulose.[15] Furthermore, delignification of barks is more difficult due to the presence of suberin, and its more condensed lignin structure.[15,19] Additionally, the high ash content in bark interferes with the recovery of pulping chemicals.[26] Moreover, lignin undergoes irreversible repolymerization during these traditional processes, making downstream conversion into chemicals extremely challenging.[8,25,27]

Because bark has a lower carbohydrate and a higher lignin content than wood,[11,15] a lignin-focused strategy might prove useful for bark valorization. Recently, a so-called "lignin-first" process has been developed for lignocellulosic biomass. This process is termed Reductive Catalytic Fractionation (RCF) and copes effectively with lignin's tendency to repolymerize.[27–30] During RCF, the *in planta* lignin is solvolytically extracted from the lignocellulosic matrix, depolymerized through cleavage of the inter-unit ether bonds and reductively stabilized through the action of a redox catalyst and H_2 or a hydrogen donor. This results in a depolymerized lignin oil and a delignified pulp.[28,31] Although RCF has been originally developed for wood biorefining, a handful of studies indicate that RCF could be an interesting process for the depolymerization of both lignin and suberin in barks of different species.[32–34]

Sheldrake *et al.* performed an RCF process using barks of sycamore, spruce and cork oak in a 1,4-dioxane/water (1 : 1) solvent system using Rh/C and Pd/C as redox catalysts. They obtained up to 3.8 wt% phenolic monomers and 3.2 wt% (mono- and bifunctional) lipids from sycamore bark using Rh/C at 200 °C.[32] Furthermore, they showed that adding inorganic bases increases the yield of aliphatics and aromatics, and that the biphasic nature of a methyl tetrahydrofuran–water solvent system allows for an easier product separation.[33] Samec *et al.* studied the conversion of cork oak bark into 4-ethylguaiacol and hydrocarbons in the gasoline and diesel range.[34] Firstly, RCF of cork oak bark was carried out in an alkaline methanol–water (2 : 1) mixture at 200 °C. During this step, the carbohydrates, the methanol solvent and the formed formates can serve as hydrogen donor for the Pd/C-catalyzed transfer hydrogenolysis of lignin. The resulting process liquor was then distilled to recover 4-ethylguaiacol (2.6 wt%), while the residue was hydrodeoxygenated at 350 °C over a Pt-MoO_3/TiO_2 catalyst yielding both lignin- and suberin-derived hydrocarbons.[34]

This study investigates the biorefining of black locust (*Robinia pseudoacacia*) bark using the RCF process. Black locust is a fast-growing, nitrogen-fixating pioneer species that can be grown on marginal lands.[35] Black locust wood is highly durable and rot-resistant and therefore frequently used as construction wood (*e.g.* furniture, poles, garden and playground equipment).[35] In addition, its widespread cultivation and fast growth make it an attractive biomass feedstock. This contribution studies various aspects of RCF of black locust bark. Firstly, RCF of black locust bark is compared to black locust wood as a benchmark. Mass balances are delineated both for bark and wood. Secondly, important process parameters (*i.e.* temperature, reaction time, catalyst type, catalyst loading and hydrogen pressure) are investigated systematically for the RCF of black locust bark, thereby assessing their influence on the depolymerization of lignin and suberin present in bark. Lastly, a proof-of-concept heptane extraction is used to separate the oil resulting from RCF of black locust bark.

Experimental section

For a list of all used chemicals and materials as well as a more detailed description of the experimental procedures, the reader is referred to the ESI.†

Dry black locust bark and wood were milled and sieved to obtain sawdust fractions with a size of <500 μm and 250–500 μm respectively. These substrates were used as such for catalytic experiments. For the compositional analysis of these substrates, the reader is referred to the ESI.† A summary is shown in Fig. 1.

The reductive catalytic fractionation (RCF) experiments were performed in a 100 ml stainless steel batch reactor (Parr Instruments & Co.). In a typical reaction, 2 g black locust bark or wood was loaded into the reactor together with the catalyst (*e.g.* 0.2 g Ru/C) and methanol (40 mL). The reactor was sealed, flushed threefold with N_2, and pressurized with H_2 (10–40 bar at room temperature). Subsequently, the reaction mixture was stirred (600 rpm) and heated to 200–250 °C during 40 min. When the reaction temperature was reached, the temperature was kept constant for 1–6 h after which the reactor was cooled and depressurized at room temperature. Afterwards, the reactor contents were quantitatively collected by washing the reactor with ethanol.

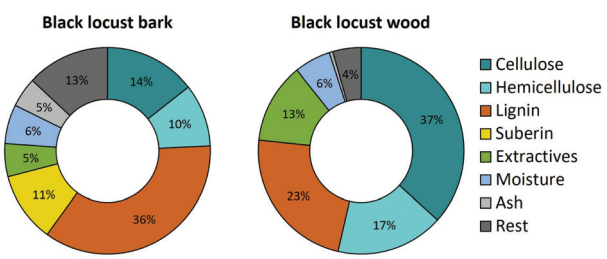

Fig. 1 Chemical composition of black locust bark and wood.

The obtained product mixture was filtered using a Por 4. fritted glass filter to separate the residual solids (bark residue and catalyst) from the liquid products. The residual solids were washed with ethanol and dried overnight at 80 °C, followed by equilibration with air humidity.

The methanol/ethanol mixture was evaporated using a rotary evaporator, yielding a viscous, brown oil. This oil was transferred quantitatively to a 10 mL vial using small amounts of ethanol. The ethanol was then again evaporated using a N_2 flow. Distilled water (5 mL) was added to the 10 mL vial with the oil and this mixture was extracted threefold with chloroform (3 × 2 mL) to separate the apolar products (mainly lignin- and suberin-derived products) from the polar products (*e.g.* glycerol and carbohydrate-derived products). The combined chloroform extracts were dried using a nitrogen flow to evaporate most of the chloroform, followed by drying overnight at 80 °C. The resulting dried oil is further referred to as 'bark oil' (or 'lignin oil' in case of wood) and its mass was used to calculate the 'bark oil yield' (and 'lignin oil yield' in case of wood). For quantitative determination of the phenolic and aliphatic monomers, 2-isopropylphenol was added as an internal standard and the oil was resolubilized in chloroform, followed by GC-FID analysis. GC-MS analysis was performed to verify the identification of the phenolic and aliphatic monomers. In addition, GPC, ^{13}C NMR, and HSQC NMR were performed to characterize the complete bark oil.

As a proof-of-concept, further downstream separation of the bark oil was performed *via* heptane extraction. Approximately 0.3 g bark oil was extracted twice with 4 mL heptane at 70 °C under continuous stirring during 1 h.

The carbohydrate content of the solid residue was determined using a standard total sugar procedure, adapted with hydrolysis conditions for cellulose-rich materials. The essential steps of this procedure are (i) a two-step H_2SO_4-catalyzed hydrolysis, (ii) reduction of the released sugars with $NaBH_4$, (iii) acetylation of the polyols with acetic anhydride, and (iv) extraction of the acetylated products with *in situ* formed ethyl acetate, followed by (v) GC-FID analysis. Each sample was analyzed in triplicate.

Results and discussion

Compositional analysis of black locust bark and wood

As a starting point of this study, the composition of the black locust bark (<500 μm) and black locust wood (250–500 μm) was determined, which is depicted in Fig. 1. All values are expressed relative to the raw black locust bark/wood. For the detailed analytical procedures, the reader is referred to the ESI.† Extractives were determined *via* an EtOH/toluene (1 : 2) extraction using a Soxtec Avanti apparatus. The extracted compounds amount to 5.2 wt% of the bark and 12.6 wt% of the wood. The suberin content was determined on pre-extracted black locust bark *via* alkaline methanolysis of the ester bonds present in suberin. The suberin content was found to be 11.0 wt% of the raw bark. The suberin-free bark and the extracted wood were used for the determination of the Klason lignin content *via* acid hydrolysis of the carbohydrate fraction. The acid-insoluble lignin ('Klason lignin') accounted for 32.9 wt% of the bark and 19.7 wt% of the wood, while the acid-soluble lignin content was 2.9 wt% and 3.3 wt%, respectively. The carbohydrate fraction of the bark and wood were determined *via* an hydrolysis, reduction and acetylation sequence (ESI†). The total carbohydrate content in bark was found to be 24.2 wt%. Glucose accounted for 14.4 wt% (approximately the corresponding cellulose content), the other carbohydrates (L-arabinose 4.5 wt%, D-xylose 2.6 wt%, D-mannose 1.1 wt%, D-galactose 1.6 wt%) accounted for 9.8 wt% (approximating the hemicellulose content). In wood, the total carbohydrate content was 53.6 wt%. Glucose content was found to be 36.7 wt% (representing the cellulose content), while the other carbohydrates (L-arabinose 1.0 wt%, D-xylose 13.8 wt%, D-mannose 1.4 wt%, D-galactose 0.8 wt%) accounted for 16.9 wt% (taken as the hemicellulose content). Moisture content was similar in bark and wood, 6.1 wt% and 5.7 wt%, respectively. Ash content was 4.7 wt% in bark, compared to 0.5 wt% in wood. In summary, the bark has a lower carbohydrate content and higher lignin content than wood. Furthermore black locust bark contains suberin, and has a higher ash content than wood. It is noted that the mass closure for wood is better than for bark. 13 wt% of the bark could not be assigned, showing that bark is chemically a more complex material.

Proof-of-concept

Black locust bark contains a significant amount of lignin (35.7 wt%) and suberin (11.0 wt%). Therefore, RCF of black locust bark was carried out as a proof-of-concept of a lignin-focused strategy for bark valorization. It is expected that both lignin and suberin will undergo depolymerization because ether bonds (in lignin) and ester bonds (in suberin) can be cleaved readily *via* solvolysis under typical RCF conditions (MeOH, 200–250 °C).

A process overview of RCF of black locust bark is shown in Fig. 2. In this proof-of-concept experiment, 2 g of black locust bark (<500 μm), 0.2 g of Ru/C catalyst and 40 mL methanol were added to a 100 mL Parr batch reactor. The mixture was pressurized with hydrogen (40 bar at room temperature), stirred (600 rpm), and heated to 235 °C (total pressure of 120 bar), which was maintained for 4 h. After cooling, the reaction mixture was collected and filtered. The residual solids (bark residue and catalyst) were washed with ethanol. The resulting bark residue yielded 41.4 wt% of the initial bark. The solvent was evaporated, and the residual components were separated through liquid/liquid extraction (chloroform/water). The compounds in the chloroform phase were isolated through solvent evaporation, yielding a dark viscous oil. This product stream yielded 32.6 wt% of the initial bark and is further referred to as 'bark oil'. Analysis of this bark oil using GC-FID showed a total phenolic monomer yield of 3.3 wt% relative to the bark. The phenolic monomers comprise both lignin-derived monomers (propyl-, propanol-, propenyl- and

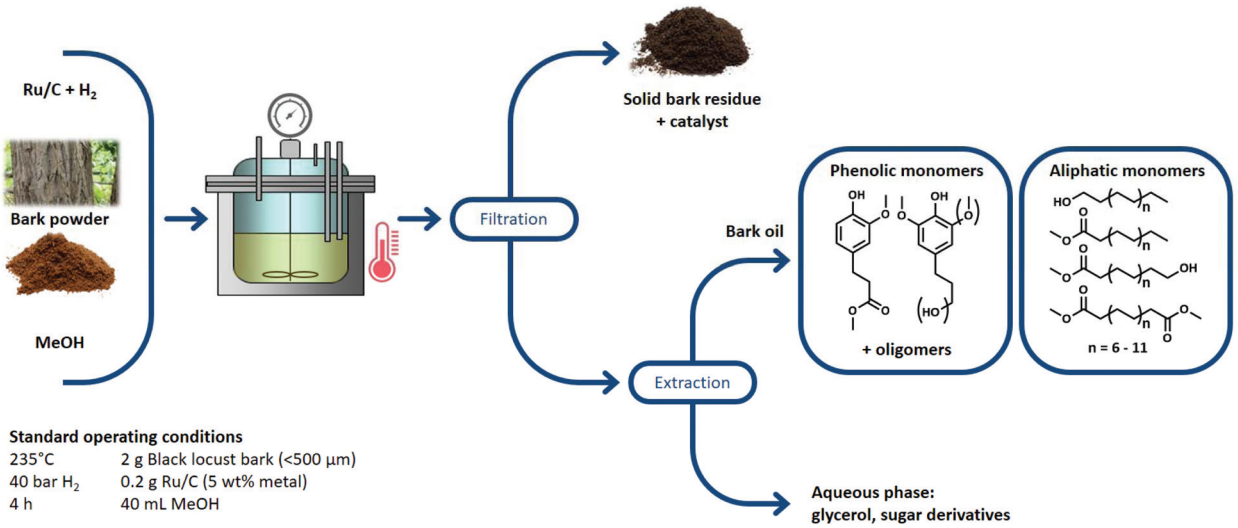

Fig. 2 General scheme of the RCF process of black locust bark and downstream separation. Filtration of the reaction mixture results in a solid bark residue. Soluble products are separated through liquid/liquid extraction (chloroform/water) into a bark oil, containing mainly lignin- and suberin-derived products, and an aqueous phase.

ethyl-substituted guaiacol/syringol) and the suberin-associated methyl (dihydro)ferulate. In addition, the bark oil contains long-chain aliphatic monomers, which mainly originate from suberin and account for 9.2 wt% of the bark. These monomers have an aliphatic chain length of 16 to 26 carbon atoms. They predominantly comprise α,ω-bifunctional molecules (*i.e.* α,ω-dimethyl esters and ω-OH methyl esters), while a smaller fraction comprises monofunctional molecules (*i.e.* alkanols and methyl esters). Most of the aliphatic monomers are saturated, except for dimethyl octadec-9-enedioate and methyl 18-hydroxyoctadec-9-enoate, which still (partly) retain their double bond after the RCF process. A detailed overview of the obtained phenolic and aliphatic monomers can be found in Table S1.† The bifunctional nature of these aliphatic monomers makes them interesting molecules for polymer, *viz.* polyester[36] and polyurethane,[37] applications.[22]

RCF of black locust bark *versus* wood

As a benchmark, RCF of black locust bark was compared to RCF of wood from the same tree. Black locust is a hardwood species, and therefore the results upon RCF of black locust wood are expected to be in line with previous studies using hardwoods (*e.g.* birch,[28,38–41] poplar,[42–44] eucalyptus[45,46]).

Typical RCF conditions (MeOH, 235 °C, 4 h, 40 bar H_2 at RT) with two catalysts (Pd/C and Ru/C) were used to compare black locust bark and wood. For both samples the same downstream analytical procedures were used. Results are summarized in Fig. 3. Firstly, these results show that the solids retention (*i.e.* the solid fraction after RCF) is higher for wood (56.1 and 52.3 wt%, with Pd/C and Ru/C, respectively) than for bark (40.4 and 41.4 wt%). Secondly, these results indicate that the yield of the obtained oil is much higher for bark (33.9 and 32.6 wt%) than for wood (22.2 and 22.6 wt%). This difference is mainly ascribed to the presence of suberin-derived

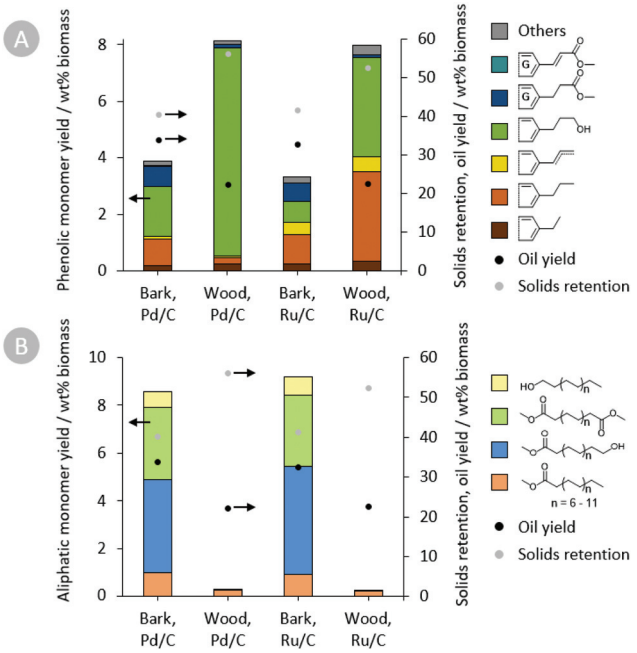

Fig. 3 Comparison of RCF of black locust bark and wood using Pd/C and Ru/C catalysts. (A) Phenolic monomers and (B) aliphatic monomers. Reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g Ru/C or Pd/C, 40 bar H_2, 235 °C, 4 h.

aliphatics in the bark oil, which are absent in the lignin oil of wood. As shown in Fig. 3, RCF of wood yields almost no aliphatic monomers, in line with the absence of suberin in wood, whereas in bark this fraction accounts for 9 wt% of the bark. The aliphatic monomer selectivity is similar with Ru/C and Pd/C, indicating no effect of the catalyst on the aliphatic functional groups.

Considering the obtained phenolic compounds, differences between bark and wood are substantial. Firstly, methyl dihydroferulate, a component derived from suberin-associated ferulic acid (*via* esterification with methanol and hydrogenation) is a major product in bark oil, whereas it is almost not present in wood lignin oil. Secondly, the total phenolic monomer yield (relative to the biomass) is considerably higher for wood, even though the lignin content of bark is higher (35.7 wt% *vs.* 23.0 wt% in wood). The low phenolic monomer yield from bark indicates a less extensive lignin extraction and depolymerization compared to wood, under these particular reaction conditions. This is confirmed by comparing the residual lignin content of the solid residues (*vide infra*) and GPC chromatograms of the obtained oils (Fig. 4). GPC analysis shows a highly depolymerized lignin oil from wood (large monomer signals, small oligomer signals), while the bark oil contains a relatively large amount of phenolic oligomers. This can be explained by a lower S/G ratio of bark lignin, resulting in a more condensed structure with fewer cleavable inter-unit ether bonds.[19,20] The S/G ratio of the phenolic monomers (without ferulates) is 0.90 and 0.85 for bark (Pd/C and Ru/C), while these values are 2.24 and 2.40 for wood.

Next to the difference in the degree of depolymerization, the lignin monomer selectivity shows dissimilarities when using black locust bark or wood (Fig. 3). To compare the selectivity differences between wood and bark, ferulate components were disregarded, as they are not present in wood. For Ru/C catalyzed reactions, the selectivity towards propyl-G/S is similar in bark and wood, *viz.* 39% and 40%, respectively. However, for propanol-G/S, the selectivity is highest in wood, *viz.* 45% *versus* 28% in bark. On the other hand, the selectivity towards propenyl-G/S is higher in bark (17%) than in wood (7%). For reactions with Pd/C, the selectivity towards propanol-G/S was very high in wood (92%), which is in line with earlier work on RCF of birch wood.[1] For bark, the propanol-G/S selectivity was only 56%. These changes in selectivity for lignin monomers, both in Ru/C- and Pd/C-catalyzed reactions, might be attributed to interactions of bark components with the catalyst surface, thereby altering the catalyst activity and/or selectivity. However, the interacting components and the nature of these interactions (*e.g.* competitive adsorption) remain to be elucidated.

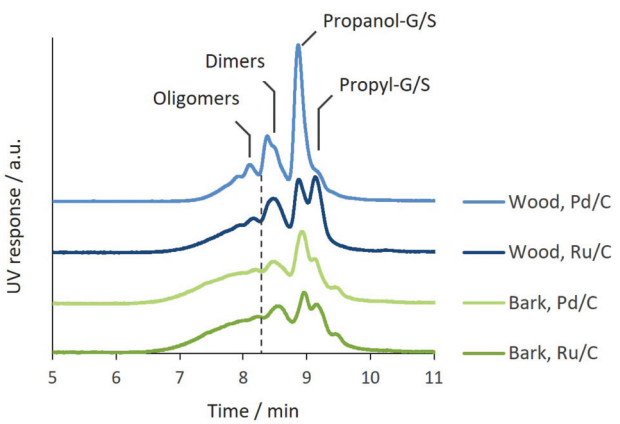

Fig. 4 GPC of chloroform oils resulting from RCF of bark and wood. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g Pd/C or Ru/C, 40 bar H_2, 235 °C, 4 h.

HSQC NMR (Fig. 5) of the oil from bark and wood supports the identification of the different obtained products. In bark oil, various signals correspond to the suberin-derived aliphatics (aliphatic chains, methyl ester groups, primary –OH groups). These signals are much less pronounced in the lignin oil from wood, where they could arise from aliphatic extractives still present in wood. The signals corresponding to the main lignin side chains (propyl-, propanol-) are present in both bark and wood oil, although they are more pronounced in the wood lignin oil. Furthermore, the NMR spectrum of bark oil contains signals corresponding to ferulates, which are absent in the lignin oil from wood. Fig. S4† shows the ^{13}C NMR spectra of the aromatic region of the same bark and wood oil samples. These spectra corroborate the higher S/G ratio in wood lignin oil than in bark oil.

In order to obtain a more complete mass balance of the RCF process for black locust bark and wood, reactions were carried out using commercial nickel catalyst pellets (Ni on silica, crushed to 0.5–1 mm). Afterwards, the nickel pellets were magnetically separated from the residual solids (~99 wt% of the catalyst pellets were recovered), thereby obtaining a catalyst-free bark/wood residue which could be used for compositional analysis. The composition of the raw substrates and their residue after reaction is given in Fig. 6. As already mentioned, the solids retention (*i.e.* the solid fraction after RCF) is higher for wood than for bark. This is due to the large portion of carbohydrates present in wood which remain in the solid pulp after RCF. Cellulose is largely retained, both for bark and for wood. In contrast, the hemicellulose content is strongly reduced upon RCF in case of bark (from 10 to 3 wt%), while it is well retained in case of wood (from 17 to 14 wt%). This suggests that black locust bark hemicellulose is less resistant to solvolysis compared to wood hemicellulose. A possible explanation could be found in the hemicellulose composition of bark and wood. Black locust bark contains a larger fraction of arabinose, galactose and mannose, and a smaller fraction of xylose compared to black locust wood. The xylan backbone appears to be more resistant to solvolysis, while the other carbohydrates are released more easily upon RCF (Fig. S5†). The lignin content in the bark residue is significantly higher than in the wood residue indicating incomplete delignification. This phenomenon could be (partially) explained by a more condensed lignin structure in bark, as suggested by the lower S/G ratio.

To get more insight in the structure of the bark and wood and their solid residues, scanning electron microscopy (SEM) was performed on these catalyst-free samples (Fig. 7). Additional SEM images at other magnifications can be found in the ESI (Fig. S6†). These images show the clear morphological differences between bark and wood particles. Wood (250–500 μm) has a more fibrous, particulate structure, while

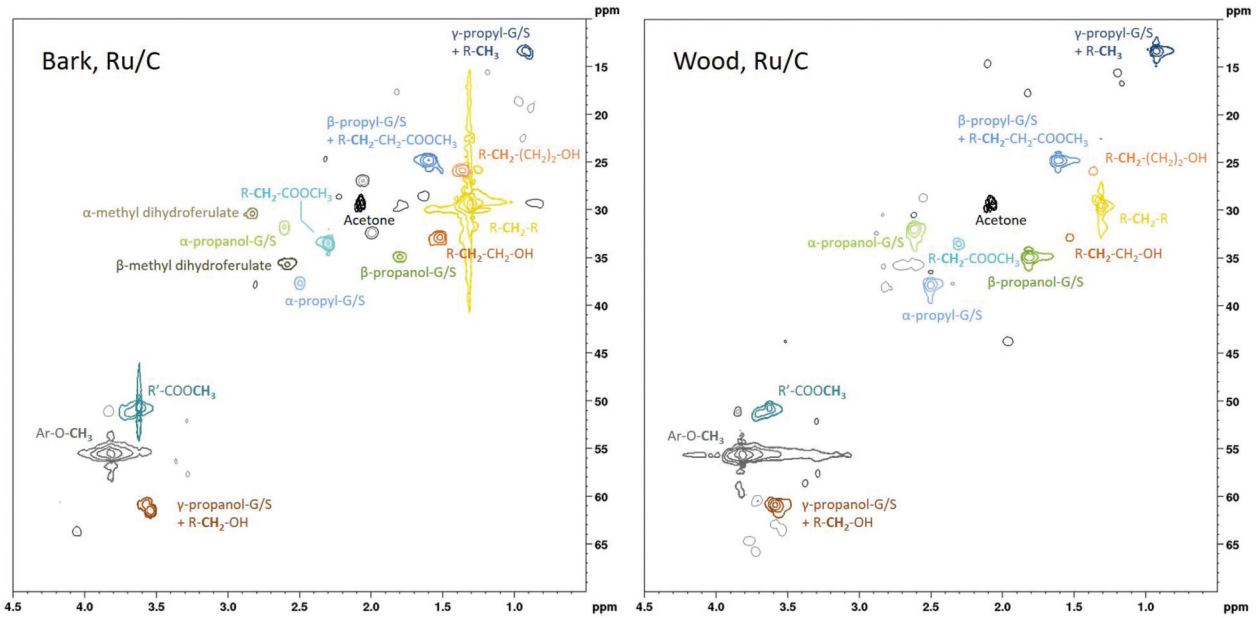

Fig. 5 $^{1}H-^{13}C$ HSQC NMR spectrum of the chloroform oil resulting from RCF of bark or wood. Signals were assigned in accordance to literature and Chemdraw predictions.[1] RCF reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g Ru/C, 40 bar H_2, 235 °C, 4 h. R = aliphatic chain, R′ = aliphatic chain or alkyl phenol.

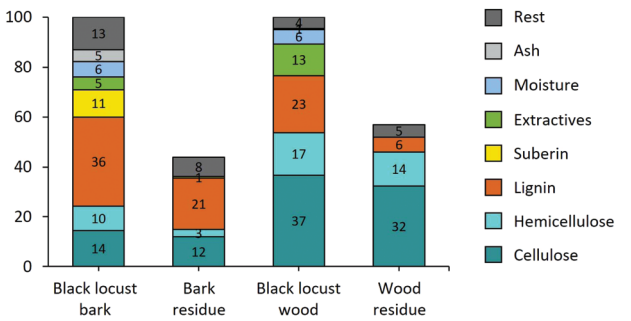

Fig. 6 Compositional analysis of raw black locust bark and wood and their solid residues after RCF processing. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g Ni/SiO_2 catalyst pellets, 40 bar H_2, 235 °C, 4 h. For the analytical procedures, the reader is referred to the ESI.†

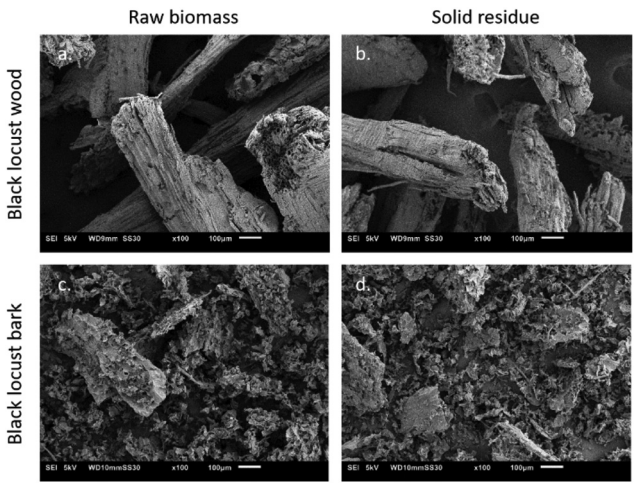

Fig. 7 Scanning electron microscopy images of the raw biomass and solid RCF residue at 100× magnification. Other magnifications (50×–1000×) can be found in the ESI (Fig. S6†). RCF reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.2 g Ni 5256 pellets, 40 bar H_2, 235 °C, 4 h. For the analytical procedures, the reader is referred to the ESI.†

bark (<500 μm) is composed of numerous small flakes, with some larger particles in between. Next, the raw substrates and the solid, catalyst-free residues from RCF were compared. Even though 57 wt% of the bark and 44 wt% of the wood is solubilized upon RCF, it can be seen that the morphology of the solids, both for bark and for wood, is well retained. As an additional structural analysis, X-ray diffraction (XRD) was performed to assess the crystallinity and polymorphism of the cellulose. Fig. S7† shows the X-ray diffractograms of raw bark and wood, and their solid residues. From this figure, it can be deduced that raw wood is more crystalline than bark. Furthermore, the crystallinity of wood clearly increases upon RCF, explained by the removal of amorphous lignin, leaving the crystalline cellulose intact. For bark, the residue is not crystalline at all, which can be explained by a lower cellulose content and possibly less crystalline cellulose.[47] Both for bark and wood, the cellulose allomorph appears to be cellulose type I, based on their X-ray diffractograms (Fig. S7†).[48]

Influence of temperature and reaction time

To keep track of the depolymerization of both lignin and suberin, RCF of black locust bark was performed at different temperatures and different reaction times (Fig. 8). Bark oil

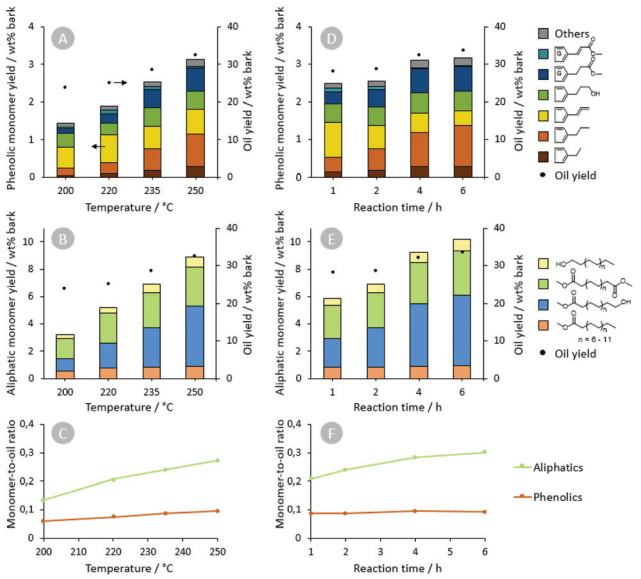

Fig. 8 Influence of the temperature (A, B and C) and reaction time (D, E and F) on the RCF of black locust bark. Effects on the bark oil yield, phenolic (A and D) and aliphatic (B and E) monomers yield and monomer-to-oil ratio (C and F). Reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g Ru/C, 20 bar H_2. Temperature variation (A, B and C) was done with 2 h reaction time. Reaction time variation (D, E and F) was done at 235 °C.

yield, phenolic monomer yield and aliphatic monomer yield all increase with an increasing temperature or reaction time (~process severity). Also the monomer-to-oil ratio, defined as wt% aliphatic or phenolic monomers/wt% bark oil,[49] increases with increasing temperature and reaction time, indicating a more complete depolymerization at higher process severity.

When comparing phenolic monomer yields, it is clear that the reaction temperature is important to obtain a high monomer yield (1.4 wt% bark at 200 °C, 3.1 wt% at 250 °C). The reaction time, on the other hand, exerts a minor influence (2.5 wt% bark at 1 h, 3.2 wt% at 6 h), indicating that depolymerization is happening fast (mainly during the first hour) at 235 °C. The main phenolic monomers are methyl dihydroferulate and propanol-, propenyl- and propyl-G/S. The selectivity towards propyl-G/S increases with increasing temperature or reaction time, which is accompanied by a decreasing selectivity towards propenyl-G/S, indicating an improved hydrogenation at higher process severity. GPC analysis of the bark oils obtained at varying temperature and reaction time (Fig. S8†) shows that lower process severities result in a higher selectivity towards phenolic oligomers and thus a less efficient depolymerization activity.

Also for the aliphatic monomers, a higher temperature or reaction time results in a higher monomer yield. Especially the yield of the ω-OH methyl esters increases greatly with increasing process severity. This observation is in line with previous studies on alkaline methanolysis of cork, showing the release of the ω-OH acids at the more severe conditions (*i.e.* higher sodium methoxide loadings). A possible explanation is that these ω-OH acids are located deep within the suberin structure and are thus less accessible.[50,51] The possible hydrogenation of α,ω-dimethyl esters into ω-OH methyl esters can be ruled out because the selectivity towards ω-OH methyl esters is similar in the blank and the catalyzed reactions (*vide infra*).

Influence of catalyst type

Next, several hydrogenation catalysts, known for their applicability in RCF of other substrates, were tested in the RCF of black locust bark. Both supported noble metal catalysts (Ru/C,[28,52] Ru/Al_2O_3,[46,53] Pd/C[40,54]) as non-noble metal catalysts (RANEY® Ni,[42] Ni/SiO_2, copper chromite[55]) were compared under typical RCF conditions (MeOH, 250 °C, 2 h, 20 bar H_2 at RT). The phenolic monomer, aliphatic monomer, and bark oil yield are presented in Fig. 9. The bark oil yield is substantially lower for the blank reaction, possibly due to partial redeposition of condensed lignin products.

The phenolic monomer yields are highest with Pd/C and Ni 5249P (nickel, 64% on silica), both 3.9 wt% of the bark, indicating a fast reductive stabilization of the phenolic intermediates. The selectivity towards propanol-G/S is also highest for Ni 5249P (41%) and Pd/C (31%), whereas the selectivity towards propyl-G/S is highest for Pd/C (29%) and Ru/C (27%). These differences in selectivity are also observed *via* GPC analysis of the bark oil with different catalysts (Fig. S9†).

In an attempt to rationalize the differences in phenolic monomer yield between catalysts, the total phenolic monomer yield was plotted against the fraction of unsaturated phenolic monomers (*i.e.* methyl ferulate and propenyl-G/S) (Fig. 10). It is observed that a negative correlation exists between both measures. This indicates that catalysts with a higher hydrogenation capacity (less unsaturated monomers) are better at

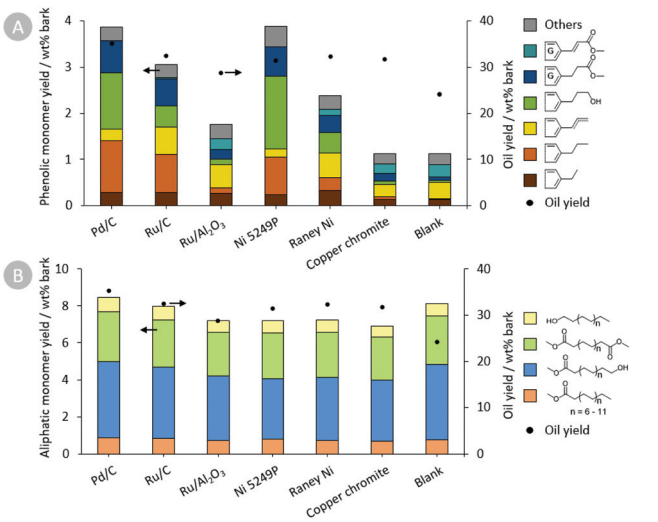

Fig. 9 Screening of different hydrogenation catalysts for the RCF of black locust bark. Effect on (A) phenolic monomers and (B) aliphatic monomers. Reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g catalyst, 20 bar H_2 (blank: 6 bar N_2, no catalyst), 250 °C, 2 h. Supported catalysts: Pd/C, Ru/C and Ru/Al_2O_3 have 5 wt% metal loading, Ni 5249P has a 64 wt% Ni loading on silica.

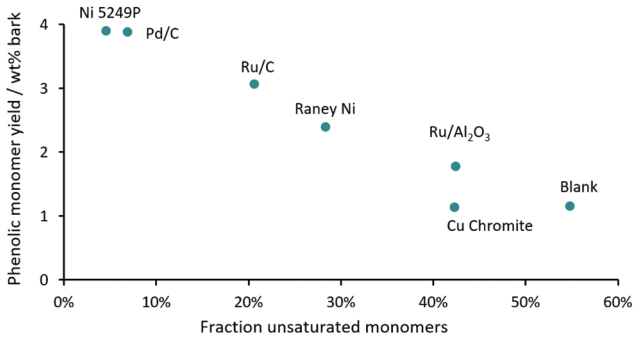

Fig. 10 Total phenolic monomer yield (see Fig. 9A) plotted against fraction unsaturated phenolic monomers (*i.e.* propenyl-G/S and methyl ferulate) for various hydrogenation catalysts.

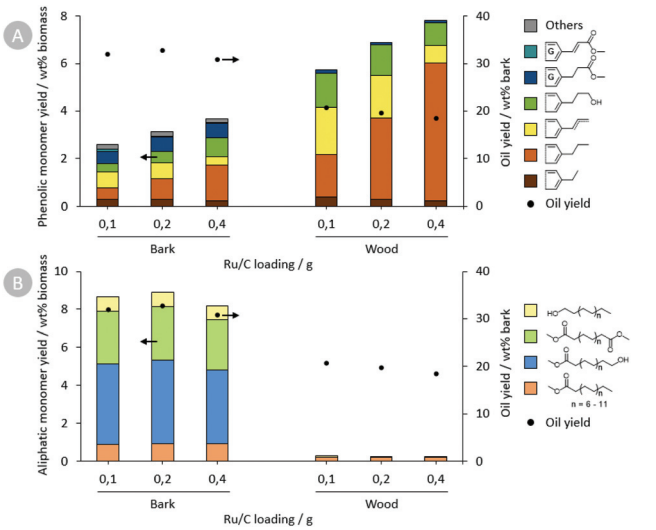

Fig. 11 Influence of catalyst (Ru/C) loading on the RCF of black locust bark and wood. Effect on (A) phenolic monomers and (B) aliphatic monomers. Reaction conditions: 40 mL MeOH, 2 g black locust bark or wood, 0.1–0.4 g Ru/C, 20 bar H_2, 250 °C, 2 h.

stabilizing phenolic intermediates, leading to a higher monomer yield. In earlier work, it was shown that a high degree of unsaturation corresponds with more extensive repolymerization.[56,57]

By comparing the unsaturated phenolic monomer yields, it can be seen that methyl ferulate is hydrogenated faster than propenyl-G/S. With the most active hydrogenation catalysts (Ru/C, Ni 5249P and Pd/C), no methyl ferulate was detected, whereas propenyl-G/S was still present (in small amounts). Also the total ferulate yield (*i.e.* methyl ferulate and methyl dihydro ferulate) is less sensitive towards the choice of hydrogenation catalyst than the other phenolic monomers. This implies that the ferulic acid-derived intermediates formed upon depolymerization (*i.e.* methyl ferulate) are less sensitive to repolymerization than the lignin-derived intermediates (*i.e.* coniferyl and sinapyl alcohol).[56]

The aliphatic monomer yields on the other hand are all very similar (6.9–8.5 wt% bark), indicating a negligible influence of the catalyst properties on suberin depolymerization. The selectivity towards α,ω-dimethyl esters, ω-OH methyl esters, methyl esters and alkanols are approximately equal for all catalysts tested, and similar to that of catalyst-free reactions, suggesting that no hydrogenation of aliphatic ester/alcohol groups occurs during RCF.

Additionally, the influence of H_2 pressure (10–40 bar at RT) was assessed for Ru/C- and Pd/C-catalyzed RCF of bark (Fig. S10 and S11†). Increasing the H_2 pressure causes an increase in total phenolic monomer yield. At 10 bar H_2 pressure, the total phenolic monomer yields are 2.9 and 3.3 wt% bark, with Ru/C and Pd/C respectively, while at 40 bar H_2 these are 3.3 and 3.9 wt% bark. The increase in phenolic monomer yield at higher H_2 pressure is accompanied by an increase in selectivity towards propanol-G/S and a decrease towards propenyl-G/S. The effect of H_2 pressure on the aliphatic monomers is minimal. This is in line with the chemistry requiring esterification instead of redox chemistry.

Influence of catalyst loading

Next, the influence of catalyst (Ru/C) loading on RCF of black locust bark was assessed, and results were benchmarked against those obtained with RCF of wood (Fig. 11). Reactions were performed with 0.1–0.4 g Ru/C, which corresponds to a catalyst loading of 5–20 wt% relative to the biomass. Typical RCF conditions (250 °C, 2 h, 20 bar H_2 at RT) were used. It is clear that, within this range, the Ru/C catalyst loading strongly affects phenolic monomer yield and selectivity. As depicted in Fig. 11, a rise in the catalyst loading increases the total phenolic monomer yield, both for bark and for wood. In bark, the total ferulate yield is only slightly influenced by the Ru/C loading, whereas the yield of other phenolic monomers is affected more substantially. This observation again corroborates the above mentioned hypothesis that the ferulate-derived intermediates are less sensitive to repolymerization than lignin-derived intermediates such as coniferyl and sinapyl alcohol.

When comparing the non-ferulate phenolic monomers, it is clear that a higher catalyst loading favors a higher yield of propyl-G/S and a lower yield of propenyl-G/S. As suggested by Renders *et al.*, the intermediates coniferyl or sinapyl alcohol formed upon solvolytic lignin depolymerization can either undergo hydrogenation to propanol-G/S (R2), hydrogenolysis to propenyl-G/S followed by hydrogenation to propyl-G/S (R3 + R6), or repolymerization (R4) (for the reaction network, see Fig. S13†).[46] Under the investigated conditions, reactions R3 + R6 prevail over R2, as evidenced by the higher combined yield of propyl- and propenyl-G/S than that of propanol-G/S. Upon increasing the catalyst loading, less repolymerization (R4) occurs, leading to a higher phenolic monomer yield. Furthermore, the rate of propenyl-G/S hydrogenation (R6) increases, leading to a high propyl-G/S yield. These trends are observed with both bark and wood as substrate.

The influence of the Ru/C loading on the aliphatic monomer yield from bark is negligible, corroborating the minimal role of redox catalysis in suberin depolymerization.

Separation of the bark oil: heptane extraction

Previous work has shown that hexane can be used to effectively separate the apolar monomers from the lignin oil.[28] Following a similar approach, the bark oil from black locust bark was separated *via* heptane extraction (extracted twice at 70 °C, see ESI†). Fig. 12 shows the composition and oil yield of the starting bark oil, the heptane extract and the residue after extraction. On a weight basis, about half of the bark oil ends up in the heptane extract and the other half remains as a residue. From Fig. 12 it is clear that almost all of the aliphatic monomers, due to their hydrophobic nature, end up in the heptane extract. Additionally, the more apolar phenolic monomers (propyl- and ethyl-G/S) are extracted into the heptane phase, while the more polar phenolic monomers (propanol-G/S) remain in the residue. These findings are supported by GPC analysis (Fig. 13). Furthermore, this figure shows that the heptane phase is made up mostly of monomers and some dimers, while most of the dimers and oligomers remain in the residue.

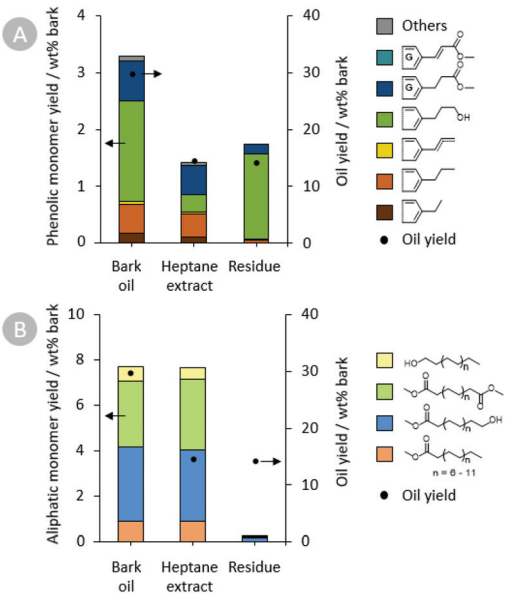

Fig. 12 Heptane extraction of bark oil resulting from RCF of black locust bark (extracted twice at 70 °C during 1 h, for the detailed procedure, see ESI†). Distribution of (A) phenolic monomers and (B) aliphatic monomers in the bark oil, heptane extract and residue. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g Ni 5249P, 40 bar H_2, 235 °C, 4 h.

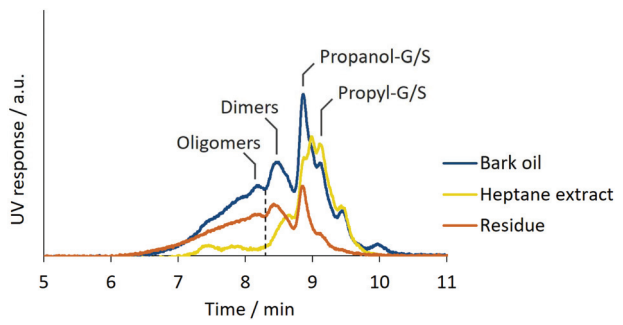

Fig. 13 GPC of bark oil, heptane extract and residue. RCF reaction conditions: 40 mL MeOH, 2 g black locust bark, 0.2 g Ni 5249P, 40 bar H_2, 235 °C, 4 h. Area under the curves is set proportional to the oil yield (*i.e.* bark oil, heptane extract and heptane residue).

Conclusions

In this contribution, a biorefinery for bark was investigated, a low-value and abundant residue. Given the high lignin content of bark, a lignin-focused strategy was used. More specifically, a reductive catalytic fractionation (RCF) process was carried out on black locust bark. RCF encompasses the solvolytic extraction and depolymerization of lignin and suberin, followed by the reductive stabilization of the lignin fragments. This way, black locust bark could be fractionated into (i) a solid phase, containing mainly carbohydrates and residual lignin, (ii) an aqueous phase, and (iii) an oil phase, containing aliphatic, suberin-derived monomers and lignin mono-, di- and oligomers. The highest bark oil yield (35.1 wt%) was obtained with Pd/C at 250 °C, during 2 hours and at 20 bar H_2 pressure.

The extent of lignin and suberin conversion is mainly governed by the 'process severity', *i.e.* a combination of temperature and time. On the other hand, parameters that govern catalyst activity (*e.g.* catalyst type, loading, H_2 pressure) only affect the chemical stabilization of lignin fragments, thereby determining phenolic monomer yield and selectivity. Suberin disassembly does not require redox catalytic action.

RCF of black locust bark was benchmarked against the RCF of black locust wood, resulting in a higher oil yield and lower solid retention for bark. This comparison further highlights the presence of suberin and a more condensed lignin structure in bark. Therefore, the bark lignin oil has a larger oligomer fraction, and relatively higher average molecular weight, which might be advantageous for certain mid-range oligomer applications. The unique α,ω-bifunctional nature of the suberin-derived monomers (*i.e.* diesters and ω-OH esters) makes them ideal (co-)monomers for hydrophobic polymer applications (*e.g.* polyester,[36] polyurethane[37] and polyamides[58]). As a proof-of-concept, a heptane extraction was carried out to separate the bark oil.

The bark solid residue has a different morphology and substantially lower carbohydrate content compared to typical wood-derived RCF pulps, likely requiring other valorization strategies than traditional pulp valorization.

Conflicts of interest

There are no conflicts to declare.

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