Debottlenecking a Pulp Mill by Producing Biofuels from Black Liquor in Three Steps

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By extracting lignin, pulp production can be increased without heavy investments in a new recovery boiler, the typical bottleneck of a pulp mill. The extraction is performed by using 0.20 and 0.15 weight equivalents of CO_2 and H_2SO_4 respectively. Herein, we describe lignin esterification with fatty acids using benign reagents to generate a lignin ester mixable with gas oils. The esterification is accomplished by activating the fatty acid and lignin with acetic anhydride which can be regenerated from the acetic acid recycled in this reaction. The resulting mass balance ratio is fatty acid/lignin/acetic acid (2:1:0.1). This lignin ester can be hydroprocessed to generate hydrocarbons in gasoline, aviation, and diesel range. A 300-hour continuous production of fuel was accomplished. By recirculating reagents from both the esterification step and applying a water gas shift reaction on off-gases from the hydroprocessing, a favorable overall mass balance is realized.

Introduction

Global warming is one of this century's most essential challenges. The majority of crude oil is used for transportation and thus to decrease the consumption of crude oil is an important key to reduce global warming. As electrification will take time, substituting fossil fuels for renewable ones is important for decreasing greenhouse gases in the short term. At the same time, resource allocation is another challenge with a growing population. Thus, we need to use existing resources more efficiently when possible.[1] The pulp and paper industry is the largest operating bio-refinery, where the Kraft process is the dominating technology with an annual production of 260×10^6 tons.[2] The major drawback of this process is the low yield of the high-value product, that is, pulp with yields of 45–50 wt% where the rest consists of lignin and hemicellulose. Even though some of the lignin is used as a reducing agent to re-activate the chemicals involved in the process and also to produce process heat, most of it is burnt to a low value.[3] In addition to the high-pressure steam, which can generate electricity albeit to a low value, also low-pressure steam is produced in excess and this energy has currently no use. The black liquor, an alkali water solution containing lignin, is burnt in an operation unit called "recovery boiler". The recovery boiler is the most capital expenditures (CAPEX) intensive unit in a pulp mill and thus, almost all mills operate with the recovery boiler as the bottleneck of the pulp production. When the capacity of the recovery boiler is reached, there are two options to increase the production of pulp:[4] 1) upgrading of the recovery boiler; 2) reduce the amount of black liquor that is burnt in the recovery boiler; the latter can be easily achieved by extracting the Kraft lignin (Figure 1).[5]

At least 10% of the lignin in black liquor can be removed without any adjustments to the mill.[6] However, after proper adjustments, up to 80% can be extracted. Pure Kraft lignin is not a product of Kraft pulping but has to be isolated from the black liquor. This can be accomplished by lowering the pH of the black liquor to 9.5–10.5 to precipitate the lignin. Different methods have been developed, involving inorganic acids and carbon dioxide with or without oxidation.[7,8] Precipitating lignin from black liquor with first carbon dioxide and then sulfuric acid has been commercialized and implemented in three pulp mills.[8] There is an extensive availability of lignin, accounting for approximately 50% of the production of pulp (130×10^6 tons lignin per year). For a pulp mill to take an investment decision on Lignoboost technology, they require a product with a long-time predicted demand.[9–13] Biofuels

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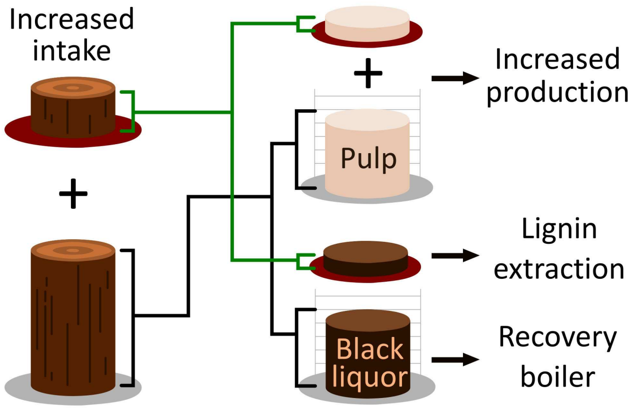


Figure 1. Pulp production increase by extracting lignin from black liquor.

compatible with current automotive engines can be considered products with unlimited demand for yet a generation in light of an estimated global fuel demand of 3.8×10^9 tons per year (2025).[14] However, Kraft lignin cannot be processed directly in current refineries exploiting fixed bed reactors, which is mainly due to low solubility in suitable carrier liquids. The transformation of lignin in the fluidized catalytic cracker (FCC) has not been successful owing to coke formation originating from the phenolics.[15–17] Previous attempts to produce drop-in quality fuels from lignin mainly explored: hydrothermal liquefaction (HTL).[18–20] HTL has been extensively studied and several bio-oils have been evaluated and further hydrotreated for drop-in fuel production.[20,21] Nonetheless, to apply HTL on lignocellulosic biomass and Kraft lignin high pressures and temperatures are required and the product still needs to be further hydroprocessed in a refinery.[22–24] Parallelly, catalytic pyrolysis of Kraft lignin has been investigated in batch, reporting moderate yields of alkanes and aromatics.[25–27] However, to date no running facilities are using these technologies, which is mainly due to the high CAPEX associated. In fact, there are no commercial plants that use Kraft lignin and no reports that support the implementation of any technology to process this raw material.

Here, we report a three-step procedure to valorize black liquor from the pulp and paper industry to biofuel. The Kraft lignin is extracted from the black liquor, esterified by a bio-derived fatty acid to enhance solubility in oil refinery streams, and finally hydro-processed in a conventional refinery set-up to produce a drop-in biofuel in gasoline, aviation and diesel range. This process has advantages over dedicated HTL or gasification, which all require major investments in high CAPEX infrastructure to handle high pressures and explosive gases.

Results and Discussion

A three-step process from black liquor to biofuel is described. Lignin is precipitated from black liquor by acidification and filtration. The precipitated lignin is esterified with a bio-based carboxylic acid to form a lignin oil.[28] The lignin oil is finally mixed with a hydrocarbon mixture and then co-processed in a hydroprocessing unit to produce valuable hydrocarbons of fuel range.

Precipitation of lignin from black liquor

An industrial process for precipitating lignin in black liquor has been developed by Theliander, Innventia, and Valmet.[8] This two step-procedure consists of a precipitation and a washing step (Figure 2 and Figure S1 in the Supporting Information). Partially evaporated black liquor from softwood (dry substance 30–45 wt%) was treated with pressurized carbon dioxide (200 kg of CO_2 per ton of lignin) that can be produced *in-situ* from the recovery boiler or the refinery (*vide infra*), to lower the pH from above 13 to below 10. The resulting slurry was then filtrated by pressure filters to give lignin cakes. The filter cakes were sprayed with concentrated sulfuric acid to fully re-protonate the lignin at pH 2 (150 kg of sulfuric acid per ton of lignin).[29] The added amount of sulfur, in form of sulfuric acid, has to be compensated with an addition of sodium hydroxide (122 kg of sodium hydroxide per ton of lignin) to re-establish the sodium/sulfur balance and merge the resulting aqueous washing solutions with the mill liquors. After partial drying, the precipitated lignin appeared as a light brown powder containing approximately 33 % of moisture. A further drying step was not desired since lignin powder with a dry content above 80 % can undergo dust explosion.[30,31] The generated lignin cannot directly be processed in existing oil refineries, mainly because the powder is not soluble in any refinery carrier liquids.

Drying of lignin

As already stated, pure Kraft lignin powder shows scarce solubility in the most common organic solvents and, even though highly hygroscopic, is insoluble in water. After filtration, lignin has a dry content of 66 wt%, which is an advantage for handling. However, water is detrimental for the following reaction and therefore, the lignin needs to be dried. Therefore, we developed a procedure to safely dry the lignin. Wet lignin with a 66 wt% dry content is mixed with fatty acids. The water is then evaporated to yield a slurry of dry lignin in fatty acids (Figure 3). Several industrial techniques can be exploited to achieve the dried slurry such as falling film,[32] thin film[33] and forced circulation[34] evaporators. This procedure has been validated in lab-scale, pilot-scale (25 kg of lignin per batch) and demonstration-scale (200 kg of lignin per batch) to yield dry lignin in fatty acids. In a demonstration plant, 200 kg of lignin [133.3 kg of dry lignin + 66.7 kg of water] and 266.6 kg of fatty

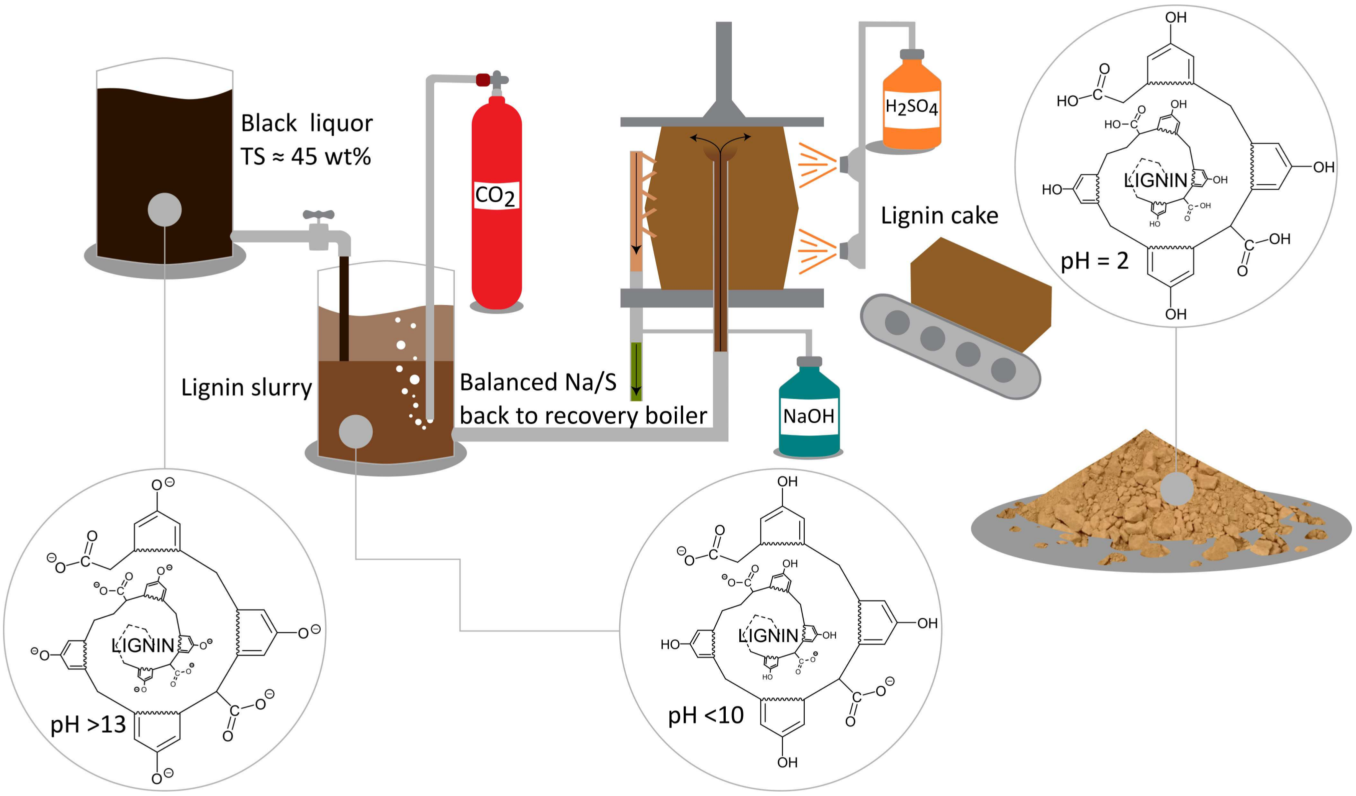


Figure 2. Lignin precipitation.

Figure 3. Lignin drying.

acid (**FA**), in form of Tall Oil Fatty Acid (TOFA), were mixed to give a slurry (**A**). The resulting mixture was set under vacuum and heated to 140 °C. Water was evaporated from the slurry and the reactor vented to yield a dewatered slurry (**B**). Thus, the dried lignin can be stored safely as a slurry ready to undergo further transformations.

Esterification of lignin

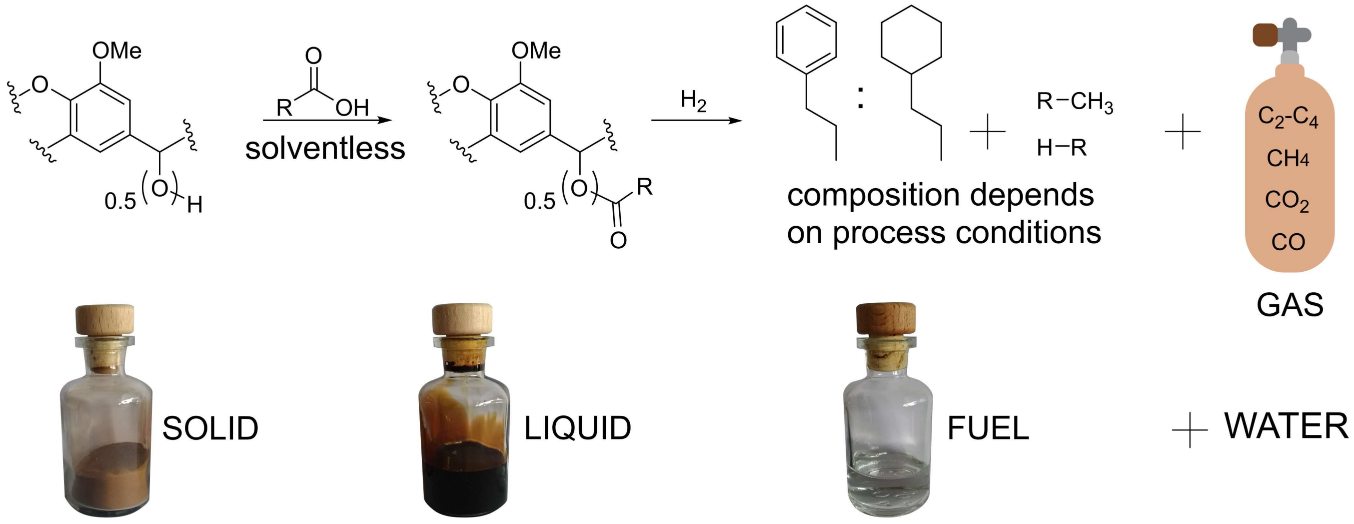
A known method to solubilize lignin in organic solvents is to esterify it with fatty acids.[35,36] In this study, TOFA has been used as a source of fatty acid. Former procedures have reported the usage of thionyl chloride[37] or oxalyl chloride[38] to produce reactive acyl chlorides *in-situ*. This is not a desirable pathway for several reasons: 1) Large amounts of chlorides are left in the lignin ester product, which is not compatible with the catalyst bed involved in the refining step and would then require an extra purification step; 2) The reaction between lignin and the reactants is exothermic and therefore challenging in large scales; 3) In addition, hydrochloric acid is generated and requires a stoichiometric addition of a base to neutralize the mixture. We envisioned a process that would circumvent the shortcomings described above by developing a novel esterification protocol using only acetic acid derivatives and an organocatalyst. The reaction is a one-pot process and described in Table 1 (reactor described in Figure S5).

Pyridine was used as catalyst, mainly because it can be easily recycled by distillation, however, different aromatic amines have been investigated and give comparable yields.[39] To the dry slurry (**B**) comprising 133 kg of dried lignin in 266 kg of fatty acid, 20 kg of catalyst and 93 kg of acetic anhydride were added at 140 °C to form a mixture (**C**). Then, the temperature was raised to 180 °C. The reaction was run at 180 °C for 30–45 min under mechanical stirring and reduced pressure. The reduced pressure pushes the equilibrium towards the lignin fatty esters, where acetic acid is distilled off, yielding esterified lignin and unreacted FA. Above 70 % of acetyl groups were recovered as acetic acid, while 28 % remained bound to the lignin in intermediate mixture **D**. However, this ratio can be

Table 1. Approximate reaction medium composition over time [wu].

	A	B	C	D	Lignin oil	Recovered
LB lignin	100	100	100	180	180	–
FA	200	200	200	120	120	–
Catalyst	–	–	15	15	<1	13.2
Ac_2O	–	–	70	10[a]	10[a]	50[b]
H_2O	50	–	–	–	–	–

[a] As acetyl groups. [b] As AcOH.



Scheme 1. Kraft lignin converted into biofuel through esterification and hydrotreatment.

altered by changing the reaction time. Above 90% of the catalyst was recovered by fractional distillation where the remaining aliquot will undergo hydrotreatment (Scheme 1). During the esterification process, the slurry is converted into a mixture comprising esterified lignin and free fatty acids. This product can now be pumped at 100 °C (2600 mPa s), making its handling and transportation sufficient. To make the esterified lignin soluble in fatty acids, the fatty ester moieties should be above 45 mol% with respect to the initial free hydroxy group. The final product was discharged from the reactor. Acetic acid (66 kg) and pyridine (17.5 kg) were collected, of which the pyridine catalyst can be directly recycled. The acetic acid will be used to regenerate the acetic anhydride in a separate operating unit.

The elemental analysis of lignin oil shows 79% of C, 11.4% of H, 42 ppm of N, 9.7% of O and 0.2% of S. GPC analysis clearly shows a shift to lower retention time of the lignin oil while compared to the initial Kraft lignin, involving a higher molecular weight [M_w(lignin oil) = 10 kDa; M_w(lignin) = 3.5 kDa], confirming the success of the esterification step (Figure 4). It should be noted, that both the drying, and esterification processes can be performed by using a surplus of low-pressure steam from the pulp mill, thus the energy balance becomes favorable.

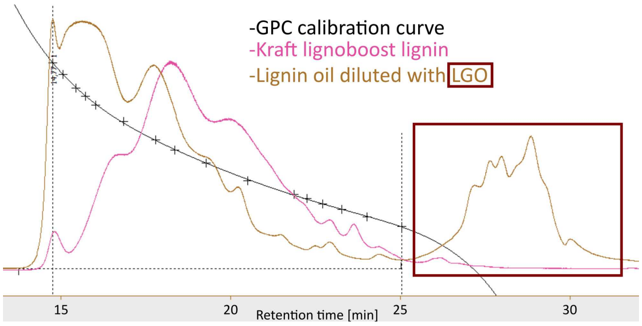
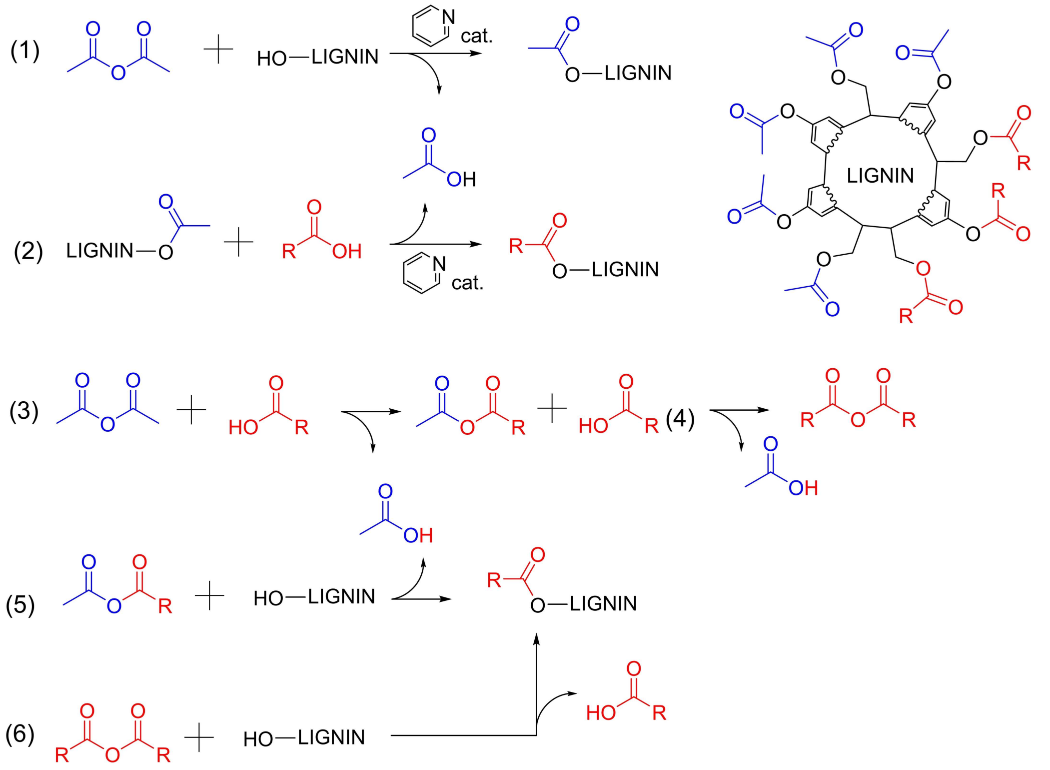


Figure 4. Gel-permeation chromatogram of Kraft Lignoboost lignin and lignin oil/feed mixture.

Reaction mechanisms during esterification

Several reactions may occur during lignin esterification (Scheme 2). Acetic anhydride can react with hydroxy groups of lignin to give acetates catalyzed by pyridine (1).[40,41] The same catalyst can promote the reaction between fatty acid and lignin acetates yielding fatty esters of lignin (2). Acetic anhydride can also react directly with fatty acids to give mixed acetic fatty acid anhydrides and symmetrical fatty acid anhydride (3 and 4).[42] Mixed acetic fatty acid anhydrides can react with the free hydroxy group of lignin to yield both fatty acylated and acetylated moieties (5), where symmetrical fatty



Scheme 2. Reaction scheme.

acid anhydride can only yield fatty acylated lignin (6). Ester acidolysis performed by free fatty acid on aliphatic lignin acetates is also possible under those reaction conditions.[43]

To elucidate the reaction mechanism and the role of the reactants during lignin esterification, several control reactions were performed (Table 2 and Table S2). To facilitate analysis, stearic acid and oleic acids were used in these reactions. By reacting Kraft lignin with a fatty acid, no product was observed both in the presence and absence of a catalyst (Table 2, entries 1 and 2). Negligible reactivity was observed with acetic acid (Table 2, entry 3). In accordance with previous reports, the Kraft lignin was fully acetylated by acetic anhydride in presence of a catalyst to yield Kraft lignin acetate (KLA; Table 2, entry 4). Replacing acetic anhydride with fatty acid anhydride resulted in a very low degree of esterification, probably due to the increased steric hindrance provided by the fatty chain (Table 2, entry 5). KLA was used as a substrate in the presence of only fatty acid, however low reactivity was observed (Table 2, entry 6), while good yields were obtained in the presence of both fatty acid and organocatalyst (Table 2, entry 7). These results support a reaction mechanism in which the lignin is firstly transformed into KLA by acetic anhydride and pyridine and then undergoes trans-esterification driven by the removal of acetic acid and the excess of fatty acids, catalyzed by pyridine [Scheme 2, reactions (1) and (2)].

To further verify our hypothesis, we performed an additional mechanistic study exploiting ^{13}C-labeled compounds (e.g., ^{13}C

Table 2. Control reactions.[a]

Entry	Substrate	Stearic acid [g]	Anhydride	Pyridine [mg]	Degree of ester [%]
1	KL	1 (1.1 equiv)	–	75	0
2	KL	1 (1.1 equiv)	–	–	0
3	KL	1 (1.1 equiv)	–	75	0
4	KL[b]	–	acetic (excess)	75	$>$99 (KLA)
5	KL[b]	–	stearic (excess)	75	$<$5 (stearic ester)[c]
6	KLA[d]	1 (1.1 equiv)		–	$<$5 (stearic ester)[c]
7	KLA[d]	1 (1.1 equiv)		75	$\approx$30 (stearic ester)[c]

[a] Reaction conditions (unless otherwise stated): 667 mg of Kraft lignin (TS 66 %) to 1 g of stearic acid was subjected to vigorous stirring at 130 °C until a homogenous slurry was reached. Then vacuum was applied to remove water (when present) and kept for 5 min. The system was then vented and, if required, pyridine and anhydride were added. The reaction mixture was heated to 180 °C. After 30 min, vacuum was applied to remove acetic acid and pyridine until completion. [b] Dry KL, substrate amount = 500 mg. [c] Estimated by NMR spectroscopy. [d] Fully acetylated Kraft lignin, substrate amount = 636 mg.

oleic acid and ^{13}C acetic anhydride; see the Supporting Information, Section S3.3.1). The isotopic label allowed us to quantify, relative to lignin, the degree of esterification and to discriminate among the different kind of esters (i.e., aliphatic/aromatic and acyl/acetyl esters). The real-time analysis study shows a rapid increment of the degree of esterification after the addition of the acetic anhydride to the reaction mixture initially giving mostly acetates as product (Figure 5). By prolonging the reaction time and applying vacuum, the composition of esters shifted towards the oleates. Interestingly, the study shows how mainly the aromatic acetates are transformed into oleate esters (Figure 5).

Organocatalysis

Our group has investigated the performance of several nitrogen-containing organocatalysts for fatty esterification of lignin, reporting methyl-imidazole as the best candidate in our previous study.[28] However, to simplify the separation of the organocatalyst from the acetic acid/catalyst mixture simple pyridine was chosen as the most valid alternative. Suitable boiling point and price/availability made this aromatic compound the best choice. Concerning the toxicity of pyridine, it has to be considered that almost 90% of it is recovered and remerged into the stream while the rest undergo hydrotreatment yielding hydrocarbons, which is acceptable for the refinery.

Acetic anhydride production

Acetic anhydride can be produced from acetic acid through the established ketene method.[44] The carboxylic acid is dehydrated in gas phase at high temperatures and the condensation of two molecules lead to acetic anhydride.[45] Thus, 0.7 mass equivalents of acetic anhydride to lignin is required. Approximately 0.9 mass equivalents of acetic acid are needed for the transformation to acetic anhydride (92% of yield). Approximately 28% of the acetyl groups are lost/incorporated into esterified lignin and have to be compensated for by fresh acetic acid. The external requirement of acetic acid amounts to 0.387 mass equivalents, required to compensate for the loss during the transformation. Moreover, the high temperature required for the ketene formation cannot be sustained by the steam provided by the mill, so an external source of energy would be needed. We calculated that 200 kg of gasoil (46 MJ kg^{-1}) is required per ton of acetic anhydride produced via the ketene method, 140 kg of gasoil (6.4 GJ) is then needed to process 1 ton of lignin. However, the increase in pulp production is also associated with a surplus of bark (23 MJ kg^{-1}), which is commonly burnt. The increased bark production amounts to approximately 100 kg per ton of processed (2.3 GJ). Moreover, from the HT step, 94 kg of C_3–C_4 gaseous HC (49 MJ kg^{-1}) are produced (4.6 GJ). By exploiting those aliquots of byproduct, the external needing for fuel would be reduced to zero.

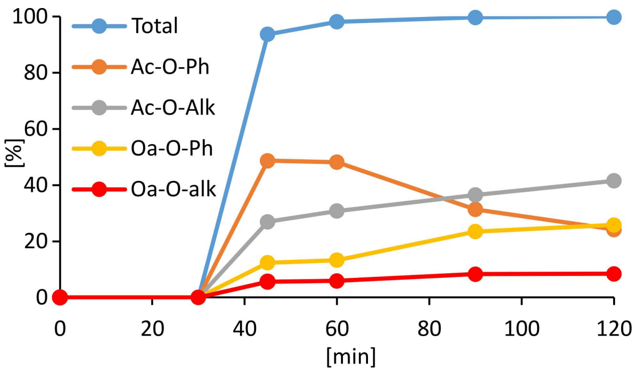


Figure 5. Esterification of KL with ^{13}C-labeled oleic acid and acetic anhydride over time. Relative abundances are given for aromatic acetates (Ac-O–Ph), aliphatic acetates (Ac–O-Alk), aromatic oleates (Oa-O–Ph), and aliphatic oleates (Oa-O-Alk).

Hydrotreatment

To process lignin in a fixed bed reactor, the feed needs to be fully soluble in carrier liquids such as different types of gas oils. Indeed, the above-described lignin oil is fully soluble in light gas oil (LGO). To control the exotherm generated during the hydrotreatment and the coke formation, the oxygen content in the feed should not exceed 15% and this was accomplished by blending lignin oil with LGO and TOFA to give a lignin/TOFA/LGO ratio of 10: 60: 30 accounting the fatty acid ester moieties on lignin as free fatty acids (TOFA).The hydrodeoxygenation of the feed was performed in a high-throughput unit with an applied operation pressure of 120 bar of pure hydrogen gas and a liquid-hourly space velocity (LHSV) of 0.60 h^{-1} (Section S4). The test was performed at 360 °C. The catalysts used in the study were two commercial NiMo catalysts widely used for hydro-desulfurization processes of which catalyst A is more active than catalyst B.[46] Unfortunately, owing to the commercial nature of the catalysts, further analysis was not permitted by the producers. However, NiMo catalysts in combination with lignin and TOFA hydrotreatment have been extensively studied and several reports have been published on the topic.[47–53] The catalysts were loaded as extrudate material with around 1.6 mm diameter and 2–4 mm length. The extrudates were embedded in small SiC particles to fill up the void space and assure plug-flow operation and proper catalyst wetting. To evaluate extrudates instead of powdered catalysts allows mass transfer effects in the catalyst particle and thus gives a more complete view of the tested system. This is a well-established approach for industrially relevant testing of hydroprocessing catalysts and trickle-bed applications under laboratory conditions, without crushing the catalysts to powder size.[54] The total liquid products were typically collected once per day. The gas-phase was analyzed by online GC roughly two to three times per day. The lignin oil feed underwent full hydrodeoxygenation to yield, in both the studied cases, 5.6% of gases, mainly carbon dioxide/mon-

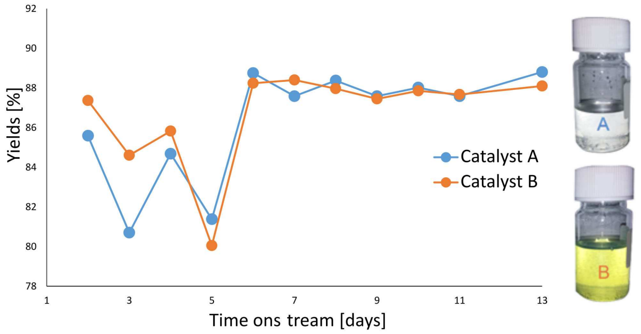


Figure 6. Liquid recovery generated by hydrotreatment of the lignin/TOFA/LGO feed for a period of 13 days (300 h) on stream. The yields for samples A (blue) and B (orange) are given, the boiling range is 180–345 °C. The yield is based on the overall hydrocarbon outcome as obtained by simulated distillation (ASTM D7213).

Table 4. Detailed simulated distillation table of the recovered liquid fraction of day 8.

T [°C]	A [wt %]	B [wt %]
50–70	0.1	0.1
70–100	0.8	0.6
100–125	0.9	0.6
125–150	0.9	0.8
150–180	2.0	2.1
180–312[a]	57.3	54.6
312–345	34.8	37.1
> 345	3.2	4.0

[a] The temperature point 312 °C was chosen to better separate C_{17} from C_{18} alkanes.

oxide and light hydrocarbons (C_{1-4} HC), and 84.4 % of liquid hydrocarbon fraction (Table 3).

Water was generated in approximately 10 %. Optionally, the oxygen-free liquid product can be recycled as carrier liquid to dilute the untreated lignin oil instead of fossil-derived hydrocarbon oil. This would result in a 100 % bio-based product.[55] The hydrotreatment test was successfully run for 300 h (13 days) on stream and did not show any increase in pressure drop. After an initial fluctuation in terms of yields, owing to the stabilization of the reactor, stable yields within 1 % of discrepancy were obtained from day 6 (Figure 6).

The lignin/TOFA/LGO mixture was converted mostly into fuel in a diesel boiling range, 180–345 °C (Table 4). From Figure 6, it can be discerned that the system became stable after 6 days and that there was only a marginal difference in reactivity between the catalysts with respect to product yield. However, the color of the product mixtures was visibly different, where catalyst A gave a transparent product and catalyst B gave a slightly yellowish product. To get more insight into the reactivity difference between the two catalysts, the liquid fractions were analyzed by 2-dimensional gas chromatography (ASTM UOP990, ESI), the results are summarized in Table 3. Sample A was composed of linear C_{9-22} alkanes in 66.9 %, where C_{17-18} contributed with 59.8 %. IsoC_{9-21} alkanes amounted to 7.3 % (4.4 % C_{9-16}), and naphthenes to 23.10 % (19.2 % C_{9-16}). Generally, < 3 % of aromatic compounds of which 2.1 % substituted benzenes detected. Sample B gave a different chemical composition, where linear C_{9-22} alkanes contributed with 59.1 % (53.3 % of C_{17-18}), of which 6.9 % were accounted as isoC_{9-21} alkanes (4.5 % C_{9-16}), and 20.9 % as naphthenes (18.0 % C_{9-16}). The aromatic fraction was notably higher and amounted to 13.3 %, where alkyl benzenes contributed with 11.5 % and this is in accordance with the slightly yellow color of the product. Simulated distillation of the liquid fractions gave an average of 96 % of gasoline-aviation-diesel fraction, b.p. 70–345 °C, and less than 4 % of high boiling hydrocarbons b.p. > 345 °C (Table 4).

Elemental analysis confirmed the absence of oxygen (reached LOD), and a level of sulfur in accordance with the Euro V fuel standard (ASTM D5453; i.e., 10 ppm). From the 2D GC analysis, it is evident that catalyst A is more active in the hydrodearomatization than catalyst B (19.4 % vs 17.6 % of naphthenes). The aromatization of linear alkanes was more evident in catalyst B where the 11 % of aromatics is most likely produced from the aromatization of long aliphatic chain such as C_{17-18}. The different outcome between the two runs demonstrates that the hydrotreatment is tangible and that different products can be obtained by slightly adjusting the reaction conditions. However, simulated distillation did not show any difference. The only exception was the

Table 3. Hydrotreatment outcome of 1 : 6 : 3 Kraft lignin/TOFA/LLGO.

Gas 5.6 wt%	HC liquid fraction 84.4 wt%	A [wt %]	B [wt %]
C_{2-4} 0.6 %	**Linear C_{9-22}**	**56.5**	**49.9**
CH_4 1.1 %	→Linear C_{9-12};	1.4	1.1
CO_2 3.0 %	→Linear C_{17-18} ; *(C_{18}/C_{17})*	50.5;	45.0;
		(1.3)	*(1.5)*
CO 0.7 %	→Linear $C_{13-16+19-20}$;	4.6	3.8
H_2S 0.2 %	**Iso C_{9-219}**	**6.2**	**5.8**
	→isoC_{9-16};	3.7	3.8
	Naphthenes	**19.4**	**17.6**
	→Naphthenes C_{7-8};	0.2	0.2
	→Naphthenes C_{9-16};	16.2	15.2
	Aromatic	**2.3**	**11.2**
	→substituted benzenes	1.8	9.7
Coke < 0.1 wt%, water 10 wt%.			

discrepancy between the fractions 180–312 °C and 312–345 °C owing to difference in degree of decarboxylation between samples A and B (Figure 7). The gas composition from both samples were similar to each other within the error of the experiment. The average chemical composition is shown in Table 3.

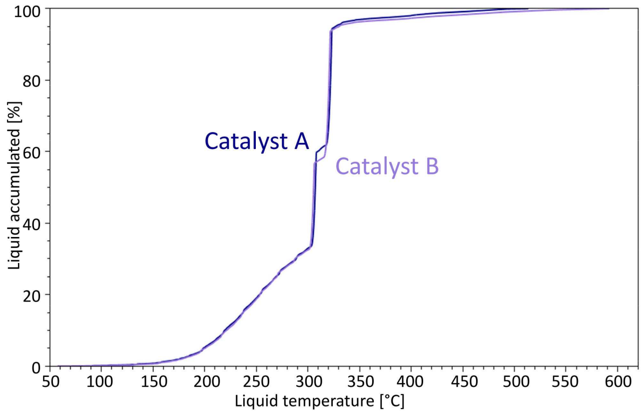
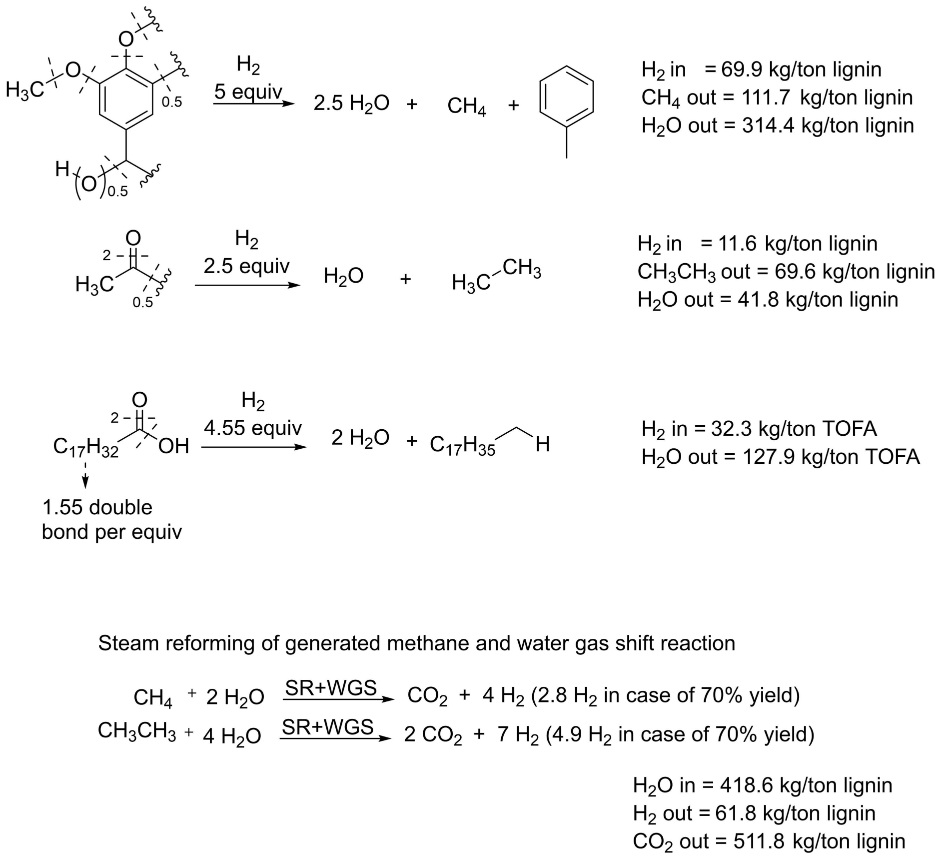


Figure 7. Simulated distillation of liquid fraction of day 8.

Hydrogen

Based on the elemental analysis, our average inter-unit comprises a molecular formula of $C_8O_{2.5}H_7$ (Scheme 3). We recommend interested readers to recent articles from the groups of Crestini and Argyropoulos and Bruijnincx that revisit the structure of Kraft lignin.[56,57] To give full deoxygenation of feed would require 280 kg of hydrogen gas, where 69 kg are needed for the mere lignin hydrotreatment, 11 kg for the acetyl groups and 199 kg to hydrotreat the fatty acid fraction. However, some of the TOFA used in the feed (4.133 weight unit) is used only as early-stage carrier liquid. Future optimization of the process involving an inert early-stage carrier liquid would further reduce the hydrogen demand. The most common way to produce H_2 gas is by steam reforming (SR) of methane combined with water gas shift (WGS), but also higher gaseous HC can be exploited.[58] Moreover, SR and WGS produce 9 ton of carbon dioxide per ton of hydrogen gas, and this would increase the carbon footprint.[59] In the case of HDO of lignin, it is possible to utilize the biogas generated as a byproduct during the hydrotreatment. SR and WGS would give 2.8 moles of hydrogen per mole of methane and 4.9 moles per mole of ethane considering the yield as 70 % (Scheme 3). As every inter-unit in softwood requires 5 equivalents of hydrogen to achieve alkylbenzenes, toluene in our equation, the net consumption of hydrogen is only 1.4 equivalents per inter-unit



Scheme 3. Hydrotreatment pathways.

linkage.[60] This equates to only 19.7 kg of hydrogen gas per ton of lignin. Thus, the only byproduct besides water is carbon dioxide. Interestingly, one ton of lignin will generate 512 kg of carbon dioxide that can be used in the precipitation step of black liquor, closing the cycle as the demand is 200 kg. The carbon dioxide is plant-derived and therefore considered a green molecule.

Mass balance for converting lignin into alkylbenzene

To simplify the mass balance calculations, we will estimate the mass balance for 1 weight unit (wu) of lignin (Table 5 and Figure 8). To generate 1.5 wu of wet lignin, 5 wu of black liquor (BL; 20 % lignin content) is required. For the precipitation step, 0.2 wu of carbon dioxide, 0.15 wu of sulfuric acid, and 0.122 wu of sodium hydroxide are required. The resulting 1.5 wu of wet lignin is then dried and esterified in 2 wu of TOFA. The activation is performed by acetic anhydride, which is generated from acetic acid. Some of the acetic acid is not recovered but incorporated into the esterified lignin. Therefore, the mass balance of the activation reagent is 0.387 wu of acetic acid in this specific example. As discussed above, the hydroprocessing of the lignin part would require 0.081 wu of hydrogen and generated 0.062 wu of hydrogen (70 % yield). By performing the WGS and SR, only 0.019 wu of hydrogen is required and 0.512 wu of carbon dioxide is generated in the process to convert the lignin part into alkylbenzene. The carbon dioxide can be used in the precipitation step. Consequently, the net mass balance estimation becomes very attractive (Table 6). For 1 wu of Kraft lignin corresponding to 5 wu of black liquor, only 0.15 wu of sulfuric acid and 0.122 wu of sodium hydroxide is required. For the esterification, 2 wu of tall oil fatty acid and 0.387 wu of acetic acid is needed. To hydroprocess this, 4.133 wu of TOFA as early-stage carrier liquid and 3.1 wu of

Table 5. Mass flow.

Lignoboost In [wu]	Lignoboost Out [wu]	Esterification In [wu]	Esterification Out [wu]	Ac_2O In [wu]	Ac_2O Out [wu]	HT In [wu]	HT Out [wu]	SR + WGS In [wu]	SR + WGS Out [wu]
5 black liq.	1 lignin	1 lignin	3.1 lignin oil	0.5 recov. AcOH	0.7 Ac_2O	3.1 lignin oil	8.679 fuel HC	0.182 CH_4 + CH_3CH_3	0.062 H_2
→1 lignin	4.472 green liq.	2 TOFA	→1 lignin	0.387 fresh AcOH	0.115 H_2O	4.133 TOFA (carrier)	→3.1 carrier HC	0.419 H_2O	0.512 CO_2
→1 salts	→3 H_2O	0.7 Ac_2O	→2 TOFA		0.072 loss	3.1 LGO (carrier)	0.268 heavy HC		0.028 loss
0.2 CO_2	→1.472 salts		→0.1 acetyl			0.280 H_2	0.094 gas HC		
0.150 H_2SO_4			0.5 recov. AcOH				0.318 CO_2		
0.122 NaOH			0.1 loss				0.182 CH_4 + CH_3CH_3		
							1.060 H_2O		

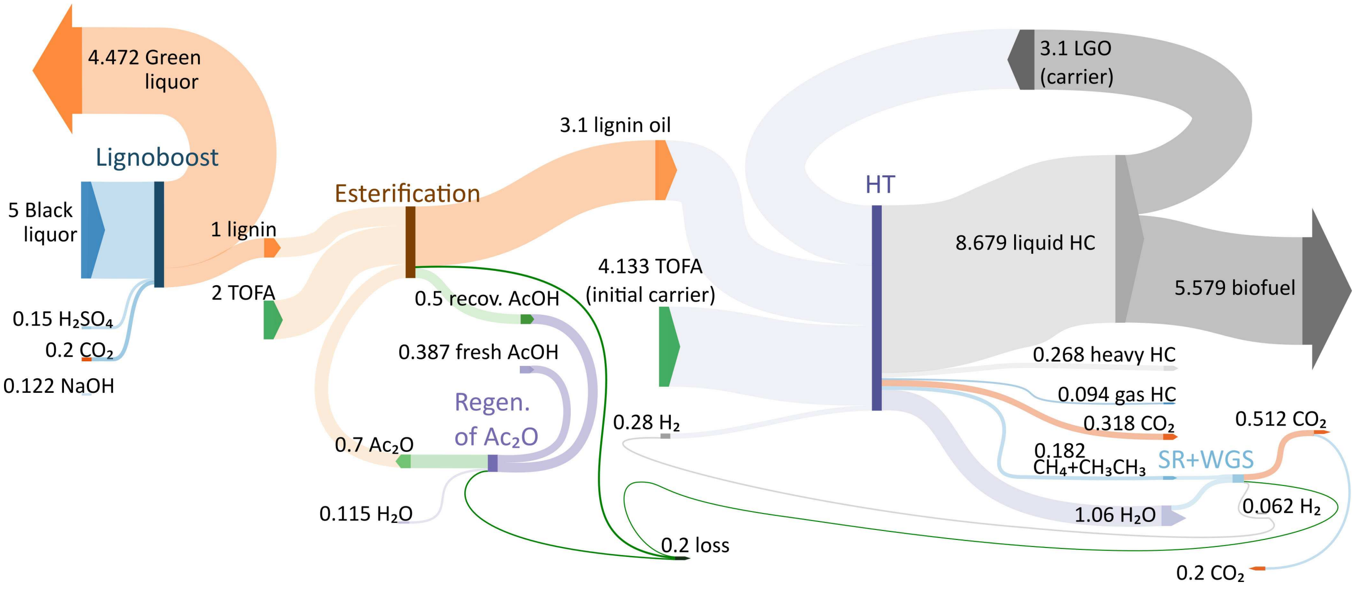


Figure 8. Sankey diagram of the overall process.

Table 6. Total net mass balance.

In ↓ [wu]	Out ↑ [wu]
5 black liquor→1 lignin	5.579 biofuel
0.150 H_2SO_4	0.268 heavy HC
0.122 NaOH	0.756 H_2O
0.387 AcOH	0.730 CO_2
0.218 H_2	4.472 green liquor
6.133 TOFA→4.133 as carrier	0.200 losses

LGO are merged together to generate a suitable feed for the hydrotreater that consumes only 0.280 wu of hydrogen gas, where 0.081 are estimated to be involved in the partially acetylated lignin HDO and the remaining 0.199 wu are used for the fatty acid fraction. Moreover, the inorganics contained in the black liquor are recycled from the precipitation step to the recovery boiler to generate green liquor in the pulp mill. Some mass losses are associated with the esterification step, the production of the acetic anhydride and the steam reforming, 0.1 wu, 0.072 wu and 0.028 wu respectively.

Discussion

Incentives for pulp mills

As described in the introduction, current Kraft pulp mills produce pulp (~50% yield), extractives (<5%), and excess energy. As the recovery boiler is the limiting operation in all pulp mills, there are two options to increase pulp production in the pulp mill: 1) change the recovery boiler to one with a higher capacity; or 2) extract lignin. As many pulp mills cannot take an investment in a new recovery boiler, extracting lignin from the process is an attractive option. 10–20% of lignin can be extracted from the black liquor with no adjustments to the infrastructure. A medium-sized pulp mill of 500 kty^{-1} pulp production can thus extract up to 30–60 kty^{-1} of lignin. As a rule of thumb, the pulp mill can increase pulp production by the same amount of lignin that is extracted. As the additional pulp produced can be considered as "marginal tonnage" the profit is considerable on just the pulp. Considering that the lignin produced can be valorized, the value of the extracted lignin can increase from its current heating value. Therefore, to produce lignin oil would enable the pulp mills to get revenues from a different product. Importantly, the energy demand for producing lignin oil can be covered by low-pressure steam in the pulp mill. As the pulp mill can increase the pulp production, the same amount of high-pressure steam will be generated and this can still be used for producing green electricity, even though this is not so profitable at the moment.

Incentives for the oil refineries

Europe has legislated that by 2021, a 6% greenhouse gas reduction should be accomplished by the retailers of fuels. Sweden has become a front-runner and by 2030 a 70% greenhouse gas emission reduction should be achieved. At the same time, EU legislation starting from 2021 dictates that 14% of all fuel should be bio-based of which 3.5% should be advanced biofuel from 2030. Only the 3.5% equals to 14 million tons of advanced biofuels. The sources of biofuel largely comprise: ethanol from sugar cane, palm oil and palm oil fatty acid distillate, and used cooking oils. Palm oil and its distillate were recently exempted from the list of accepted biofeeds because of rain-forest deforestation issues.[61] Preem in Sweden and UPM in Finland currently hydrotreat tall oil in their refineries to produce forestry derived green diesel. At the moment, there are no natural feeds to produce gasoline, only sugar cane ethanol can be added (max 10%). The lignin, hydrotreated by the proposed route, can produce hydrocarbons in C_7–C_{15} range and, depending on catalyst choice and reaction parameters, aromatic or naphthenic compounds can be generated. Hence, lignin can be converted into gasoline, aviation or diesel fuel depending on the demand. Using the described technology, linear fatty acids will be deoxygenated and partially decarboxylated to generate diesel fuel. Therefore, lignin can contribute to supply the demand for gasoline and aviation fuel and this is a major advantage of the presented technology. Thus, the refinery can increase their production of biofuels, and also expand from mainly diesel, by implementing the presented technology.

Conclusions

Debottlenecking current pulp mills by extracting the lignin from the black liquor enables an increase of the pulp production in a pulp mill without investing in a CAPEX intensive recovery boiler. As the pulp production is increased by using the same infrastructure, chemicals, and energy, the marginal tonnage becomes alluring. The lignin in the black liquor can be precipitated by lowering the pH by using first carbon dioxide and then sulfuric acid. In currently established procedures, this lignin does not have any worth besides its heating value. By esterifying the lignin with a bio-derived fatty acid, the generated lignin ester becomes lipophilic and soluble in gas oils. The solubility of the lignin ester in the gas oils is key for enabling transformation in the current refinery infrastructure. It was demonstrated that the feed can be coprocessed with gas oils. Indeed, the feed was hydroprocessed for 300 h in continuous flow to produce a biofuel in which 84% of the products were in the gasoline-aviation-diesel range. By recirculating acetic acid in the esterification step and applying a water-gas shift reaction of the off-gases from the hydrotreatment, the net mass balance of biofuels from Kraft lignin becomes very attractive.

Experimental Section

Materials

Commercial reagents were purchased from Sigma-Aldrich and were utilized without further purification. Kraft black liquor and LignoBoost Kraft lignin were provided by Valmet. Tall oil fatty acid (TOFA) was provided by Preem AB.

Lignoboost Kraft lignin isolation

Kraft lignin was isolated at Bäckhammar LignoDemo, a demonstration-scale lignin extraction facility, from Kraft black liquor according to the LignoBoost procedure.[8] The water content of lignin product after lignin isolation and washing was 33 wt% calculated by gravimetric analysis.

LignoBoost Kraft lignin esterification

To a 600 L reactor was added TOFA (266.7 kg) together with LignoBoost Kraft lignin (200 kg, 66% dry substance). The mixture was vigorously mixed at room temperature and then heated to 130 °C under vacuum to remove 66 kg of water through distillation. The homogeneous catalyst pyridine (20 kg) and acetic anhydride (93 kg) were combined with the slurry. The resulting mixture was then heated at 180 °C, and after 30 min pressure was lowered to remove up to 50 kg of acetic acid and 17.5 kg of pyridine through distillation. The resulting mixture, amounting in total to 413 kg, was cooled to 100 °C and pumped out of the reactor.

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Conflict of Interest

Joseph Samec is a professor at Stockholm University and a co-founder of RenFuel.

Keywords: biofuels · organocatalysis · lignin · hydrothermal synthesis · pulp mill

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