

## EN590 Road Diesel from Black Liquor in 4 steps

Joakim Löfstedt,<sup>a</sup> Christian Dahlstrand,<sup>a</sup> Alexander Orebom,<sup>a</sup> Gerrit Meuzelaar,<sup>a</sup> Supaporn Sawadjoon,<sup>a</sup> Maxim V. Galkin,<sup>b</sup> Peter Agback,<sup>c</sup> Åsa Håkansson,<sup>d</sup> Martin Wimby,<sup>e</sup> Elena Corresa,<sup>f</sup> Yannick Mathieu,<sup>f</sup> Laurent Sauvanaud,<sup>f</sup> Sören Eriksson,<sup>d\*</sup> Avelino Corma<sup>f\*</sup> and Joseph S. M. Samec<sup>a,b\*</sup>

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Precipitated Kraft lignin from black liquor was converted into biodiesel in three steps. A mild Ni-catalyzed transfer hydrogenolysis using 2-propanol generated a lignin residue. An organocatalyzed esterification of the lignin residue with tall oil fatty acid gave a light gas oil soluble esterified lignin residue. The esterified lignin residue was coprocessed with light gas oil in a continous hydrotreater to produce EN590 Road diesel.

Biofuels are attractive alternatives to petroleum based fuels because they do not cause a net addition of carbon dioxide to the atmosphere, since the carbon dioxide evolved from combustion is recycled to new biomass in the carbon cycle.<sup>1 2 3</sup> Biofuels from eatable biomass, referred to as 1<sup>st</sup> generation biofuels, have been questioned both from ethical and energy efficiency viewpoints. Therefore, much attention has been focused on biofuels from lignocellulose (2<sup>nd</sup> generation biofuels). As the cellulose part of the wood currently yields high value products, it would be worthwhile to use the lignin part, that constitute almost 50% of the total energy in biomass.<sup>4</sup> Biofuels from lignin are sometimes referred to as 3<sup>rd</sup> generation biofuels.<sup>5 6 7 8 9</sup> Currently the lignin is mainly used to regenerate process chemicals and give process heat during chemical pulping (Fig. 1).<sup>10 11</sup> However, the recovery boiler is generally the limiting step in pulping. Furthermore, there is usually a surplus of energy generated in the pulping process. Therefore, different strategies to extract the lignin from black liquor to increase pulp production have been developed. Precipitation of the Kraft lignin by acidification of the black liquor has been commercialized where two plants are

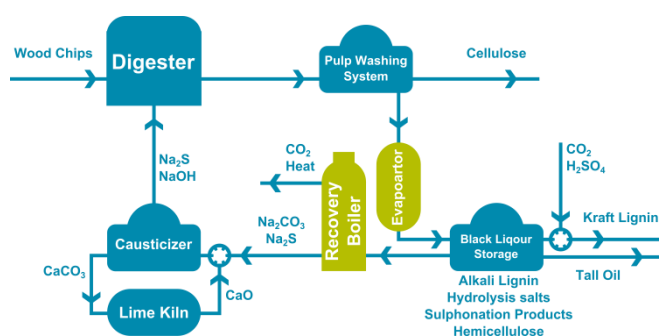


Fig. 1 The Kraft process.

currently operating.<sup>12 13 14 15</sup> Other techniques for recovering the lignin in black liquor, such as membrane filtration, are also being developed.<sup>16 17</sup>

Lignin is a challenging biopolymer to study and transform. Therefore, most academic studies have used lignin model compounds<sup>5-9, 18, 19, 20, 21</sup>. Alternatively, organosolv lignin, a non-commercial source of lignin has been used in these studies. Commercial lignin sources, such as precipitated Kraft lignin, are still a major challenge to transform. The chemical structure of the lignin residue in black liquor has been changed where new C–C bonds have been generated from condensation reactions.<sup>22</sup>

Lately, few reports appeared in which lignin from the Kraft process was used as a raw material in biofuel production.<sup>23</sup> However, specialized conditions were employed. For example an additional solvent was used. This solvent may also be transformed during the hydrodeoxygenation reactions and cannot easily be recycled due to resemblance to the products, which would give an additional cost to the process.

A challenge to produce biofuels is to use existing sources of raw materials, technologies, and logistics. A key to success is to generate a feed that is compatible with an existing oil refinery operation to produce standardized gasoline and diesel. One strategy is to co-process a petroleum-based feed blended with a bio-feed containing lignin. However, lignin is not compatible in existing refinery processes.

<sup>a</sup> Renfuel AB.

<sup>b</sup> Department of Chemistry, BMC, Uppsala University, Husargatan 3, 751 23, Uppsala, Sweden.

<sup>c</sup> Department of Chemistry, Uppsala BioCenter, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-75007 Uppsala, Sweden

<sup>d</sup> Preem AB.

<sup>e</sup> Valmet AB.

<sup>f</sup> Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València, Avda dels Tarongers s/n, 46022, Valencia, Spain.

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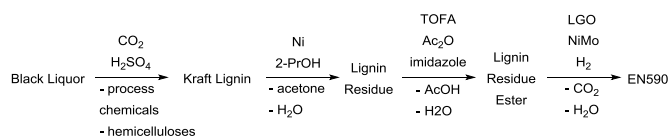


Fig. 2. 4-step process carried out in this work to obtain road diesel.

We hereby report the generation of biodiesel from precipitated Kraft lignin, through a mild Ni-catalyzed transfer hydrogenolysis reaction that generated a lignin residue that was easily separated from the solvent and catalyst (Fig. 2). This residue was esterified with tall oil by organocatalysis to form an esterified lignin residue that was soluble in light gas oil. A mixture of esterified lignin residue and gasoil was then hydroprocessed using a commercial NiMo catalyst in a flow reactor to produce fully deoxygenated biodiesel with EN590 specifications (Figure 2).

Ni-catalyzed transfer hydrogenolysis of Lignoboost lignin using isopropanol, as H-donor, was performed at 140°C and 8.5 bar for 16 hours.<sup>24</sup> After the reaction was completed, the generated lignin residue was easily separated from the catalyst by filtration and from the solvent by distillation. The molecular weight of the formed lignin residue was not significantly reduced, according to the GPC diagram (ESI, Figure S1). As can be seen in by HSQC analysis, the Kraft lignin was partially reduced. (Fig. 3). Noteworthy, keto functions (**S'** and **G'**) and benzylic alcohols (**A** and **A'**) were reduced. Furthermore, ether bonds were cleaved (**A**, **A'**, **B**, and **C**). These bonds were reductively cleaved in a transfer hydrogenolysis reaction (ESI, Figure S3). Acetone, from the transfer dehydrogenation of 2-propanol was observed in the solvent mixture after the reaction. However, the resulting material did not show any

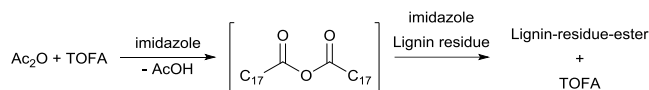
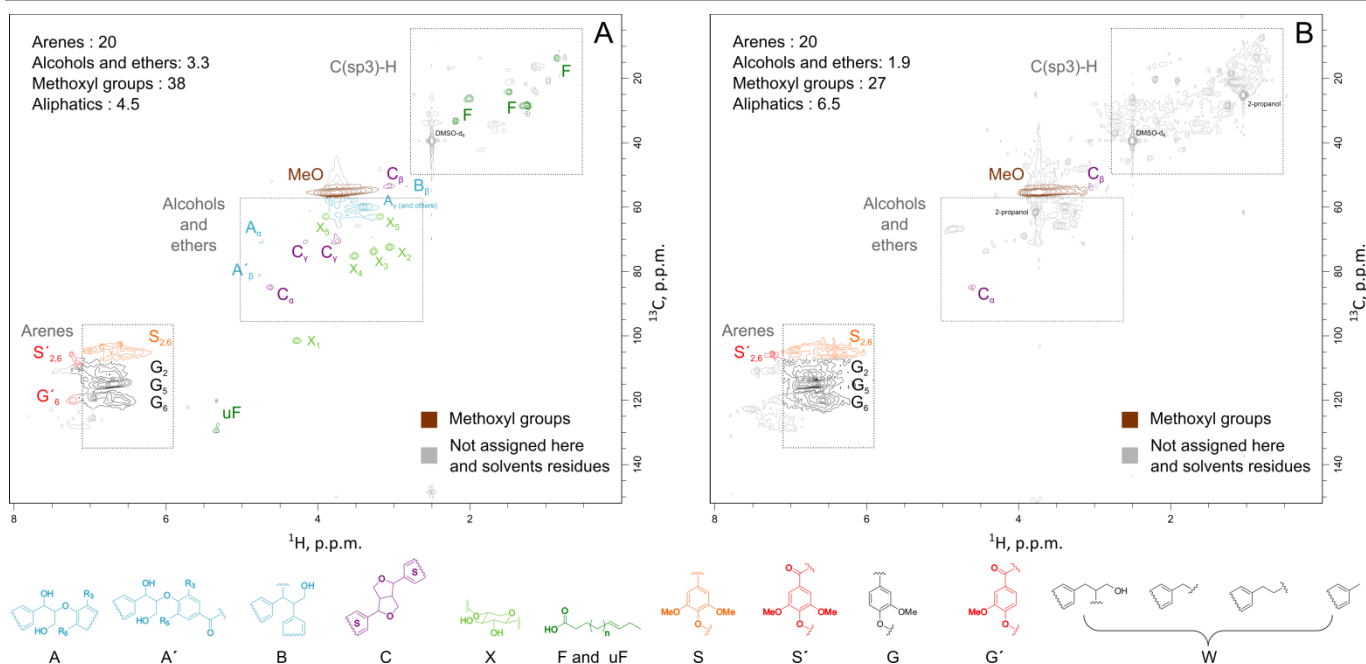


Fig. 4 Esterification of the lignin residue with *in-situ* prepared TOFA anhydride.

improved solubility properties in light gas oil. At this stage, the lignin-based material was then not compatible with an existing refinery process. Increasing hydrogen pressure in the hydrogenolysis is not a preferred option. Ni is known to promote C–O bond cleavage in biaryl ethers at higher pressures<sup>25, 26</sup>, and at even higher pressures saturated alcohols and hydrocarbons are generated.<sup>27</sup>

In order to solubilize the lignin residue another strategy was envisaged. It is known that certain hydrotreaters can hydroprocess cofeeds of vegetable oils and light gas oils<sup>28</sup>. We hypothesized that if the lignin residue was covalently bond to a vegetable oil this product would become more soluble in light gas oil (LGO). Tall oil fatty acid (TOFA) is a distillate from crude tall oil that is currently used as a feed in oil refineries to produce 2<sup>nd</sup> generation hydrotreated vegetable oils<sup>29</sup>. TOFA mainly contains oleic and linoleic acids<sup>30</sup>. As the lignin residue contain hydroxyl groups both as phenols and benzylic and aliphatic alcohols, an esterification of the lignin hydroxyl groups by the carboxylic acids in TOFA was envisaged.<sup>31</sup> An esterification reaction of the lignin residue by the corresponding fatty acid anhydride was performed. The fatty acid anhydride was conveniently generated *in-situ* by mixing TOFA with acetic anhydride using N-methyl imidazole as catalyst.<sup>32, 33 34 35</sup> At the beginning of the reaction the lignin residue and the mixed anhydride in raw tall oil diesel formed a heterogeneous slurry.



**Fig. 3** Complete HSQC spectra of: **A** – precipitated Kraft lignin, **B** - after Ni treatment. Structures found in the dissolved lignin: (A)  $\beta$ -O-4', (A')  $\beta$ -O-4' with a conjugated carbonyl or carboxyl group, (B)  $\beta$ -1', (C) resinol, (X) xylan, (F, uF) saturated and unsaturated fatty acids or esters, (S) syringyl unit, (S') oxidised syringyl unit, (G) guaiacyl unit, (G') oxidised guaiacyl unit, (W) proposed lignin fragments for the Ni treated lignin (S.I.).

However after two hours, the slurry had become a homogeneous solution. By  $^1\text{H}$  NMR spectroscopy, it was determined that the esterified lignin residue (ELR) consisted of 1.2:1 ratio of TOFA:lignin monomer unit (ESI). Gratifyingly, this ELR was soluble in light gas oil. By  $^{31}\text{P}$  NMR spectroscopy, it was determined that a large part of the phenolic and benzylic alcohols were esterified (ESI, Figure S8).

A major challenge in the conversion of biomass including lignin-derived bio-oils in a conventional hydrotreater is the high oxygen content. Compared to mineral oils that have a negligible oxygen content ( $\text{O/C} \leq 0.03$ ), the lignin residue before esterification has a higher oxygen content ( $\text{O/C} = 0.25$ ). During hydro-processing in a hydrotreater, the oxygen in the feed is reductively removed as water in an exothermic reaction. Controlling this exothermic reaction is a challenge in the hydro-processing of a biomass containing feed.<sup>7-9</sup> A way to circumvent the exotherm is to co-process the bio component with a less reactive mineral oil. This has successfully been employed in several oil refineries. One example is the co-processing of TOFA and LGO in a hydrotreater.

Then, a mixture of TOFA, ELR and LGO was hydroprocessed in a fixed bed reactor using a presulfided commercial NiMo-catalyst. This type of catalyst is typically used for hydro-desulfuration of mineral oil feeds in petroleum industry. It should be noted that more specialized catalysts are available for biomass containing feeds.<sup>28-29</sup> The catalyst was presulfided in-situ at 400°C with a stream of 10%  $\text{H}_2\text{S}$  in  $\text{H}_2$  (120 mL/min) for 12 hours prior to use. After this, the system was pressurized at 65 bar with hydrogen and temperature stabilized to operation setpoint. Then the feed was injected continuously and samples taken every 12 hours.

As reference, a commercial feed comprising TOFA/LGO (70:30) was processed. This feed was easily hydrotreated and showed stabilized yields after 50 hours. Analysis of the product mixture showed a major peak corresponding to a  $\text{C}_{18}$  straight chain alkane and a minor peak for a  $\text{C}_{17}$  straight chain alkane (ESI, Figure S12). This is in accordance to a high degree of a hydrodeoxygenation pathway favored over a decarboxylation pathway. This is confirmed by the higher water yield compared to the carbon dioxide yield.

The feed containing an esterified lignin residue TOFA/ELR/LGO (27:43:30; corresponding to 15wt% lignin) was also successfully hydrotreated. Deactivation by coke was small enough to allow a stable operation for more than 50 hours as for the reference feed. As expected, the hydrogen consumption increased compared to the reference run as well as the formation of water and carbon dioxide due to the higher oxygen content of the feed (ESI, Table S4). The gas yield, mainly carbon dioxide and methane, increased slightly. Extra methane may be formed from the cleavage of the methoxy groups in the lignin. Under the same processing conditions, the lignin containing feed yielded less middle distillate (bp 216-359°C) and more heavies (bp > 359°C) than the reference feed. The composition

of liquid product exhibited a decrease in saturates from 89% to 82%, an increase of monoaromatics from 9.8% to 15% and an increase of polyaromatics from 1 to 2%.

**Table 1.** Product distribution of different feeds after hydroprocessing. 340°C, 65 bar.

Run ID	1	2	3
Feed composition	TOFA:LGO 70:30	TOFA:ELR <sup>a</sup> :LGO 27:43:30	TOFA:ELR <sup>a</sup> :RTD 27:43:30
WHSV ( $\text{h}^{-1}$ )	1.0	1.0	0.7
Yields (wt%)			
Total gases	2.68	4.84	5.16
of which: $\text{CO}_2$	2.02	2.72	2.96
$\text{CH}_4$	0.33	1.15	1.21
Water	5.4	9.0	8.4
Total liquids	91.9	85.7	86.3
-216	10.7	12.0	10.6
216-359	79.2	65.9	68.2
359+	2.0	8.1	7.5
Liquid composition			
Saturates	89.2	82.1	82.5
Monoaromatics	9.8	15.6	15.5
Poly-aromatics	1.0	2.3	1.9

<sup>a</sup> Total amount of precipitated lignin in the composition is 15 wt%.

As a result, the density of the liquid increased from 0.82 to 0.84 g/ml. Product yields and liquid composition were little affected when the Weight Hourly Space Velocity (WHSV) was decreased from 1.0 to 0.7  $\text{h}^{-1}$ . Therefore, the incorporation of lignin into the feed allows tuning the properties of the hydroprocessed diesel. This is especially important when fatty acids are hydroprocessed, because they tend to yield linear saturated alkanes of lower density and higher cold point. One issue may be the formation of BTX that may be formed upon deoxygenation of lignin monomers. Fortunately, BTX content of the hydroprocessed product remained below 0.3% (ESI, Table S3). Meanwhile, an increase in highly substituted, longer chain monoaromatics (Propyl benzene and larger) was observed in the product mixture. Thereby, the hydro-processing did not cleave to a large extent the C-C bonds between the alkyl chains and aromatic groups in the lignin monomers. TAN number was measured at 0.0 for all of the hydroprocessed products, which indicates a total conversion of acid functions. This was confirmed by the disappearance of the band corresponding to the carbonyl group and the strong decrease of the band corresponding to the hydroxyl group of phenols in the IR spectra (ESI, Figure S13), and is also consistent with NMR studies (HSQC/HMBC, figures S14-16), which states that all carbon oxygen bonds are removed. So, in accordance with oxygen mass balance made from  $\text{CO}_2$  and water yields, we expect an oxygen content lower than 0.1wt% for all the hydroprocessed products. It should be noted that the properties of the hydroprocessed products obtained from

esterified lignin residue in tall oil, concerning distillation curve, composition and density, fits well into EN590 specifications of road diesel.

## Conclusions

The conversion of commercial precipitated Kraft lignin to EN590 road diesel has been achieved in 3 steps. A mild transfer hydrogenolysis was followed by an esterification with tall oil to generate a soluble lignin ester that was soluble in mineral oil. Simulated refinery hydrotreatment gave a fully deoxygenated product with specification that qualifies for EN590 road diesel.

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