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

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1. General considerations

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

**Gel permeation chromatography** was performed using a YL 9110 HPLC-GPC system (YL Instrument Co., Ltd., Dongan-gu, Anyang-si, Kyounggi-do, 431-836, Republic of Korea) equipped with 3 Styrage® columns (HR 0.5, HR 1, HR 3, 7.8×300 mm respectively) mounted in series (eluent THF, flow rate 1 mL/min, injection volume 50 μL) and an UV detector (254 nm). The system was calibrated by using ReadyCal-Kit polystyrene (MP 266, 682, 1250, 2280, 3470, 4920, 9130, 15700, 21500, 28000, 44200, 66000 Da). All the samples were dissolved in THF and filtered through a syringe filter (PTFE 15mm, 0.2μm).

**Elemental analysis** was performed by Analytische Laboratorien GmbH in Germany.

**ICP** analysis for metal content in lignin and lignin oil was determined by using a Spectro Ciros CCD ICP AES after treating the samples in aqua regia and hydrogen peroxide.

$^1$H, $^{31}$P, $^{13}$C and 2D NMR spectroscopy were recorded on an Agilent 400-MR (400 MHz, 162 MHz and 101 MHz) spectrometer. Chemical shifts are given in ppm (δ) relative to CHCl₃ signal (7.26 ppm for $^1$H) as an internal standard. For $^{31}$P NMR analysis the samples (30mg) were phosphorylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), according to a published procedure using N-hydroxy-5-norbornene-2,3-dicarboximide as internal standard.$^{1,2}$

**2D GC-MS** was performed using an Agilent 7890 with a ZX1 two-stage thermal modulator according to Test method UOP 990-11. The operating conditions were the following: Primary column: HP-PONA 50m x 0.2mm x0.5μm; Secondary column: Supelcowax 1.8m x 0.1mm x 0.2μm; Carrier gas: Hydrogen; Flow rate: 1.5ml/min; Split flow ratio: 100:1; Injection temperature: 280°C; Initial oven temperature: 40°C; Initial hold time: 10min; Programming rate A: 1.5°C/min; Intermediate temperature: 153°C; Programming rate B: 2.0°C/min; Final temperature: 280°C; Final hold time: 11.17min; Hot jet temperature program: 120°C (10min) to 280°C at 1.5°C/min; Detector temperature: 280°C; Sample size: 0.2 μl; Modulation period: 9 sec.
2. Lignin isolation

Kraft lignin was isolated, in Bäckhammar LignoDemo, a demonstration scale lignin extraction facility, from Kraft black liquor according to the LignoBoost procedure. Water content of lignin product after lignin isolation and washing was 33 wt% calculated by gravimetric analysis.

Under normal conditions (high pH), lignin is completely soluble in black liquor and will remain in solution due to its hydrophilic nature. By lowering the pH of the black liquor, the lignin precipitates due to negative dissociated groups accepting protons and lignin agglomerates will start to bind together (at about pH 11.5-11). If pH continues to drop, lignin will further precipitate until most of it is insoluble. In the LignoBoost process the pH of the black liquor is lowered to pH 10 by injecting CO₂ gas (45-60 kg/ton black liquor DS) in to the black liquor at high pressure (>10 bar). After precipitation the black liquor/lignin slurry is transferred to a pressure filter where an alkaline lignin cake is produced. The cake has a total dry solid of 60-65% and consists roughly of 50% lignin and 50% lignin lean black liquor. Lignin cakes from the filtration procedure is transported via belt conveyors to a re-suspension step where it is mixed with water and fresh sulphuric acid (re-suspension suspended solids is about 15-20%). The pH of the suspension is about 2.5. Gases formed (i.e. H₂S and CO₂) during the low pH re-slurrying step are transported back and utilized as precipitation gas. The re-suspended slurry is transferred to a second filtration, which is a combined filtration and washing step. After cake formation the residue is washed with acidified water (pH 2.5 using H₂SO₄) to wash away the impurities, primarily Na and other inorganic substances. Figure S1 below shows a simplified process schedule.

Figure S1 A simplified process schedule of the LignoBoost technology.
2.1. Lignin characterization

The lignin obtained from the previous step was dried and analysed by Gel Permeation Chromatography to determine the molecular weight distribution. Mn: 1310; Mw: 3541 and PD: 2.7.

$^{31}$P NMR was used to analyse and quantify the free hydroxyl group available on lignin. Total Lignin-OH 6.49 mmol/g of which 4.07 mmol/g phenolic, 0.46 mmol/g carboxylic, and 1.96 mmol/g aliphatic.

![Figure S2 LB Kraft lignin $^{31}$P NMR spectrum](image)

Table S1 LB Kraft lignin elemental analysis

| C    | H     | N    | S    | O     | Na    |
|------|-------|------|------|-------|-------|
| 64-66% | 5.7-5.8% | <0.1% | 2-2.25% | 26-27.5% | 0.1-0.2% |

![Kraft lignin](image)

![Figure S3 LB Kraft lignin $^1$H NMR spectrum](image)
Figure S4 LB Kraft lignin HSQC spectrum.
3. Lignin oil

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

Figure S5 Drawing of the pilot reactor (600L). From the left; condensate vessel, reactor vessel, circulation loop with recirculation pump.
3.1. Lignin oil characterization

Gel permeation chromatography and NMR were also exploited to follow the lignin esterification reaction. Lignin oil molecular weight distribution analysis gave Mn: 2266; Mw: 10469 and PD: 4.6.

![Figure S6 GPC chromatogram of Lignoboost lignin and lignin oil diluted with LGO.](image)

1H NMR was used to follow the esterification reaction over time when using stearic acid as the only fatty acid. Particularly, the signal of alpha proton of stearate esters were used as reference for the success of the reaction. However, due to signal overlap was not possible to quantify the esterification degree by NMR.

![Figure S7 Lignin oil 1H NMR spectrum.](image)
Figure S8 1H NMR of lignin oil at different reaction time. The triplet at 2.47 ppm represent the alpha carbon of aromatic lignin stearate.

Figure S9 Lignin oil HSQC spectrum.
3.2. Degree of esterification

Mass balance is taken into account to calculate the ratio fatty/acetic esterification of lignin oil. $^{31}$P NMR reports 6.5 mol of free hydroxyl groups per kilogram of lignin. It is possible to calculate the amount of acetyl groups bounded and, since no OH groups are left after the reaction, the amount of fatty esters by difference from the extra mass of Lignin oil. Acetylation contributes as +42 g/mol to the lignin oil while compared to the slurry before the reaction, while fatty esterification is considered -18 g/mol.

\[
\text{Lignin Oil mass} - \text{Lignin mass} - \text{Fatty Acid mass} = x \times \left( 42 \frac{g}{mol} \right) + \left( \text{Lignin OH mol/kg} - x \right) \times \left( -18 \frac{g}{mol} \right)
\]

\[
x \% = \frac{\text{Lignin Oil mass} - \text{Lignin mass} - \text{Fatty Acid mass} + (18 g/mol \times \text{Lignin OH mol/kg})}{(42 + 18) g/mol \times \text{Lignin OH mol/kg}} \times 100
\]

Thus, the mass of the product lignin oil is 413.0 kg, where the initial mass of lignin is 133.3 kg, the initial mass of fatty acid is 266.7 kg and the estimated free OH-groups of lignin corresponds to 6.5 mol/kg. Acetylation (x) corresponds to 55 mol%. Since no free hydroxyl groups remains after the completion of reaction, the degree of fatty esterification is 45 mol%.
3.3. Mechanistic study

A general control reaction consisted in adding 667 mg of Kraft Lignoboost lignin (TS 66\%) to 1 g of stearic acid under vigorous stirring at 130 °C until homogenous slurry is reached. Then vacuum was applied to remove water and kept for 5 minute. The system is then vented and 75 mg of pyridine and 350 mg of acetic anhydride were added. The reaction mixture is heated up to 180 °C. After 30 minutes vacuum is applied to remove acetic acid and pyridine until completion. Acetylated lignin was obtained according to following procedure: 1.0 g of dried lignin was combined with 20 mL of dry pyridine and 20 mL of acetic anhydride under stirring at room temperature for 24 h. Approximately 150 mL of an aqueous solution of HCl (pH 1) were added, the solids filtered under vacuum and washed with deionized water. The resulting powder were dried at 60 °C for 24 h. Stearic anhydride was produced according to published procedure. The degree of esterification was calculated as reported in section 3.2.

| Entry | substrate | stearic acid | anhydride | pyridine | Mass yield | Approximate degree of esterification (%) |
|-------|-----------|--------------|------------|----------|------------|-----------------------------------------|
| 1     | KL 0.5 g  | 1 g (1.1 equiv) | -         | -        | 1.497 g    | 0                                       |
| 2     | KL 0.5 g  | 1 g (1.1 equiv) | -         | 75 mg    | 1.489 g    | 0                                       |
| 3     | KL 0.5 g  | -            | Acetic 10 mL (large excess) | 75 mg | 0.639 g$^1$ | >99 (KLA) |
| 4     | KL 0.5 g  | -            | Stearic 1.75 g (2 equiv corresponding to 1.81 g of acid) | 75 mg | 1.839 g$^1$ | <5 (stearic ester) |
| 5     | KLA 0.637 g (corresponding to 0.5 of KL) | 1 g (1.1 equiv) | -         | 1.626 g | <5 (stearic ester) |
| 6     | KLA 0.637 g (corresponding to 0.5 of KL) | 1 g (1.1 equiv) | 75 mg    | 1.579 g  | ≈30 (stearic ester) |

$^1$ excess of anhydride was quenched with distilled water, then vacuum was applied to remove the remaining water and the eventual acetic acid.
3.3.1. $^{13}$C labelling study

To better evaluate the mechanism of esterification, commercially available oleic acid-$1^{-13}$C, 99 atom % $^{13}$C ($^{13}$C OA) and acetic anhydride-$1,1^{-13}$C$_2$ 99 atom % $^{13}$C ($^{13}$C Ac$_2$O) were utilised in a time study. A general reaction consisted in adding into a crimp seal vial 50 mg of dry Kraft lignin to 112 μL of $^{13}$C OA (100mg) and an excess, due to the reduced scale, of 4-methyl pyridine as organocatalyst (100 μl). The mixture was heated for 30 min at 130 °C, then 32 μl of $^{13}$C Ac$_2$O were added to the mixture by using a micro syringe. The mixture was let react for 30 min at 130 °C, then the temperature was raised up to 190 °C and after 30 min vacuum was applied for another 30 min. Samples corresponding to reaction time of 30, 45, 60, 90 and 120 minutes were produced. After the end of the reaction the vial was cooled down in an ice bath and extracted with 0.9 mL of CDCl$_3$. The extractives were filtrated, collected into a NMR tube and analysed directly. $^1$HNMR, HMBC and $^{13}$C NMR analysis were run on the samples. The signal corresponding to the methoxy groups of lignin was integrated as 1 on the $^1$H spectra, the residual signal of CHCl$_3$ (7.26 ppm) was used as internal standard to normalize and integrated as IS. HMBC was used to qualitatively assign the integral intervals of the esters on the $^{13}$C spectra, i.e. phenolic acetates (Ac-O-Ph) 166.6 - 169.4 ppm, alkyl acetates (Ac-O-Alk) 169.4 - 171.2 ppm, phenolic oleates (Oa-O-Ph) 171.2 - 172.8 ppm and alkyl oleates (Oa-O-Alk) 172.8 - 174.0 ppm (Figure S6). Signal derived from $^{13}$CDCl$_3$ was integrated as IS to normalize the integrals of the esters to the corresponding amount of lignin. Total amount of esters of the sample corresponding to reaction time 120 min was set as 100% in our calculations (Table S3).

![Figure S10 HMBC spectrum of sample corresponding to reaction time 120 min.](image_url)
Table S3 Lignin ester analysis.

| Reaction time (min) | 30  | 45  | 60  | 90  | 120 |
|---------------------|-----|-----|-----|-----|-----|
| Ac-O-Ph (%)         | -   | 48.7| 48.2| 31.4| 24.2|
| Ac-O-Alk (%)        | -   | 26.9| 30.8| 36.5| 41.5|
| Oa-O-Ph (%)         | -   | 12.4| 13.3| 23.5| 25.8|
| Oa-O-alk (%)        | -   | 5.6 | 5.9 | 8.3 | 8.4 |
| Total esters (%)    | 0.0 | 93.7| 98.1| 99.7| 100.0|
Figure S11 $^{13}$C NMR spectra of $^{13}$C labelling time study.
4. Hydro-treatment:
Catalyst activation by in-situ sulfidation was performed prior to the test in order to obtain a defined activation state and avoid slow re-sulfidation, in particular of the passivation layer, during the initial days of testing. The activation protocol was as follows (note, GTO is the ratio of hydrogen to oil flow rate in [NL(H2)/l(oil, 70 °C)]; LHSV in [ml(oil, 70 °C)/h/ml(catalyst)]):

1. Mounting, nitrogen purge, leak testing at 130 barg (first with nitrogen than with 10% hydrogen/nitrogen), then pressure down to ambient pressure.
2. Nitrogen purge (1.4 NL/h per reactor position), ambient pressure, reactor temperature 60°C, duration 30 min.
3. Hydrogen purge (1.4 NL/h per reactor position), ambient pressure, reactor temperature 60°C, duration 30 min.
4. Pressure up (5 bar/min) to 45 barg under hydrogen flow.
5. Soaking with activation feedstock, LHSV 2.68 l/h, at reduced hydrogen flow (0.44 NL/h per reactor position), duration 30 min.
6. Temperature ramp 60 to 100°C at 20°C/h, LHSV 2.1 l/h, hydrogen flow at 0.44 NL/h per reactor position.
7. Increase of hydrogen flow to 3.41 NL/h per reactor position, GTO 500, LHSV remains at 2.1 l/h.
8. Temperature ramp 100 to 250°C – plate 1 at 10°C/h, plate 2 at 20°C/h.
9. Hold time at 250°C, minimum 8 h – plate 1 for 23 h, plate 2 for 8 h.
10. Temperature ramp 250 to 320°C at 5°C/h.
11. Hold time at 320°C, minimum 6 h – plate 1 for 6 h (re-run for 10 h), plate 2 for 6 h.
12. Heat/cool to test temperature at 5°C/h.
13. Pressure up to 120 barg at 15 bar/15 min.
14. Feed change to test feedstock, adjusting LHSV to 0.6 l/h and GTO 1000.

A 16-fold high-throughput trickle bed reactor system was used for the test campaign (Figure S4).

Figure S12 Picture of the high throughput testing unit – a 16-fold trickle bed system with 4x4-heater.
The following process parameters can be accommodated by this testing system:

- Number of Reactors: 16 (4x4 heating concept)
- Temperature [°C]: up to 450°C
- Pressure [bar]: 160
- Operation mode: up- or downflow
- Catalyst volume [ml]: up to 6.5
- Reactor inner diameter [mm]: 5mm, 6mm, 8mm
- Liquid flow [mL/min]: Up to 6.5 ml/h per reactor
- Gas flows [NL/h]: 0.5-10 NL/h per reactor
- Feeds: 1 common liquid feed
- Gases: H₂, N₂
- Online-analytics: online: Gas phase HC, H₂, H₂S, CO, CO₂

The general test conditions are as follows:

- Reactor pressure 120 barg with pure hydrogen.
- Hydrogen to oil ratio (GTO) 1000: 1 [Nl/l].
- LHSV 0.6 1/h.
- Reactor temperature was 360°C.

Note, GTO is the ratio of hydrogen to oil flow rate in [Nl(H₂)/l(oil, 15°C)]; LHSV in [ml(oil,15°C)/h/ml(catalyst)]. For converting LHSV into the corresponding oil flow rate, the reactor volume of the isothermal zone for the reactor inner diameter of 4.72 mm (isothermal zone 200 mm, volume 3.5 ml) was defined as reference volume. This definition is necessary since the catalyst filling exceeds the isothermal zone for several reactors and to a different extent, and a few reactors with larger diameter were chosen in plate 2. Since the activity correlates exponentially with temperature, the zones outside the isothermal zone with lower temperature contribute to a lower extent to the overall conversion. Hence for comparison, the isothermal volume was used as base case corresponding to LHSV 0.6 1/h. The pre- and post-isothermal zones were in some cases filled in order to capture very reactive compounds and hence suppress unwanted side reactions.
4.1. Gas product yields by online-GC

*Table S4 Gas yields and composition.*

| Gas composition | Yield excluding unconverted H₂ [%] | Yield excluding unconverted H₂ and DMDS by products [%] | Yield excluding unconverted H₂ and DMDS by products assuming 10% water [%] |
|-----------------|----------------------------------|-------------------------------------------------------|---------------------------------------------------------------------|
| NH₃             | < 0.1 %                          | < 0.1 %                                               | < 0.1 %                                                             |
| CO              | 0.9                              | 0.9                                                   | 0.8                                                                 |
| CO₂             | 3.3                              | 3.4                                                   | 3.0                                                                 |
| CH₄             | 0.6                              | 0.6                                                   | 0.6                                                                 |
| C₂-C₄           | 1.1                              | 1.1                                                   | 1.0                                                                 |
| H₂S             | 0.2                              | 0.2                                                   | 0.2                                                                 |
| CH₄-DMDS        | 1.2                              |                                                       |                                                                      |
| H₂S-DMDS        | 0.7                              |                                                       |                                                                      |
| Gas fraction    | 8.0                              | 6.2                                                   | 5.6                                                                 |
| Liquid fraction | 92.0                             | 93.8                                                  | 84.4                                                                |
| Sum Gas+Liquid  | 100.0                            | 100.0                                                 | 90.0                                                                |

*Table S5 Hydrotreatment feed elemental analysis*

| C     | H     | N     | S     | O     | Metals |
|-------|-------|-------|-------|-------|--------|
| 78.9% | 11.4% | 42 ppm| 0.2%  | 9.7%  | <15 ppm|

4.2. Hydrocarbon liquid fraction chemical characterization

2D GC-MS was used to determine the chemical composition of the liquid fraction coming from the hydrotreating unit.

*Table S6 Hydrocarbon liquid fraction chemical composition.*

| Wt%    | Alkanes (%) | Iso-paraffin (%) | Napthenes (%) | Aromatics (%) | Indanes (%) | Diaromatics (%) |
|--------|-------------|------------------|---------------|---------------|-------------|-----------------|
| Sample A | 66.83       | 7.33             | 23.14         | 2.10          | 0.62        | -               |
| Sample B | 59.80       | 6.94             | 19.91         | 4.45          | 7.21        | 1.71            |
Figure S13 2D GC-MS chromatogram of Sample A.
Figure S14 2D GC-MS chromatogram of Sample B.
Figure S15 Accumulated Simulated Distillation plot for Catalysts A and B for the days 9, 10, 11 and 13.