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BL2F

Transforming Black Liquor to Biofuel

Research and Innovation Action

H2020-LC-SC3-2019-NZE-RES-CC

D3.3 - Report on 2nd stage HDO

WP3 - Task 3.2.2 Second stage HDO

Date 20.3.2024

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Grant Agreement n°884111.

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Document Information

Grant agreement	884111
Project title	Black Liquor to Fuel by Efficient Hydrothermal Application integrated to Pulp Mill
Project acronym	BL2F
Project coordinator	Prof. Dr. Tero Joronen
Project duration	1st April 2020 – 31th March 2024 (48 Months)
Related work package	WP 3 - Upgrading and application testing
Related task(s)	Task 3.2.2 Second stage HDO
Lead organisation	VTT
Contributing partner(s)	Neste, Ranido
Due date	31.3.2024
Submission date	20.3.2024
Dissemination level	Public

History

Date	Version	Submitted by	Reviewed by	Comments
8.3.2024	1.0	Sari Rautiainen	Babak Armand, Maximilian Wörner	Draft for reviewers
19.3.2024	2.0	Sari Rautiainen		Final version

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Abbreviations and acronyms

Acronym	Description
BL	Black liquor
DMDS	Dimethyldisulfide
DoD	Degree of deoxygenation
HDO	Hydrodeoxygenation
ICP-OES	Inductively coupled plasma - optical emission spectrometry
IHDO	Integrated hydrothermal
KF	Karl-Fischer

Executive Summary

This report reviews the work done in the non-hydrothermal upgrading of black liquor-based HTL biocrude. According to the BL2F process concept, the liquid HTL product, containing water and majority of the organic fraction of the black liquor, is first upgraded in an integrated hydrothermal hydrodeoxygenation to increase the stability and to reduce the oxygen content of the biocrude. A second upgrading step is carried out at an oil refinery to further improve the quality of the fuel intermediate. Due to the delays in commissioning the TAU HTL-pilot reactor, the hydrothermal HDO experiments in Task 3.2.1 were carried out mainly using model compounds and lignocellulosic HTL biocrude obtained from Aarhus university. The non-hydrothermal upgrading in Task 3.2.2 was therefore carried out using a small sample of purified biocrude obtained from the TAU pilot.

The BL-based biocrude was hydrotreated in a batch reactor using a sulfided NiMo-catalyst at 350 °C and with 50 bar H_2 loading. Two product fractions formed in the process, a light top fraction, which contained some dodecane from the catalyst sulfidation, and a more viscous bottom fraction. Analysis of the elemental composition showed that the oxygen content of the biocrude decreased from 18 wt% to less than 10 wt% during the upgrading. Furthermore, the sulfur content decreased from about 2 wt% to less than 0.2 wt% in both product fractions. Compared to the unsatisfactory results obtained in the hydrothermal hydrodeoxygenation, reported in D3.2, these results show that the direct hydrodeoxygenation is a more promising method to upgrade the BL-based biocrude.

Keywords

Black liquor, Upgrading, Hydrodeoxygenation, Fuel

1 Introduction

The Black Liquor to Fuel project aims to valorise black liquor (BL), an abundant side stream from pulp mills, into marine and aviation fuels. According to the project concept, the black liquor is processed by hydrothermal liquefaction in supercritical conditions to separate the cooking salts in brine and to produce an HTL product from the organic fraction (Figure 1). In the first stage, the biocrude along with the aqueous fraction is upgraded in integrated hydrothermal hydrodeoxygenation (IHDO) process step. In the second stage, the biocrude is further upgraded by hydrotreatment in the absence of water. As a result, a transportation fuel intermediate or component with low oxygen and sulfur content is obtained.

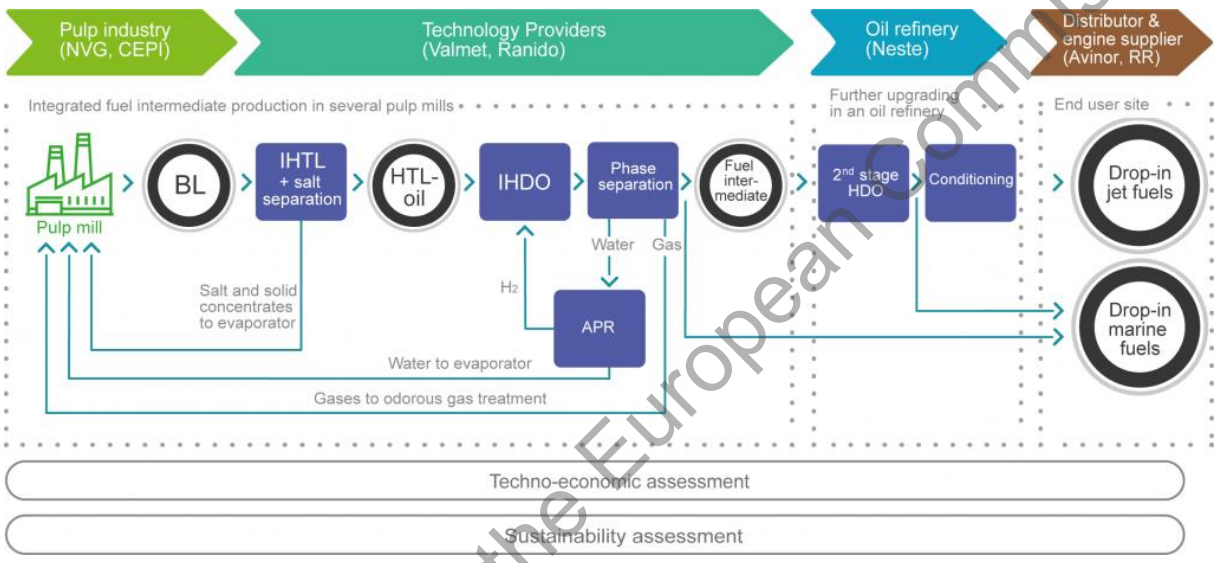

Figure 1. Scheme of the BL2F process concept.

The hydrothermal HDO, the first step of the upgrading, was studied in task 3.2.1 and reported in D3.2. Due to the lack of real BL-based feedstock, the work was conducted using model compounds and lignocellulosic HTL biocrude obtained from Aarhus University. Based on the model compound experiments, it was concluded that full deoxygenation of the phenolics is very challenging in aqueous conditions. Furthermore, hydrothermal HDO of the Aarhus biocrude in the presence of water gave rather low yields of the upgraded bio-oil (40-60 wt%), and significant amounts of coke formed especially in SCW (up to 40 wt%). The degree of deoxygenation remained low (maximum 10%) in all experiments. Due to the non-representative and aged composition of the biocrude, however, these results cannot be directly applied to the BL-based biocrude. Moreover, the execution of hydrothermal HDO experiments in batch mode is challenging due to e.g. oil-water solubility problems when heating and cooling the reactor.

The delayed commissioning of the TAU pilot forced us to modify the original plan of task 3.2.2. Since there was no real BL-based feedstock available for T3.2.1, we could not produce the intended BL-based partly deoxygenated fuel intermediate for T3.2.2. Moreover, the HTL process in TAU pilot produced different product streams than originally planned. The biocrude was extracted from the products and separated from solid hydrochar. A 60 g sample of purified

biocrude from top product was delivered to VTT from TAU for the HDO testing. The unsatisfactory results in the hydrothermal HDO prompted us to use this sample directly for the non-hydrothermal HDO tests.

The hydrotreatment of HTL biocrude from various sources has been reported in several studies.[1] However, to our knowledge, there is no prior art in upgrading of black liquor-based HTL biocrude. Sulfided NiMo and CoMo catalysts are commonly used in the desulfurisation of crude oil fractions at oil refineries as well as for hydrodeoxygenation of biocrudes and vegetable oils. Therefore, a sulfided NiMo/γ-Al_2O_3 was selected as catalyst for the HDO of BL-based biocrude. Typically, the hydrotreatment is carried out at 350-400 °C with hydrogen partial pressures starting from 40 bar. Based on these, we chose to carry out the experiment at 350 °C and charged the cold reactor with 50 bar H_2. Reaction time was set at 3 h. The BL-based biocrude was analysed before and after the HDO experiment to investigate the changes in the elemental composition. A limited number of analyses could be carried out due to the low quantity of the product.

2 Materials and methods

2.1 Materials

The purified biocrude was produced at TAU pilot reactor in hydrothermal liquefaction of black liquor. The biocrude was extracted from the HTL top product and separated from solid hydrochar. The NiMo/γ-Al_2O_3 catalyst was prepared by Ranido. The catalyst contained 8.83% NiO and 41.06% MoO_3 and the particle size was <0.1 mm. The catalyst was sulfided *in-situ* prior to use.

2.2 Experimental setup

The batch experiment was performed in a Büchi glasuster 200 mL high pressure autoclave reactor. First, the catalyst was sulfided by measuring 3 g of NiMo/γ-Al_2O_3, 3 ml dimethyldisulfide (DMDS) and 23 g dodecane into the reactor. The reactor was sealed and flushed three times with nitrogen. 30 bar hydrogen gas was loaded at room temperature, and the sulfidation was run at 350 °C for 4 h. After the sulfidation, excess solvent was removed from the reactor. For the HDO experiment, 33 g of the biocrude was added to the reactor. The reactor was sealed again and flushed three times with nitrogen. 50 bar hydrogen gas was loaded at room temperature, and the experiment was run at 350 °C and stirring rate of 600 rpm for 3 h.

2.3 Sample work-up

After the hydrotreatment, the sample mixture was collected from the autoclave and transferred to a glass bottle. At room temperature the sample contained two phases, i.e. liquid phase on top and sticky slurry phase at the bottom. Heating of sample at 40 °C for 30 min was tested to see if the sample forms a homogeneous phase or not. The sample did not form a homogeneous mixture after heat treatment. Therefore, sample was separated into top oil phase and bottom phase. To remove the catalyst particles from the bottom phase, filtration was carried out after dissolving the sample to ethyl acetate and sonicating for 30 min to form a liquid slurry. Glass

microfiber filter, 692 with 1µm particle retention was used in filtration. After filtration, the ethyl acetate phase was collected in a round bottom flask and residual solids were allowed to dry under fume hood to constant weight. Rotary evaporation was carried out at bath temperature of 40 °C and gradually increased to 60 °C and 240 mbar vacuum. Operation was stopped when condensation stopped.

2.4 Analytics

2.4.1 Water content

The volumetric Karl-Fischer (KF) titrations were performed with an apparatus of Metrohm Omnis Titrator according to ASTM E203. A one-component solution (Combititrant 5, Merck) was used as titrating agent and Chloroform/methanol (1:3 V/V) as working medium. The endpoint of the titration was detected with a platinum electrode. The KF apparatus is tested by analyzing pure water. Sample size was about 250 mg – 1g. After weighing, the sample was brought into the titration vessel of the KF apparatus. Each sample was measured twice and results are averaged.

2.4.2 Total acid number (TAN)

TAN was determined by potentiometric titration using Metrohm 888 Titrando equipment with Metrohm LL Solvotrode-Glass electrode. Sample size was about 250 mg – 1g. Sample was diluted in isopropanol and brought into the titration vessel of the instrument. Titripur (Tetra-n-butylammoniumhydroxidi solution in 2-propanol/methanol, Merck) was used as a titrating agent. Self-characterized pyrolysis bio-oil was used as a control sample.

2.4.3 Density and viscosity

The viscosity and density of the oil samples were determined by injecting a known volume into Anton Parr SVM3000 Stabinger Viscometer. Both viscosity and density were measured at 15 and 40 °C.

2.4.4 CHNS/O

Carbon, hydrogen, nitrogen and sulfur contents of the oil samples were determined using an Elementar Rapid Vario MACRO CUBE analyzer, following ASTM D5291 method. The operating temperature in the tube furnace was 1150 °C. Oxygen content of the oil samples was determined using an Elementar Rapid Vario OXY CUBE. The method was based on ASTM D5622-16. The operating temperature in the tube furnace was 1450 °C.

2.4.5 Simulated distillation

Simulated distillation of the oil sample was performed according to ASTM D2887 method using Agilent 7890A GC system equipped with a flame ionization detector. Calibration of the equipment was carried out by Agilent boiling point calibration No 1 (5080-8716) having a carbon range of C5 - C40. Reference gas oil supplied by Agilent was used as a control sample.

2.4.6 ICP-OES

Concentrations of K, Mo, Na, Ni and S was measured with ICP-OES (5110 SVDV, Agilent Tecnologies). The samples were first treated in microwave (Ethos Up, Milestone) with acid-

assisted digestion method by weighting 0.4 g sample into the microwave tubes. Then 9 mL concentrated HNO_3 (*Empura 65%, Merck*) and 1 mL H_2O_2 (*Suprapur 30%, Merck*) were added. The tubes were closed and placed in the microwave digestion system. Following digestion method was run: 1) temperature was increased to 210 °C in 20 minutes, 2) temperature was held at 210 °C for 15 minutes. After the samples had cooled down, they were diluted to 25 ml with Merck type I water.

The solutions were analysed with ICP-OES equipment and further diluted with 1 % nitric acid (*Empure 65%, Merck*) when needed. Representative background correction was done, and dilution factors were taken into account in the results. Multi elemental standard solutions provided by Inorganic Ventures and Merck were used as calibration standards and control samples.

3 Results

For the hydrotreatment of the biocrude, the NiMo/γ-Al_2O_3 catalyst was first sulfided *in-situ* using DMDS as sulfiding agent and dodecane as the solvent. After the sulfidation, excess solvent was removed and the sulfided catalyst was left in the reactor along with a small amount of dodecane. The mass balances of the samples are listed in Table 1. The purified biocrude from TAU was hydrotreated at 350 °C and 50 bar hydrogen cold pressure for 3 h. Due to the viscous nature of the biocrude, about 70 wt% of the charged biocrude, dodecane and catalysts was recovered from the reactor after the experiment (Figure 2)Figure 2. Biocrude before and after the hydrotreatment.. The product separated into lighter top phase and a viscous bottom phase, from which the solids were separated by filtration (Figure 3).

Table 1. Mass balances

Input		Products	
Biocrude	33 g	Bottom phase	10.6 g
Dodecane[a]	9.61 g	Top phase	13.3 g
Catalyst	3.03 g	Solids	3 g
Total recovered	36.3 g	Total[b]	26.9 g

[a] Dodecane remaining in the reactor after sulfidation. [b] Some material lost due to incomplete recovery.

Figure 2. Biocrude before and after the hydrotreatment.

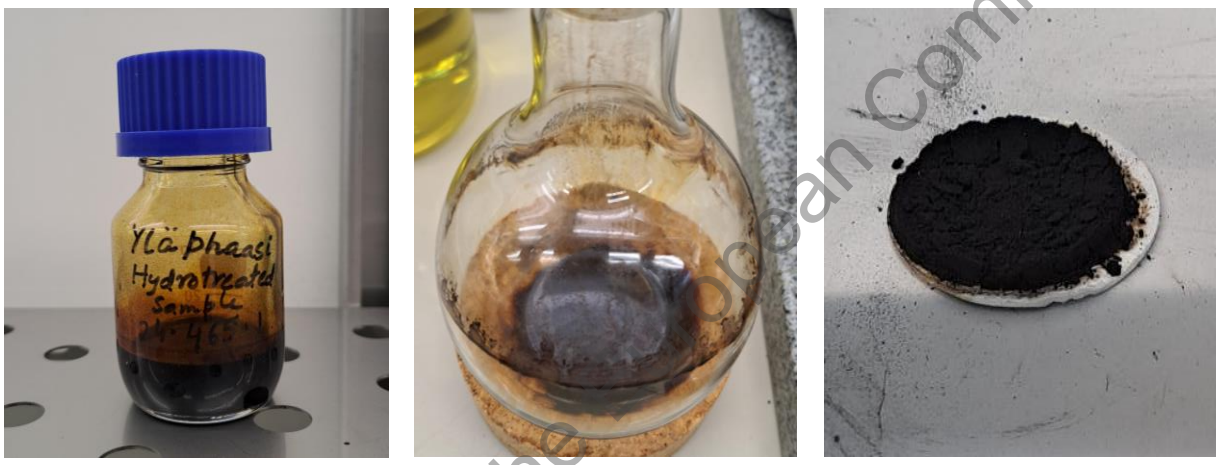

Figure 3. The hydrotreated sample separated into top phase (left), bottom phase (centre) and solids (right).

The results presented in Table 2 show that the NiMo/γ-Al_2O_3 catalyst and the hydrotreatment conditions applied are effective for the removal of oxygen, sulfur and acid content of the biocrude. The oxygen content of the biocrude was 18.5 wt% which was reduced to 3.7 and 9.8 wt% in the top and bottom product phases, respectively. Although the measured contents of oxygen in the product samples are lower than the actual amounts due to the presence of some dodecane left from the catalyst sulfidation step, however, considering the low amount of dodecane, the oxygen removal efficiency at second-stage HDO conditions was verified. As can be seen in Table 2, the sulfur content of the biocrude was almost completely removed over the NiMo/γ-Al_2O_3 catalyst, and the total acid number (TAN) was significantly reduced from 96.7 mgKOH/g in the biocrude to 3.6 and 13.1 mgKOH/g in the top and bottom product phases, respectively, indicating the effective removal of acidic compounds through the hydrotreatment process. The effective desulfurisation was confirmed by ICP analysis (Table 3).

Table 2. Sample properties

Sample	Elemental composition						Water (wt%)	TAN (mg KOH/g)
	C	H	N	S	O (meas.)	O (diff.)		
Biocrude	70.18 ± 0.9	6.87 ± 0.07	0.42 ± 0.01	2.00 ± 0.06	18.5 ± 0.9	20.5 ± 0.9	4.4	96.7 ± 0.3
Top phase	85.62 ± 0.07	12.18 ± 0.2	0.17 ± 0.01	0.07 ± 0.01*	3.7 ± 0.3	2 ± 0.2	<0.5	3.6 ± 0.1
Bottom phase	81.17 ± 0.6	8.47 ± 0.1	0.35 ± 0.04	0.18 ± 0.04*	9.8 ± 0.2	9.8 ± 0.4	<0.5	13.1 ± 0.7

* Inaccurate due to low amount.

Table 3. ICP analysis of residual metals

Sample	Elemental composition (ppm)				
	Na	K	Mo	Ni	S
Biocrude	67.5	<1.6	10.2	5.3	24320
Top phase	<6.2	<1.9	10.8	5.9	1408
Bottom phase	32.7	<1.9	49.7	9.7	1694

As shown in Table 4, the density and viscosity values of the top phase product closely resemble those of fossil-based fuels. The density of the top phase product at 15 °C is 0.877 kg/l which is close to that of kerosene (0.78-0.81 kg/l), diesel (0.78-0.86 kg/l) and gasoline (0.72–0.76 kg/l).[2,3] The viscosity of the product at 40 °C (2.7 mm^2/s) is also close to the viscosity of diesel (3 mm^2/s).[2]

Table 4. Top phase viscosity and density.

Viscosity @ 15 °C	Kin. Viscosity @ 15 °C	Density @ 15 °C
5.439 ± 0.002	6.204 ± 0.003	0.877 ± 0.000
Viscosity @ 40 °C	**Kin. Viscosity @ 40 °C**	**Density @ 40 °C**
2.705 ± 0.004	3.154 ± 0.005	0.858 ± 0.000

Simulated distillation analysis was carried out to investigate the boiling point distribution of the top phase of the catalytically hydrotreated product. As shown in Figure 4, a wide range of molecular weight with the boiling points from 50 to 420 °C was observed, indicating the presence of different distillate fractions (e.g., gasoline and diesel cuts) in the product sample. The distillate at the boiling point of around 216 °C corresponds to the dodecane solvent left from catalyst sulfidation, which its share matches well with the ratio of the amount of the remaining dodecane (9.61 g) to the amount of the top phase product (13.3 g).

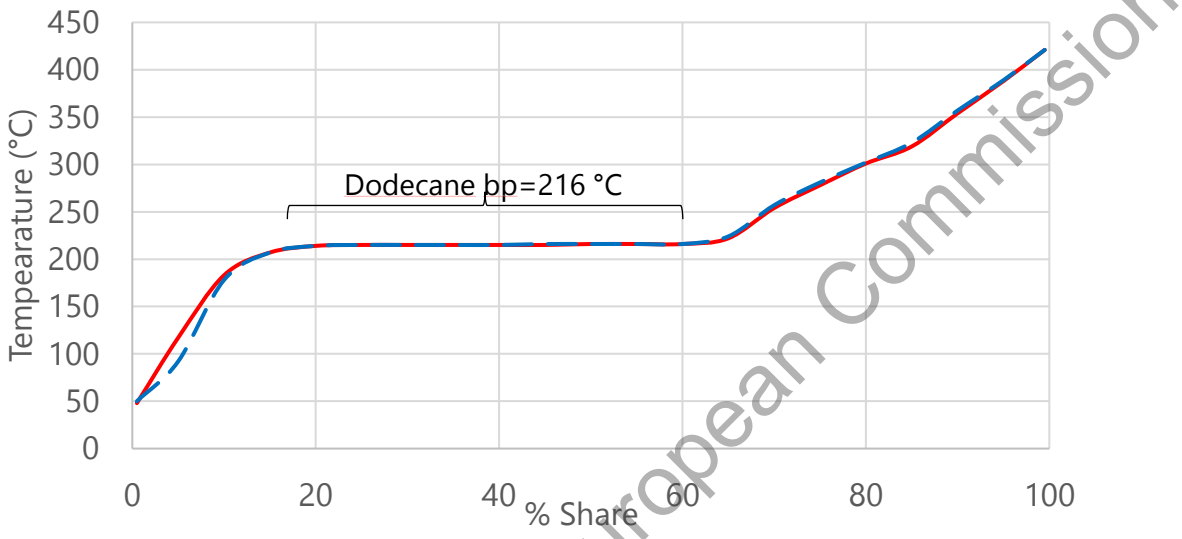

Figure 4. Simulated distillation of top phase in the region 50-420 °C. The two lines correspond to two parallel measurements.

4 Summary and future prospects

This report summarises the work done on the upgrading of black liquor-based HTL biocrude in BL2F Task 3.2.2. A small amount of biocrude, separated from the HTL products at TAU pilot reactor, was hydrotreated in a batch reactor at VTT. The analyses of the hydrotreated products indicate that the alumina-supported nickel-molybdenum sulfide is an active catalyst for hydrotreatment at the selected reaction conditions (350 °C; initial hydrogen pressure of 50 bar; reaction duration of 3 h). Deoxygenation and desulfurisation were achieved and, moreover, the acid content of the biocrude decreased significantly. Even though the top phase contained some residual dodecane from catalyst sulfidation, the improved chemical properties as well as the physical features (e.g., density and viscosity) of the top phase oil indicate the potential of the hydrotreated oil for further polishing to be used as fuel. Catalysts other than NiMo with different supports of distinct acidic and textural properties could also be tested for better catalytic performance. Furthermore, the optimisation of the catalyst and the reaction parameters could definitely improve the conversion and reaction selectivities, resulting in a higher quality fuel product. Overall, the results show that the non-hydrothermal hydrodeoxygenation using sulfided catalysts is a promising method for upgrading the BL-based HTL biocrude.

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