

- IDEALFUEL -

Lignin as a feedstock for renewable marine fuels

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“Development of next generation biofuel and alternative renewable fuel technologies for aviation and shipping”



Deliverable Report

D3.2 – Report on ton-scale pilot production of lignin-based HFO-like marine fuel



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Publishable summary

The EU H2020 project IDEALFUEL aims to develop an efficient and low-cost chemical pathway to convert lignocellulosic biomass into a Biogenic Heavy Fuel Oil (Bio-HFO) - with ultra-low sulfur levels - that can be used as drop-in fuel in the existing maritime fleet. While technical lignins are cheap and available in large quantities, their characteristics are not suitable for the development of high-performance marine fuels. Among others, these lignins suffer from low solubility, large molecular weight, and high sulfur content and are generally non-uniform in their chemical nature. One strategy consists in solvent fractionation of technical lignins and/or woody biomass to extract a high-quality fraction, which can be more suitable for fuels applications. A second strategy consists in the production of high-quality lignin from biomass with alternative bio-refining process. Within IDEALFUEL, the partners selected lignin/biomass solvolysis and Aldehyde-Assisted Fractionation (AAF) as the most relevant technologies for the production of high-performance lignin for fuel applications. Woody biomass solvolysis to an intermediate crude lignin oil (CLO) prior to the bio-HFO production, is one of the process solutions within IDEALFUEL project coordinated by WP2 as a way to mobilize 2nd generation biomass and has been used in order to produce the CLO feedstocks for its catalytic hydrotreatment towards Bio-HFO. In the latter process, commercially available Ru/C catalyst has been used to hydrodeoxygenate the CLO and produced a Bio-HFO composition that needs to be complied with ISO8217 for marine fuels. In this report, we present our efforts to scale up the lab-scale catalytic HDO process that was developed within WP3 of the IDEALFUEL project and was the starting point for bench scale and pilot scale activities.



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1 Introduction

This deliverable report is a consolidation of research activities within WP3 of IDEALFUEL project, that focused on developing a catalytic HDO process for the upgrade of crude lignin oil into HFO-like marine fuel; and more specifically on our efforts to scale-up the Bio-HFO production process from lab to pilot and ton-scale preparation of lignin-based HFO-like marine fuel.

As it was presented initially in the granted project proposal, the consortium and partners considered a 300 L Hastelloy batch reactor as means to catalytically hydrogenate the CLO at pilot scale. However, during the progress of the project and specifically during the lab-scale developments from partner CSIC, it was found out that the 300L reactor has operational limitations for scaling up the lab-scale process (namely the pressure). CSIC partner has done several attempts to adapt the operational conditions (temperature, pressure, reaction time, among others) of lab-scale HDO process in order to allow performing the upscaling at Vertoro facilities. Even when the adapted catalytic HDO process allows attaining Bio-HFO with the expected quality, the reduction in operational pressure was not enough to fulfil Vertoro reactor requirements. Alternatively, Vertoro started looking for other possibilities for scale-up activities within EU. The CLO amounts for all the activities of this deliverable report and tasks from WP3 has been produced by Vertoro within WP2, from woody biomass based on Vertoro's Biomass-to-CLO process at pilot scale; activities that have been reported at the deliverable D2.4. The quality of the CLO has been analysed prior to the HDO process; while the final Bio-HFO product has also been analysed to determine molecular weight reduction, viscosity and residual oxygen and water content.

2 Methods and Results

Methods

Gel Permeation Chromatography for molecular weight determination (GPC) (by VERTORO): The GPC analysis was performed using Shimadzu Prominence-I LC-2030C 3D apparatus, which was equipped with columns in series (Mixed-C and Mixed-D, Polymer Laboratories) in combination with a UV-Vis detector (at 254 nm). Both columns were calibrated with the standards of polystyrene. The eluent was tetrahydrofuran (THF) and analyses were performed around room temperature (25 °C). Automated peak integration was performed, using Shimadzu LabSolutions CS software, to calculate the approximation for the areas in the constructed GPC graphs.

Gel Permeation Chromatography for molecular weight determination (GPC) (by CSIC): GPC analyses were carried out in a SHIMADZU apparatus equipped with two columns connected in series (Mixed-C and Mixed-D, polymer Laboratories) and both a refractive index detector and an UV/Vis detector at 254 nm. The column calibration was done using polystyrene standards (from 580 to 3242000 Da). Analyses are performed at 25 °C using THF as eluent with a flow rate of 1 mL min⁻¹. Reaction samples are dissolved with the concentration of 6 mg mL⁻¹ and filtered using a 0.45 µm filter membrane prior to injection. By GPC it is possible to determine the degree of depolymerization obtained at the end of the reaction and an approximate distribution in molecular weight ranges: 77-512 Da to monomers and dimers, 512-814 Da to trimers and tetramers, and >814 Da for further oligomers.

GCxGC/FID-MS for product composition by CSIC: Product identification for the lightest product fraction was carried out using GCxGC-MS analysis. Most probable product structures were identified using the GC-MS structure predictor from their MS fragmentation pattern. An Agilent 7890A was used, equipped with an HP-INNOWAX column (30 m) and a DB-5 column (5 m), with an FID detector and coupled with an Agilent 5977A MSD mass spectrometer. The analysis was carried out according to the following temperature program: starting in 50 °C and held 1 min, then a ramp of 2.5 °C/min up to 250 °C, where holding 69 minutes.

Kinematic Viscosity measurements of Bio-HFO: All the kinematic viscosity measurements were outsourced to Q8 Research, Kuwait Petroleum International; according to **EN-ISO 3104** analytical method.

<https://q8research.com/services/laboratory-testing-and-analysis>

Oxygen content analysis of Bio-HFO: All the oxygen content analysis measurements were outsourced to ASG Analytic Service AG (www.asg-analytik.de) and measured according to **ASTM D5622 :1995**.

Results and discussion

The end goal of this work package and this deliverable report was to demonstrate the production of 2 metric tons of a sulfur-free Bio-HFO at pilot scale reactor, which meets the specifications of an HFO bunker fuel (ISO 8217 norm) (i.e. sulfur content <0.1 wt%, flashpoint >60 °C, viscosity at fuel storage conditions (T=50 °C) <1000 mm²/s, viscosity at fuel injection conditions (T=130 °C) <15 mm²/s) and deliver said marine fuel by to WP5 for 4- and 2-stroke demonstration engine tests. The departing point of these activities is the lab-scale recipe developed by partner CSIC within WP3 and preliminary reported in Deliverable 3.1. Different catalysts have been investigated for sugar-free and sugar-containing methanol lignin oils at the HDO process. High degree depolymerization of CLOs via hydrotreating at remarkably mild operation conditions have been achieved with various catalysts, i.e. Ru/C catalyst, WO_x overlay catalysts and Fe-Ni-doped CeO₂ catalysts. Optimal conditions for HDO (250 °C, ≈70-80 bar of H₂ pressure, etc.) of sugar-containing CLOs with Ru/C commercial catalyst have been determined through lab-scale testing adapted to produce mL-range solvent free bio-HFO products, which displays low O content and acceptable viscosity values within HFO specs. The standard operation conditions are also presented in Figure 1 (left).



Sample	MW Range (g/mol)	Type of Compounds	Abundance (%)	Mw (g/mol)	Pmax (bar)
CLO	8206 – 533	Oligomers	44.39	1027	-
	533 – 275	Trimers/Dimers	11.17		
	275 – 77	Dimers/Monomers	44.24		
Standard	1928 – 533	Oligomers	34.72	438	86
	533 – 275	Trimers/Dimers	22.67		
	275 – 77	Dimers/Monomers	42.61		

Figure 1. (left) Reactor setup used by CSIC to develop lab-scale recipe. Reaction conditions: Volume 25mL; Feed volume 14 mL; Lignin amount in CLO 9 wt%; 5wt% Ru/C catalyst amount 0.441 g (40% with respect to lignin); Temperature 250 °C; initial pressure 30 bar H₂; reaction time 22h. (right) Molecular weight analysis of CLO before and after the HDO process depicting also the maximum operating pressure in the reactor.

In view of these results, larger volumes of the CLO (CLO20: LIB2020_03_CLO20) were then treated with the 5wt%Ru/C catalyst in a 25 mL Autoclave Engineers reactor working at 250 °C under constant H₂ pressure to produce a total of ≈4g of solvent-free hydrotrated CLO (or bio-HFO) which was characterized by GPC, NMR and GCxGC-FID/MS. Results revealed that the produced bio-HFO had a sufficient degree of depolymerization, with a decrease in the O content (from 42 to 24wt%) and with viscosity values (300-350 mPas at 50 °C) that meet the range required for a HFO-type fuel for marine applications. The methanol content of the Bio-HFO has also been measured via headspace GCMS and found to be only 1.3 wt% (Figure 3). Therefore, standard operational conditions for the hydrotreating of CLOs from VERT with 5wt% Ru/C commercial catalyst (at 250 °C, 30 bar of initial H₂ pressure during 22 h) in the lab-scale autoclave-type reactor were established by screening of main reaction parameters (reaction time, temperature, pressure, catalyst concentration), and following reaction mixtures by GPC, NMR and GCxGC-FID/MS analyses. Under these hydrotreating conditions ≈60% depolymerization degree was reached.



Figure 2. (left) Reproducibility of CLO HDO process with respect the molecular weight distribution of the depolymerized lignin fractions and cumulative production of Bio-HFO for quality control; (right) Bio-HFO produced and analysed for its viscosity.

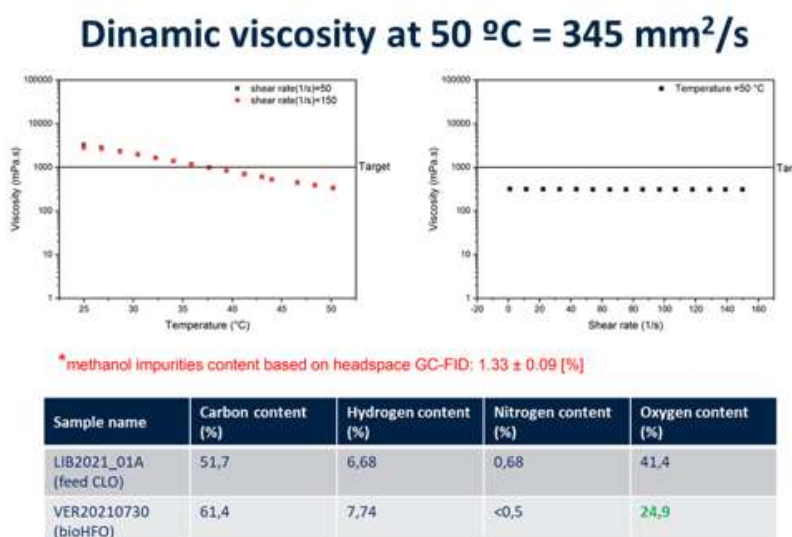


Figure 3. (Top) Viscosity of produced Bio-HFO at various temperatures and shear rates; (bottom) oxygen content analysis of CLO and final Bio-HFO product.

In addition, and due to the limitations encountered for the scaling up of the standard/optimal operational conditions above mentioned in the pilot-scale reactor at VERT facilities, additional lab-scale HDO R&D work was performed at CSIC to try to match the new operational window. Firstly, the most critical reaction parameters in HDO process of CLOs samples were determined and operational conditions adapted to accomplish larger scale reactor requirements (at VERT), such as lower temperature (≤ 235 °C), lower reaction time (≤ 10 h), and H₂ pressure (< 80 bar and close to ≈ 60 bar). Moreover, the possibility of using wet instead of pre-activated or dried Ru/C commercial catalyst was assessed with success. In other sense, the change as solvent from methanol to 2-propanol (as a stronger hydrogen donor) was unsuccessful showing a depolymerization degree of $\approx 1\%$. Furthermore, the effect on CLO concentration (CLO: methanol ratio) was evaluated, results showing similar depolymerization degrees where more concentrated CLOs samples were used, but yielding less bio-HFO.

Finally, to cope with the limitations of large reactor at VERT, the possibility of performing two consecutive HDO runs per hydrotreated CLO batch (235 °C, 30 bar of H₂, during 10 h) with fresh wet Ru/C commercial catalyst was explored. Results show a slightly higher depolymerization degree ($\approx 53\%$) than the HDO reaction at 250 °C during 22 hours ($\approx 48\%$), while the physical appearance of the solvent-free bio-HFO product after two consecutive HDO runs resembled that of the first sample of bio-HFO produced by CSIC (which had showed dynamic viscosity values within specs for HFO application).

As shown in Table 1, operating the HDO process at the lower temperatures (< 235 °C) required to maintain the total pressure at ca. 60 bar, led to lignin depolymerization degrees $\leq 30\%$, which could to be improved to any substantial extent by repeating the run with fresh catalyst under the same conditions. The average molecular weight for the hydrotreated product is in all cases > 950 Da, too high to meet the flow specs required for a bio-HFO. The results emphasize that it is not possible to achieve a sufficiently high lignin depolymerization degree at the low operation temperature imposed by the 60 bar pressure capping.

Table 1. Summary of lab-scale catalytic results for the HDO of CLO (batch WH20220524), with (lignin oligomers + C5 sugars (+FA)): Methanol mass ratio of 1:2. Reaction conditions: CLO feed (14 mL (approx. 12.4 g)); catalyst: 5%Ru/C (Fresh catalyst, 50 % water wet

Sample / Conditions	Temp. (°C)	Cat. (g)	MW Range (g/mol)	Type of Compounds	Abundance (%)	<Mw> (g/mol)	Depolymerization Level (%)	P _{max}
CLO	-	-	14423 – 533	Oligomers	62.98	1439	-	-
			533 – 275	Trimers/Dimers	16.73			
			275 – 77	Dimers/Monomers	20.29			
At 250 °C	250	1.56	6425 – 533	Oligomers	45.69	756	47	74
			533 – 275	Trimers/Dimers	21.63			
			275 – 77	Dimers/Monomers	32.67			
At 235 °C	235	1.58	9193 – 533	Oligomers	56.78	1019	29	69
			533 – 275	Trimers/Dimers	17.56			
			275 – 77	Dimers/Monomers	25.66			
P _{max} operation 60 bar	210 - 215	1.57	10228 – 533	Oligomers	58.38	1120	22	60
			533 – 275	Trimers/Dimers	16.74			
			275 – 77	Dimers/Monomers	24.88			
a) 2 ^o Run at 60 bar ^a	205	0.84	8454 – 533	Oligomers	55.52	999	30	60
			533 – 275	Trimers/Dimers	17.41			
			275 – 77	Dimers/Monomers	27.08			
b) 2 ^o Run at 60 bar ^b	210	0.85	8139 – 533	Oligomers	52.67	977	32	60
			533 – 275	Trimers/Dimers	22.04			
			275 – 77	Dimers/Monomers	25.09			

a) After the 1st run, the alcoholic fraction is separated and dried to obtain 2.1395 g of bioHFO, which is fed in the reactor for the 2nd run at P_{max} = 60 bar.

b) After the 1st run, the alcoholic fraction is separated and directly fed into the reactor for the 2nd run at P_{max} = 60 bar.

The 300L batch stirred tank reactor facility available at the Brightlands Chemelot Campus, and considered for upscaling activities within WP3 has an **operational pressure limitation of maximum 60 bar**. Considering that the project entails the catalytic conversion of lignin oils of methanol (solvent) base, this pressure limit effectively translates to a lower maximum operation temperature of T_≤170-180 °C, at which the partial pressure contributions from the gas-phase hydrogen reactant and the vapour pressure of the methanol solvent reach the maximum allowed 60 bar total pressure. Several mitigation actions have been put into play and tested for their applicability to produce the bio-HFO in the pilot-scale; and the consortium decided to outsource the pilot scale activities for the HDO process and look for alternative reactors that could accommodate the lab-recipe that was developed within WP3.

Efforts to find alternative pilot reactor for scaling Bio-HFO process: Immediately after it was communicated to Vertoro that the required operating pressure for the Bio-HFO process was above >60 bar, Vertoro started looking for alternative sites and third-parties to scaling up the process. Additionally, this has also been added in the minutes of the 4th and 5th General Assembly GA of IDEALFUEL consortium.

The first option that was investigated was VITO (www.vito.be) and its Lignoalue pilot plant for hydrogenation of lignin-based feedstocks. Vertoro asked for an indicative quotation but at the end, this option did not materialize since the commissioning schedule/plan of the Lignoalue pilot plant was not aligned with our scale-up activities and the consortium did not take the risk to proceed further.

The second option that Vertoro explored was the facilities of BTG Biomass Technology Group. BTG has several hydrotreaters available ranging from lab-scale (~1 kg/d feed) to pilot-scale (~20 kg/d feed). The hydrotreaters are based on fixed bed reactors, and each hydrotreater unit consists of 4 reactors in series. The catalyst can be BTG's proprietary catalyst (Picula™), a standard sulphided NiMo or CoMo catalyst, or -if preferred- a catalyst provided by client. Operating pressure is up to 200 bar, and temperatures are in the range of 100 to 400 °C. Vertoro visited immediately the BTG facilities and had several meetings with CTO of BTG (Bert Van de Beld) in order to establish an experimental plan that was aligned with our scale-up activities. Based on these discussions and after an NDA was signed an official quotation has been prepared by BTG for supporting us on our scale-up activities. According to the research contract quotation BTG would hydrotreat the Methanolic CLO at a pressure of 100 bar, and a temperature of 250 °C (all 4 reactors operated at same temperature), and Picula™ has been selected by Vertoro/CSIC as the desired catalyst. A lab-scale screening test will be needed prior to starting the pilot plant activities; in case the screening activity shows operational issues with this specific feedstock. The CLO feedstock would be provided by Vertoro and the hydrotreated CLO will be sent back to Vertoro and CSIC for further quality control analysis. So a GO-NO GO decision moment for pilot activities was established based on successful results of Phase A (bench scale).

Phase A: Bench scale (1 kg / day) continuous fixed bed reactor

Phase B: Pilot Scale (20 kg / day) continuous fixed bed reactor.

Vertoro, after approval from IDEALFUEL Consortium Partners, accepted the offer and proceeded immediately with the feedstock preparations for Phase A. 3 kg of concentrated methanolic CLO 50:50 w/w (mixture of lignin oligomers and methylated C5 sugars dissolved in methanol; produced within WP2) was shipped to BTG group for the execution of Phase A in December 2022. The Picula™ (NiCu/SiO₂) catalyst was provided by BTG, which is considered as a typical hydrotreatment catalyst which is used by BTG to hydrotreat pyrolysis oils. This catalyst is mainly purposed to partially deoxygenate the feed and convert mainly the sugars, which in a different case could cause coke formation. As a second step, they apply a NiMo or CoMo hydrotreatment step. They use catalyst needles and not a catalyst powder. BTG reactors could not accept powder catalyst in that system and therefore Picula™ catalyst could be used in both Phases. The bench scale hydrotreater that was utilized for Phase A is depicted in Figure 4. The bench scale hydrotreater comprises 4 reactor stages in series that are packed with catalyst extrudates. The process conditions that were applied in the system as presented in Figure 4 (right) are given below:

Mass flow CLO: 60 g CLO / hour

H₂ flow: 30 litre / hour

Pressure: 96-100 bar

Temperature: 250 °C.

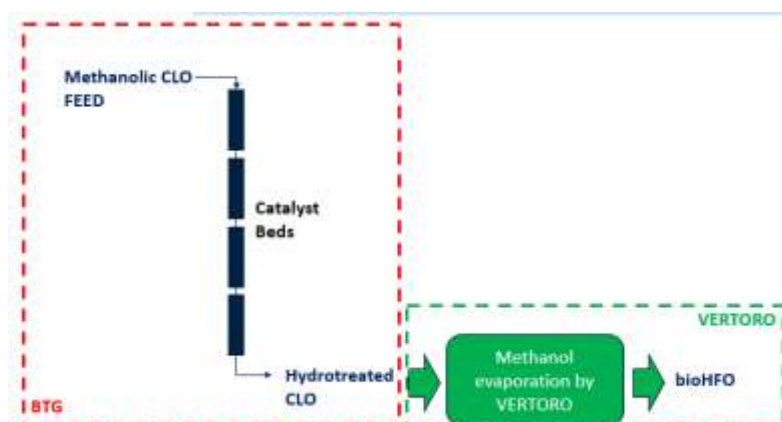


Figure 4. (left) bench scale hydrotreaters that were used for Phase A of BTG contract; (right) Battery limits for material handling with Vertoro handling the hydrotreated CLO for methanol evaporation and analysis of final Bio-HFO product.

According to the results and report written by BTG's technical team, the CLO feed was measured for its MCRT content and found to be approximately 20%. MCRT (Micro Carbon Residue Test) is a laboratory test used to determine the amount of carbonaceous residue formed after evaporation and pyrolysis of typically petroleum materials under certain conditions. MCRT is also a qualitative indicator of hydrocracking efficiency of various processes and has been used by BTG to assess the HDO process of the CLO.

Based on the hydrotreatment experiment of 14/12/2022, a pressure of 100 bar has been achieved in all 4 reactors at a temperature of 250 °C. The hydrotreater could operate for 12 hours in total. After the first 11 hours of operation a strong pressure drop was observed (Figure 5; top) and the system shut down immediately for safety purposes. After inspection of the system afterwards, it was found that there was severe carbon build-up in the inlet of reactors 1 & 2; which finally caused the pressure drop increase (Figure 5, bottom). Two samples were taken at RT= 6 hours and RT= 12 hours and Vertoro handled them further for methanol removal and quality analysis of the final Bio-HFO composition according to Figure 4.

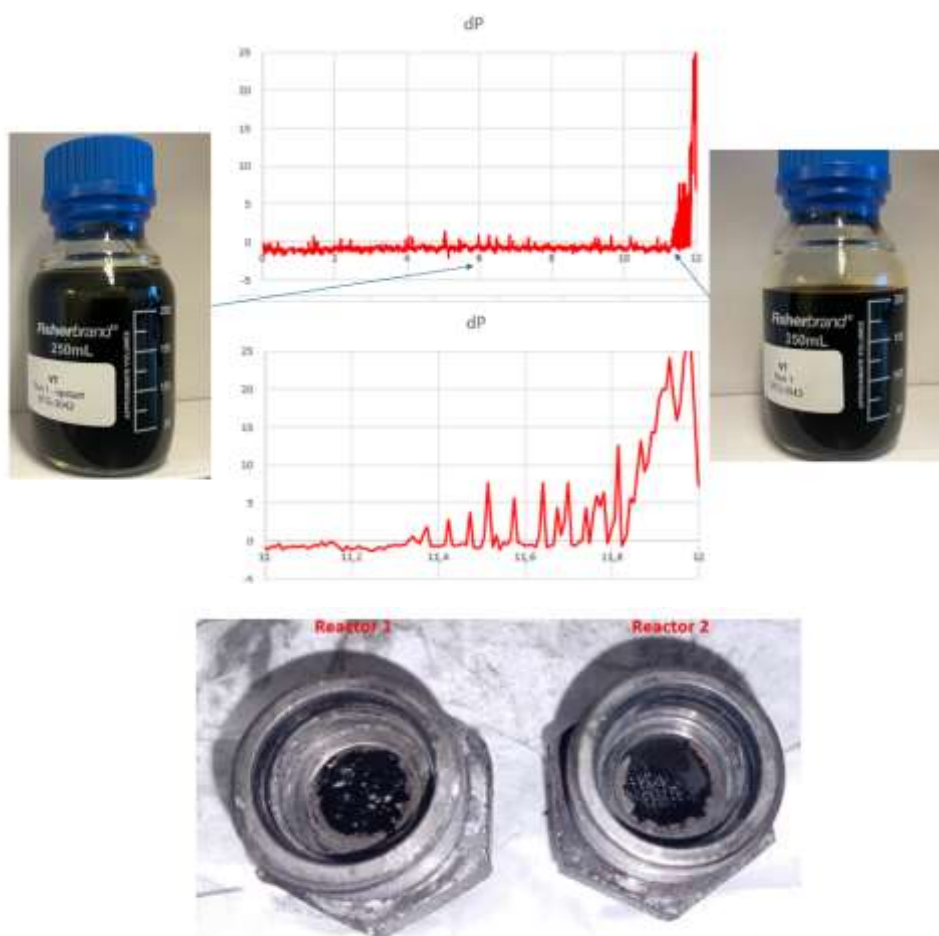


Figure 5. (top) Pressure drop during HDO of CLO at 250 °C and 100 bar H₂ pressure; (bottom) carbon build-up in reactors 1 & 2.

The two hydrotreated samples BTG-3042 and BTG-3043 that correspond to 6 and 12 hours, respectively, were treated by Vertoro downstream to remove all solvent and were sent for external analysis; namely viscosity and oxygen content. The average molecular weight distribution has been determined by both Vertoro and CSIC, while Oxygen content by ASG analytic and Viscosity measured by Q8. The Bio-HFO produced after removal of methanol from sample BTG-3042 is also depicted in Figure 6.

Table 2. Quality results of Bio-HFO produced during BTG Phase A tests

Sample	<Mw> (g/mol)	Oxygen content (%)	Viscosity at 40 C (mm ² /s)	MCRT (-)
BTG – 3042 (6 h)	903	24.1	723	4 %
BTG – 3043 (12 h)	995	30.9	N.A.	N.A.



Figure 6. Final Bio-HFO product produced from BTG-3042 hydrotreated CLO sample at BTG continuous flow reactor.

According to Table 2, results showed that significant oxygen content reduction occurred between 24-30 % (similar to lab scale results at 25 mL CSIC batch reactor), however the Mw reduction was not similar (900-990 g/mol), which might be due to re-polymerisation reactions occurred or catalyst deactivation because of coke formation on catalyst surface. We can assume that carbon deposition that was observed in the inlet of the reactors; might have also caused similar deposition on catalyst active sites. The viscosity of the Bio-HFO could only be measured at the BTG-3042 sample and was 723 mm²/s at 40 °C. This viscosity value is also similar and in alignment with the lab-scale results on Bio-HFO (Figure 3). Finally, BTG also reported the MCRT value, which found to be only 4% and is a strong indication of efficient hydrogenation degree towards low Mw components. Unfortunately, BTG classified this HDO test as unsuccessful due to carbon build-up in the reactors and the whole system. Therefore BTG, decided to repeat the same test but applying different temperature regime during the heating up stage of the reactor; namely 100-150-200-250 °C, maintaining the same operational pressure of 100 bar. Therefore, they cleaned / rinsed the whole system from carbon build-up of first test and proceeded to test 2. Again, they observed fast and strong pressure drop increase; but this time faster (between the first 3-4 hours), while no product sample could be obtained. After both unsuccessful HDO tests due to carbon deposition / reactor fouling, BTG announced to us that we got a NO-GO decision for the Phase B and the pilot hydrotreater.

Accordingly, Vertoro decided not only to continue looking for alternative reactor options to scale up the Bio-HFO process (this time at batch mode), but also to allocate resources to bench scale experiments at a 4 L batch reactor (Figure 7) in order to produce Bio-HFO samples for partners downstream that had to start working on product quality and fuel specifications. In total three batches were executed at the 4L reactor using CLO at two variations; two with composition CLO 1:1 w/w in methanol and one batch with higher dilution factor in the feed; namely CLO 1:4 w/w. The produced Bio-HFO samples are depicted in Figure 7 together with their molecular weight analysis for comparison with previous tests. All the samples



Figure 7. Bench scale 4 L Hastelloy reactor for Bio-HFO production.

were shipped not only to our partner CSIC for analysis validation (1 mL sample) but also to WP4 partners for quality control analysis in alignment with ISO8217 specifications for marine fuels. Results showed that the molecular weight of all three samples was similar and comparable to previous test for the same process conditions, but at larger reactor scale. All three samples were analysed further by partners in WP4 for other fuel related specifications.

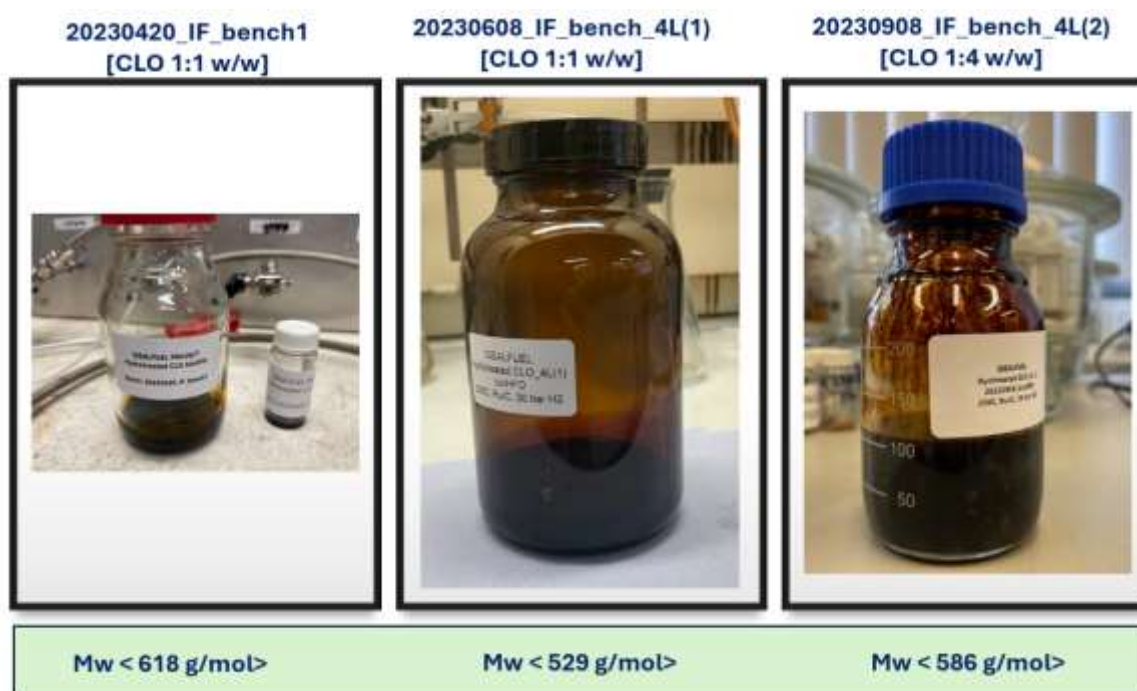


Figure 7. Bio-HFO Samples produced in the 4L batch reactor at TU/e in order to supply partners at WP4 with samples for product quality assessments. *Process conditions for CLO hydrotreatment: T = 250 °C, RT = 12 hours, 30 bar initial H₂ pressure, catalyst 5 wt% Ru/C, catalyst loading 40% based on lignin content.*

While we were working on bench scale samples in order to supply Bio-HFO to partners, we have been also actively looking for larger scale batch reactors in order to finalise the ton-scale production of Bio-HFO; in

accordance with WP3 tasks. After several months of searching through our network, we managed to find a pilot facility institute; namely **Fraunhofer Center for Chemical-Biotechnological Processes CBP** (<https://www.cbp.fraunhofer.de/en.html>). Vertoro visited the Fraunhofer pilot hall and assessed all the available options for scaling-up the Bio-HFO process. After all, in May 2023, it was communicated to us that there was one batch Hastelloy reactor available that could be used in order to apply HDO process of CLO at high temperatures and pressures; but its capacity was only 50 L. In Figure 9, we are presenting the 50L reactor that was presented to us for the Bio-HFO process.

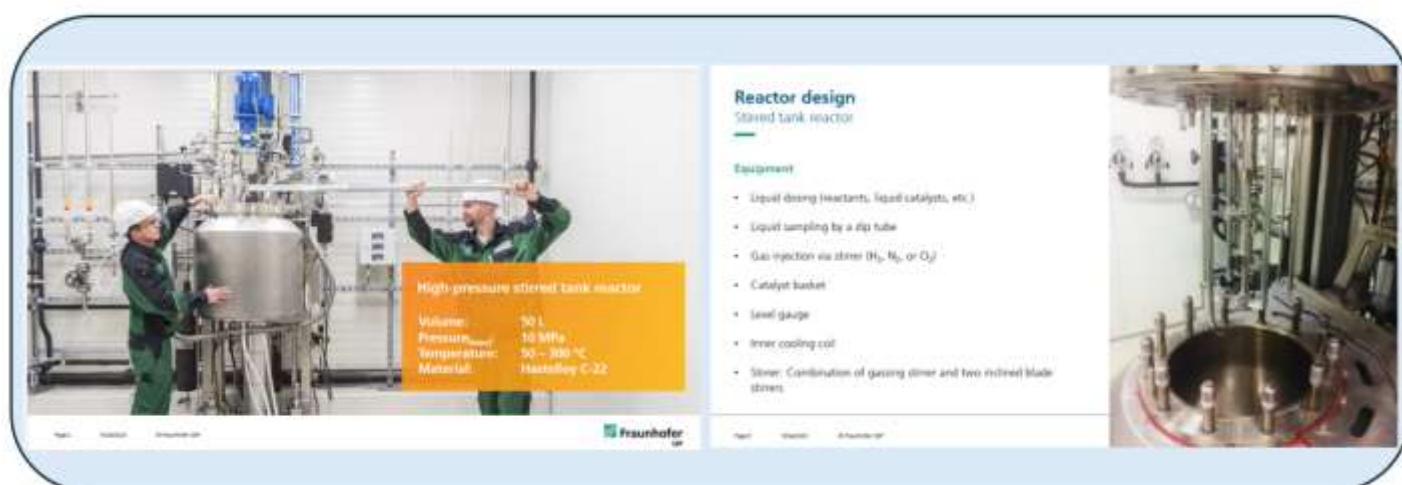


Figure 8. Fraunhofer 50 L high-pressure stirred tank reactor that could be used for scaling up the Bio-HFO process.

After communicating this option again with whole IDEALFUEL consortium, we decided to proceed with the definition of a new research contract with Fraunhofer under NDA; where we could use the 50L reactor at multiple batches to produce larger amounts of Bio-HFO for engine tests. Therefore, Vertoro proceeded with the production of CLO amounts from woody biomass (reported in WP2 deliverables) and CSIC proceeded with the purchase of 5 kg of wet 5wt% Ru/C hydrogenation catalyst (Figure 9). According to the project description and the defined campaigns, Fraunhofer Team would hydrogenate as first step 35L of CLO 1:1 (in 3 batches at fixed price of € 27,514) with the optionality open to order at least 7 more batches if the quality of the Bio-HFO was in accordance to our expectations. The order was placed in November 2023 (offer no. 20042274), and the first 3 batches were scheduled for execution in first weeks of January 2024. Unfortunately, the project manager Jakob Köchermann informed us via email communication on 03/01/2024 that during a water commissioning and preparation batch of the 50L reactor with water, the stirrer failed and broke down. After inspection by Fraunhofer it was resulted that the bearing (plain bearing) was destroyed during the water test run (January 3rd) to check the parameter set-up and time-programmed control for our project. Fraunhofer has been trying to resolve the issues by requesting feedback and technical support by

the manufacturer (<https://www.premex-reactor.com/en/>), and finally it was communicated to us that the reactor would only become available for the IDEALFUEL project in April – May 2024. This was communicated to the Project Officer of the project and a decision was made to not grant extension on the project to finalise these activities. Therefore, Vertoro requested the shipment of the feedstock CLO and catalyst back to the premises of Vertoro and CSIC respectively.

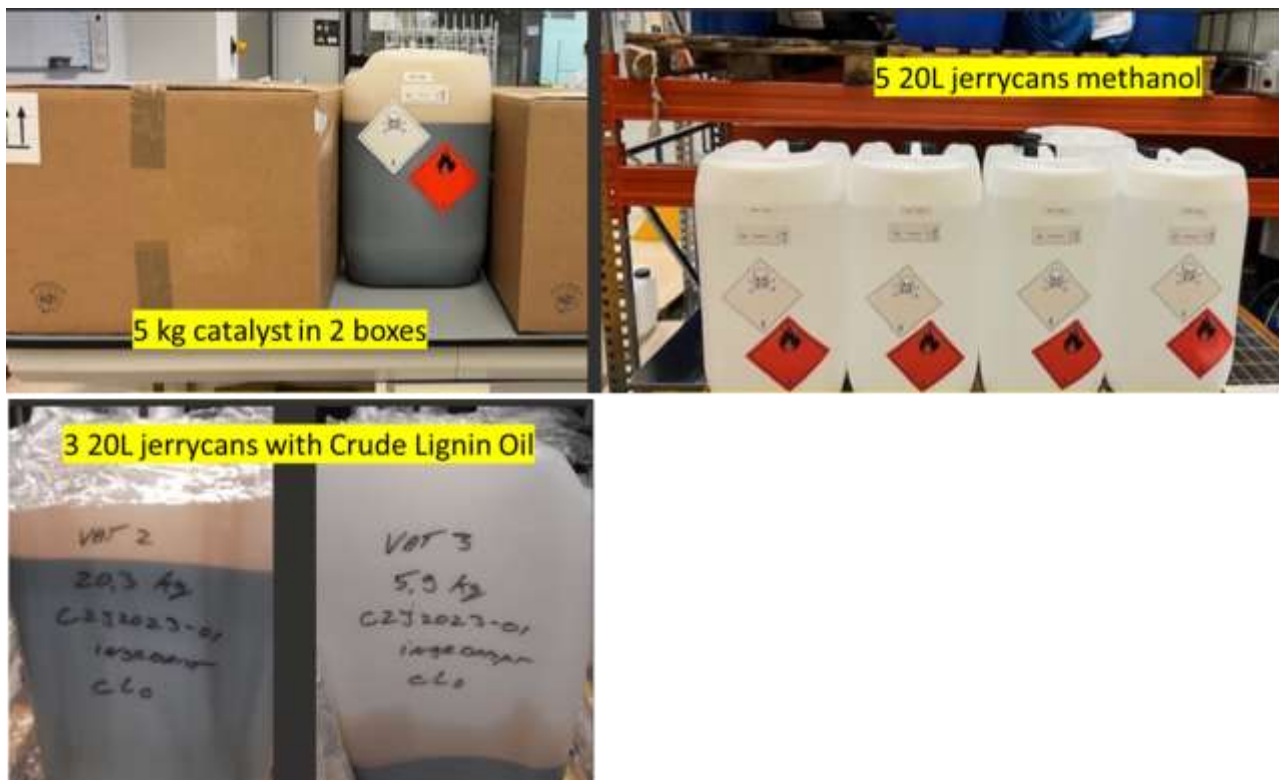


Figure 9. CLO 1:1 w/w Feedstock, fresh methanol and Ru/C catalyst that was shipped to Fraunhofer pilot facility in order to scale up the Bio-HFO process in the 50 L reactor. All raw materials were returned back to Vertoro and CSIC after cancellation of the project.

3 Conclusions

- Lab-scale recipe for catalytic HDO processing of CLOs has been successfully developed and was transferred for scale-up activities; based on positive catalytic performance of 5wt% Ru/C commercial catalyst on hydrotreating CLO at 250 °C, 80-90 bar, produced from woody biomass; delivering therefore a Bio-HFO composition with >50% oxygen content reduction, and viscosity below the maximum limit of 1000 mm²/s at 50 °C.
- Process conditions of lab-scale recipe required minimum operating pressure of 60 bar. This requirement made the scalability of the process in the 300L Batch reactor impossible due to pressure limit of 60 bar. Task Leader looked for alternative reactor options.
- A continuous pilot scale fixed bed reactor has been utilised (BTG biomass Group) in order to scale-up the hydrotreatment of CLO at 250 °C and 100 bar operating pressure, using an alternative hydrogenation catalyst (Picula™) offered by equipment owner. Bench scale assessment; prior to pilot scale operation (20 kg/hour) showed that the final Bio-HFO product exhibited significant oxygen content reduction and low viscosity (similar to lab process) for 11 hours of operation at 250 °C and 100 bar H₂ pressure; but under the presence of carbon build-up in the inlet of the reactors, and possibly on catalyst surface leading to its deactivation. This resulted in higher molecular weight distribution (approx. 900 g/mol) of the final Bio-HFO product compared to lab-scale results and low yields to oil.
- Bench scale reactions were executed in a 4L batch reactor in order to generate small-scale Bio-HFO samples for fuel quality and blending activities in other work packages. The molecular weight of the Bio-HFO samples produced was in alignment and similar ranges with lab-scale data.
- Finally, a new 50 L high-pressure stirred tank reactor was found as alternative scale-up option in Fraunhofer Institute. Large amounts of CLO were produced by Vertoro in WP2, and Ru/C catalyst has been ordered by CSIC; but at the end this scale-up campaign could not been executed due to the fact the stirrer of the reactor broke down; just before the project starts.
- If the 50L Fraunhofer reactor had not broke down, we believe that we could have produced the required amounts of Bio-HFO under the accepted properties for further research activities (molecular weight, oxygen content reduction and kinematic viscosity).

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Project partners:

#	Partner short name	Partner Full Name
1	TUE	Technische Universiteit Eindhoven
2	VERT	Vertoro BV
3	T4F	Tec4Fuels
4	BLOOM	Bloom Biorenewables Ltd
5	UNR	Uniresearch B.V.
6	WinGD	Winterthur Gas & Diesel AG
7		(Formerly SeaNRG, is now GOODFUELS #12)
8	TKMS	Thyssenkrupp Marine Systems GMBH
9	OWI	OWI – Science for Fuels gGmbH
10	CSIC	Agencia Estatal Consejo Superior De Investigaciones Cientificas
11	VARO	Varo Energy Netherlands BV
12	GOOD	GoodFuels B.V.



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