

Final report

1. Project details

Project title	Integration of Biogas production with Hydrofaction oil production – De-risking before demonstration (BiogasOil)
File no.	64021-2054
Name of the funding scheme	EUDP 2021-II
Project managing company / institution	Nature Energy Biogas A/S
CVR number (central business register)	34 61 40 91
Project partners	Steeper Energy Aps Aalborg University Seges Innovation P/S Nature Energy Construction A/S
Submission date	26 June 2024

2. Summary

English version

Nature Energy A/S considered the implementation of Steeper Energy ApS Hydrofaction® technology platform into its operations for the conversion of biogas digestate into advanced biofuels. The BiogasOil Project aimed to articulate the advantages of biogas and bio-oil production at the same site to 1) generate biofuels derived from waste feedstock; 2) to validate the quality of the biofuels; 3) determine additional biogenic wastes; 4) reduce GHG emissions from agriculture, waste management and transport.

The overall project objective was to de-risk future commercial projects based on synergies between anaerobic digestates from manure fibers, energy production, nutrients and carbon management.

Danish version

Nature Energy A/S påtænkte at anvende Steeper Energy ApS's Hydrofaction® teknologi til at konvertere afgassede gyllefibre til avancerede flydende biobrændstoffer. BiogasOil projektet har afsøgt at tydeliggøre fordelene ved at integrere biogas og bioolie produktion gennem: 1) at øge mængden af fornybar energi fra den samme mængde affaldsbiomasse; 2) at validere kvaliteten af biobrændstof; 3) vurdere yderligere affaldsbiomasser som ville være passende at behandle i denne proces; 4) reducere drivhusgasudledningerne fra landbrug, affald og transportsektoren.

Projektet har været designet til at risikofærdække forudsætninger forud for en mulig investeringsbeslutning, herunder med konsekvenser i landbruget.



The BiogasOil Project aimed to articulate the advantages of the integration of biogas and bio-oil production at the same site. The BiogasOil Project included a program of biocrude production, process products separation (including minerals and nutrients) and biocrude upgrading to advanced biofuels.

Main results and conclusions

The successful proof of concept for the conversion of digested fibres into energy-dense biocrude through Hydrothermal Liquefaction (HTL) has been achieved.

A total of five HTL campaigns were conducted using a variety of slurry formulations that included digestate fibre materials and additives to optimize biomass processing and HTL process stability.

The project's most representative HTL biocrude and HTL solids were assessed to determine the possibility of market integration in the current energy and agricultural sectors, encompassing the use of HTL solids as fertilizers and production of fuels via biocrude stand-alone upgrading and co-processing.

Successful hydrotreatment of the HTL biocrude utilizing commercial sulphided catalysts in continuous hydrotreater units was also accomplished.

Marine and diesel samples suitable for blending with conventional fuels were obtained

Perspectives and effects derived from the technology.

Integrating a biogas facility with a hydrothermal liquefaction (HTL) plant aims to revolutionize the energy market by offering a dual approach to waste management and renewable fuel production. Biogas facilities traditionally convert organic waste into methane, a valuable source of renewable energy. However, by combining biogas production with HTL technology, which converts organic matter into high-quality biocrude that can be further upgraded to produce fuels, the market gains a versatile solution capable of handling diverse feedstocks and producing a wider range of valuable products. This integration not only enhances the efficiency and output of renewable energy but also provides a sustainable alternative to fossil fuels, thereby contributing significantly to the market's efforts towards decarbonization and environmental sustainability.

3. Project objectives

Objectives of the project

1. Reduce or dissipate uncertainties based on confirming the physical production and value of the produced co-products as well as the contribution of GHG emissions reductions for the conversion of digestate fibers to biocrude and subsequently to bio-marine diesel, bio-diesel and bio-jet partially.
 - a. Quantify the mass and energy balance
 - b. Operating protocols
 - c. Optimization opportunities
2. Confirm the impact of Capital and Operating costs on future economics where early indications show that the costs of aggregating the waste biomass resources influence the business case.
3. Identify coordination, and indeed integration, opportunities to leverage existing biogas infrastructure with new Hydrofaction® plants.
4. Utilize extensive existing engineering work for a preliminary design and techno-economic evaluation of a commercial Hydrofaction® to be located at a biogas Plant using the digestate fibers from 3-5 other nearby biogas plants.

Energy technology developed and demonstrated

1. Production of a representative bio-crude based on relevant digestate fibres.
2. Demonstrate a pathway of a representative biocrude to the market by
 - a. Performing upgrading tests to "Drop In" green transportation fuels in a stand alone unit
 - b. Performing upgrading test resembling co-processing with fossil oil in a refinery
 - c. Producing physical samples of the various cuts including extensive characterization of these
 - d. Investigating options for direct use of the biocrude e.g. for marine, stationary generators, decentralized CHP, or Waste Incineration plants
3. Investigate the recovery of phosphorus and nitrogen from the process and assess the options for direct use of the mineral fraction on farmland as well as processing options to higher value conventional phosphorus and their return to agriculture.
4. A techno-economic assessment of the commercial demonstration plant with preliminary site layout and assessment of CAPEX, OPEX and side streams part of an environmental assessment.
5. Business case indicating economic feasibility and a sensitivity analysis.
6. Life cycle analysis for determination of the expected GHG savings from the biofuel products in a European context (RED II).

4. Project implementation

The project was extended from 36 mth to 42 mth due to a 7 mth break in the beginning of the project where the partners had to agree on and finalise the project agreement. Despite this the project has overall been executed according to the agreed milestone plan, only with minor adjustments to the budget and milestone plan. All these adjustments have been agreed with EUDP and have not influenced the scope of work in the project.

5. Project results

Objectives and technical results.

Throughout the BioGasOil project, great progress was made in minimizing the uncertainties associated with converting digestate fibers using Hydrofaction® technology. This was accomplished through rigorous

studies that proved the physical production process's performance as well as the worth of the created coproducts. Furthermore, a detailed quantification of mass and energy balances has been successfully accomplished, along with the establishment of operational protocols.

The project has successfully demonstrated the feasibility of producing homogeneous pumpable slurries from digestate fibers, facilitating their conversion through the Hydrofaction® process without the need for drying. Despite encountering challenges during HTL product separation, dewatering and inorganic removal to obtain a biocrude suitable for upgrading at commercial refineries, an average yield of 37 wt.% of HTL biocrude has been achieved, although lower than anticipated. Specifically, the degassed product forms a stable emulsion impeding distinct phase separation. Optimization efforts may be necessary to maximize oil recovery, including refined inorganic removal techniques and potentially implementing a multistage process with centrifuges. Further testing is imperative to refine the design for commercial implementation.

Evaluation of the HTL biocrude's potential for fuel production has been a core objective, revealing its suitability for producing blendable marine fuel and diesel. Additionally, coordination and integration opportunities have been identified to align existing biogas infrastructure with Hydrofaction® plants, exemplified by the completion of preliminary engineering designs. These designs serve as the foundation for conducting techno-economic evaluations of commercial Hydrofaction® plants at biogas facilities, leveraging digestate fibres from neighbouring plants.

Addressing technical risks has been bifurcated into two major work packages: WP2 focuses on sorting, pretreatment, handling and conversion of digested fibers in HTL, WP3 and WP4 concentrate on product characterization and biocrude upgrading. Further elaboration on the results of individual work packages and tasks follows.

Processing of Digestate Fibers in HTL

The proof of concept for the transformation of digestate fibres into biocrude and solids using hydrothermal liquefaction (HTL) was successfully completed through the work conducted in WP2 (Feedstock fibres and biocrude production) and WP3 (Physical and chemical characterization of feedstocks, products, and effluent streams). The biocrude and solids streams have the potential to be used for fuel production and fertilizers, respectively, as will be discussed later in this report. HTL experiments were conducted at the HTL pilot plant at Aalborg University. In Figure 1, a diagram of this unit is illustrated.

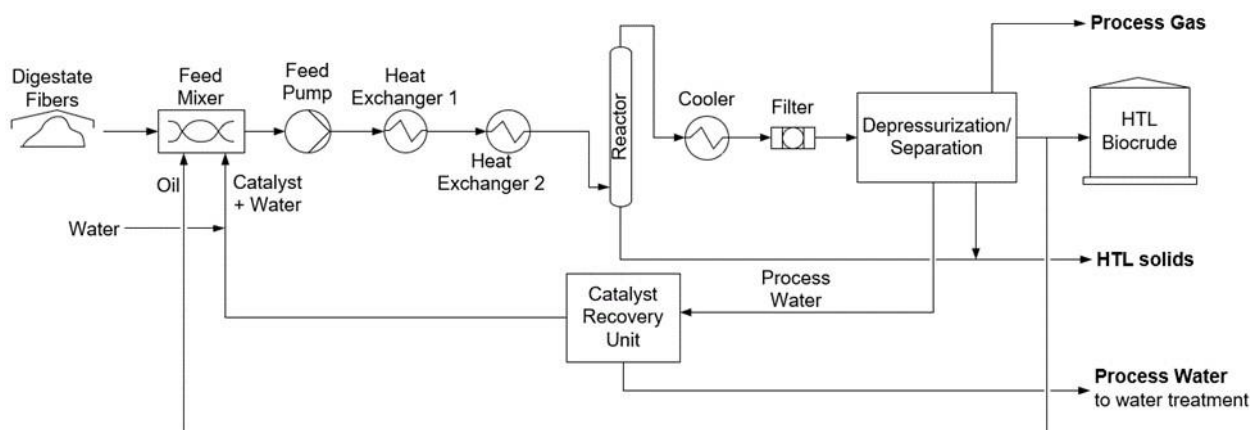


Figure 1. HTL pilot plant simplified diagram

Table 1 presents the average composition of digested fibres used as feedstock in the project. The analysis revealed that the biomass's significant fluctuations in moisture content (between 50-70 wt.%), ash content (911 wt.%), and large particle size (>6 mm) posed difficulties in optimizing biomass processing and achieving a consistent, pumpable slurry. These qualities are crucial for enhancing process profitability and ensuring seamless operation. Therefore, feedstock homogenization and subsequent particle size reduction were undertaken to create a more homogeneous feed with an average particle size of 2 mm (Fig. 2), optimal particle size defined based on lignocellulosic material successfully processed at this HTL facility with pipe internal diameter of 6 mm.

Table 1. Average composition of digestate fibers.

Analysis	Units	Method	Digestate fibers
Moisture content	[wt.%]	DL-4002	68.1
HHV (db)	[MJ/kg]	ASTM D240-19	18.7
Ash (db)	[wt.%]	ASTM D482-19	9.3
Carbohydrates (db)			
Arabinan	[wt.%]		1.3
Xylan	[wt.%]	By IC, TAPPI T249 prep ^a	15.2
Galactan	[wt.%]	By IC, TAPPI T249 prep ^a	0.5
Glucan	[wt.%]	By IC, TAPPI T249 prep ^a	21.2
Acid Insoluble Materials	[wt.%]	By IC, TAPPI T249 prep ^a	37.6
Total	[wt.%]	By IC, TAPPI T249 prep ^a	75.9
Carbohydrates, extra parameters (db)			
Hemicellulose	[wt.%]	By calculation ^b	17.1
Cellulose	[wt.%]	By calculation ^b	21.2
Elemental composition, (daf)			
C	[wt.%]	ASTM D5291 A-21	46.6
H	[wt.%]	ASTM D5291 A-21	6.2
N	[wt.%]	ASTM D5291 A-21	2.4
O	[wt.%]	By difference	43.9
S	[wt.%]	ASTM D1522 A16-E1	0.5
Cl	[wt.%]	SS-EN 1508:2011 (Mod.)	0.4

^a (% , extracted OD - ESM 310D) Analysis on acid-hydrolyzed sample; includes arabinan, xylan, mannan, galactan, glucan, and Acid Insoluble Material; ^b (% , extracted OD - ESM 310D) Determination of cellulose and hemicellulose from carbohydrate data.

The dry matter content of the digestate fibres was 14% higher (31.9 wt.%) than the optimal dry matter level of a lignocellulosic slurry (17.5 wt.%), which limits the possibility of recycling process water, an essential aspect of Hydrofaction® technology. In order to determine the ideal dry matter content (DMC) of the slurry for digestate fibres, three different slurries were prepared using Steeper Energy's slurry recipe. The slurries had varying dry matter contents of 17.5%, 20%, and 28%. Based on the pumpability tests performed using an in-house methodology, it was determined that the most appropriate mixture for the operation would consist of slurries containing 17.5% dry matter. Figure 2c includes a visual representation of the selected slurry.



a) Digestate fibers as received



b) Fibers after milling



c) Slurry

Figure 2. Digestate fibers to slurry: a) fibers as received; b) fibers after particle reduction; c) slurry with DM 17.5%

The digestate fibres were introduced into the HTL plant through the mixer, where they were combined with other slurry components, such as a homogeneous catalyst and sodium hydroxide, to control the pH of the process water after separation to around 8.5. Additionally, recycled water phase and oil recirculation are included to enhance the rheological properties of the slurry and the conversion chemistry, as is typically done in the lignocellulosic recipe. The feed slurry is introduced into the feed tank and then consistently supplied to the plant using the charge pump. The feed slurry is subjected to a pressure of 320-330 bar by the feed pump (average flow rate of 20 kg/h) and then heated to a reaction temperature ranging from 300-385°C using two heaters connected in series. Afterward, it enters the up-flow reactor with a target temperature of 385°C. The reactor's effluents were cooled before being introduced into a filtration unit and pressure let-down system. Then, the depressurized product was treated in a separation module to obtain a biocrude with low water and inorganic content. A cumulative amount of 3500kg of slurry underwent processing in multiple experiments, resulting in a total of 170 hours of accumulative oil production.

The key challenges in processing digestate fibres were the separation of the degassed product to maximize oil production and allow the removal of inorganic impurities, hence improving the oil's quality for later upgrading. The separation method employed involved a three-step gravimetric operation that extracts and treats HTL products using acid and solvent, which is comparable to how lignocellulosic materials are processed in Hydrofaction® technology. Although the HTL products were separated, the oil production per dry-ash-free biomass treated (37 wt.%) was less than the expected 44 wt.% observed in an HTL lab scale unit. The stated oil yields differ due to the creation of a strong emulsion between water and oil during degasification and separation stages, as well as poor recovery of the light fraction (BP < 110°C) from the process gas stream. HTL biocrude yields are expected to increase by optimizing light fraction recovery, recovering water-soluble organics from produced process water, recycling them back into the process as a concentrate, and improving the separation efficiency of degassed products (oil, process water, and inorganics) by incorporating solvent-assisted phases such as centrifugation, acidification, and filtration.

The HTL process predominantly produced process water and gas as byproducts, yielding 27.2 and 21.9 wt.%, respectively. Furthermore, 10.1 wt.% solid formation was observed, with the majority of the solids concentrated inside the reactor. This solids production was ascribed mainly to the digestate fibres' high ash content (9.3 wt.%). Solids production could be reduced by improving the HTL process parameters. An appropriate solid handling system is required to remove materials from the reactor during operation. Table 2 shows the mass, elemental, and energy balances determined from the campaign's average results.

Table 2. Mass, energy and elemental balance (daf)

		Digestate	Biocrude	Process Gas	Process Water	Solids	Total
Mass and Energy Balances							
Mass	wt.%	100	37.0	21.9	27.2	10.1	96.2
Energy	%	100	70.1	4.1	0.3	12.0	86.6
Elemental Balance							
C	wt.%	100	64.5	13.8	2.0	14.1	94.4
H	wt.%	100	59.8	7.0	43.4	6.6	116.8
N	wt.%	100	20.2	10.3	63.0	8.6	102.2
S	wt.%	100	14.3	5.5	78.7	3.9	102.4
O	wt.%	100	6.1	33.6	49.1	6.6	95.4

The carbon recovery from biomass to oil was 64.5 wt.%, as evidenced by the biocrude production and carbon content (81.33%). Similarly, 14.1 wt.% and 13.8 wt.% of the carbon in biomass are extracted as solid and gaseous forms, respectively. The process water included just 2 wt.% of the biomass carbon, resulting in a carbon balance closure of 94.4 wt%. The carbon balance's poor closure could be due to uncertainty caused by carbon losses in the aqueous and gaseous phases. The nitrogen and sulphur balance shows that the process water and biocrude contain the majority of the nitrogen and sulphur produced from biomass. Due to sample processing and technical constraints, the chloride balance in relation to the biomass input had a low closure (28%). The only HTL stream products discovered to contain chlorides were process water (0.39 wt.%) and a trace in HTL biocrude (30 ppm). In order to enhance the Cl balance, it is necessary to do accurate chloride analysis on fresh samples.

The water phase was found to have a high total organic carbon (TOC) of 23400 mg/l (APHA 5310B) and an ash content of 7.96 wt.%. This indicates that the process water might be concentrated and recirculated back into the process, potentially leading to an increase in oil yield and a reduction in the need for fresh catalysts. Nevertheless, it is necessary to carry out a purification process on this concentrate in order to prevent the accumulation of undesirable components such as chloride. In addition, this process requires certain purification and treatment procedures before it may be discharged. Hence, case studies that are tailored to a given site should include a thorough assessment that specifically targets key aspects of the current wastewater treatment.

Table 5 presents a detailed analysis of the composition and energy content of the gaseous product. Based on the above composition, it is evident that carbon dioxide represents the main gas produced, indicating that biomass reforming, water gas shift reaction, and decarboxylation were involved in eliminating oxygen from the biomass. Methane and other hydrocarbons with low molecular weight primarily arise from methanation and cracking processes. The elemental content of the gaseous product is 29.38 wt.% C, 1.96 wt.% H, 1.14 wt.% N, 0.14 wt.% S and 67.38 wt.% O. The HTL gas product contains mostly CO₂, but its high heating value is due to the presence of combustible substances such as hydrogen and hydrocarbons, which can be used for heat process integration.

Table 3. Product gas composition and HHV

Component	Air free, vol%	Air free, wt.%	HHV, MJ/kg
H ₂	12.05	0.66	0.926
CO ₂	77.52	92.40	0.000
CO	0.10	0.08	0.01
H ₂ S	0.15	0.14	0.001

NH ₃	3.00	1.38	0.31
CH ₄	3.51	1.52	0.84
Ethylene	0.21	0.16	0.08
Ethane	1.70	1.38	0.69
Propene	0.33	0.38	0.19
Propane	0.74	0.88	0.43
Sum C ₄	0.36	0.57	0.28
Methanol*	0.00	0.00	0.00
Ethanol*	0.21	0.26	0.08
Acetone*	0.12	0.19	0.06
Total	100	100	3.90

Gas composition was determined following the standard SS-ISO 6974

The energy extracted from the dry-ash-free HTL products, derived from biomass with an HHV of 20.1 MJ/kg entering the process, is primarily concentrated within the biocrude, representing 70% of the energy input. Although this retrieval is lower compared to that observed for forestry residues (85.6%), the production of highly energy-dense biocrude underscores the HTL technology's capacity to convert low-energy-density biomasses (20.1 MJ/kg) into high-energy-dense biocrude (39.04 MJ/kg). Approximately 12% of the energy is retained in the solids (24.8 MJ/kg), with 4% in the gas phase (HHV: 3.90 MJ/kg). The energy losses within the aqueous byproduct (0.3%) align with the carbon losses discussed above, emphasizing the need to implement an effective oil recovery strategy to harness the technology's potential.

Digestate Fibers derived HTL biocrude potential

As part of this project, HTL biocrude utilization has been assessed to explore its potential for fuel production and integration into refinery processes. The distinctive characteristics of HTL biocrude (refer to Table 2) were considered when choosing a suitable upgrading process scheme and determining an entry point within a petroleum refinery. Potential pathways for integrating HTL biocrude into the market include the necessary treatment processes for incorporating it as a component in marine fuel blending, traditional hydroprocessing technologies for diesel production, and co-processing with petroleum feedstocks. The digestate fiber-derived HTL biocrude has a high energy density, with an HHV of 39 MJ/kg. It is less oxygenated (7.22 wt.%) than lignocellulosic HTL biocrude (~10 wt.%); however, it contains a higher concentration of nitrogen (1.32 wt.%) and sulfur (0.2 wt.%). The HTL biocrude is movable and has a viscosity of 1473 cSt at 25°C (refer to Figure 3). Table 4 provides a summary of the characteristics of HTL biocrude.

Table 4. Summary of HTL biocrude characterization



Figure 3. Digestate-fibers derived HTL biocrude at 25°C

Test	Method	Unit	HTL biocrude
Water content		wt. %	0.16
Ash	ASTM D482 (Mod)	Ppm	232
Al+Silicon	ICP-OES	Ppm	<10
Micro carbon residue	ASTM D4530	wt. %	13.25
TAN	ASTM D664A	mg KOH/g	28.53
High Heating Value - HHV daf	ASTM D240	MJ/kg	39.04
Density @ 15°C	ASTM D4052/D5002	kg/m ³	1019
Kinematic Viscosity @ 50°C	ASTM D445	cSt	162
<i>Elemental analysis (daf)</i>			
Carbon	ASTM D5291	wt. %	81.33
Hydrogen	ASTM D5291	wt. %	9.93
Nitrogen	ASTM D4629	wt. %	1.32
Sulfur	ASTM D5453	wt. %	0.2
Oxygen		wt. %	7.22
H/C Molar Ratio	Calculated	molar ratio	1.45
Cl	XRF	wt. %	0.003
Flash point	ASTM D3828B	°C	58
<i>SimDis</i>			
Naphtha (IBP-190°C)	ASTM D7169	%	5.7
Middle distillates (190–343°C)	ASTM D7169	%	28.3
Heavy gas oils (343-550°C)	ASTM D7169	%	41.6
Residue (550+)	ASTM D7169	%	24.4

Diesel application

The HTL biocrude consists of 32% of compounds with a boiling point similar to that of commercial diesel (150-350°C). However, this fraction cannot be used directly as diesel fuel due to its high levels of aromatic molecules and compounds containing oxygen, sulphur, and nitrogen. These compounds are naturally present in HTL oils generated from digestate fibres. Hydrotreatment is essential for achieving the desired decreases in density, aromaticity, heteroatom content (O, N, and S) and polarity while improving the heating value and hydrogen-to-carbon ratio. Additionally, it helps to minimize the number of carboxylic acids, which contribute to the elevated Total Acid Number (TAN) of the initial HTL biocrude (28.53 mgKOH/g). Hydrotreatment also makes a higher yield of diesel fraction possible, which helps transform the biocrude's heavy component (350°C+) into molecules with a lower boiling point.

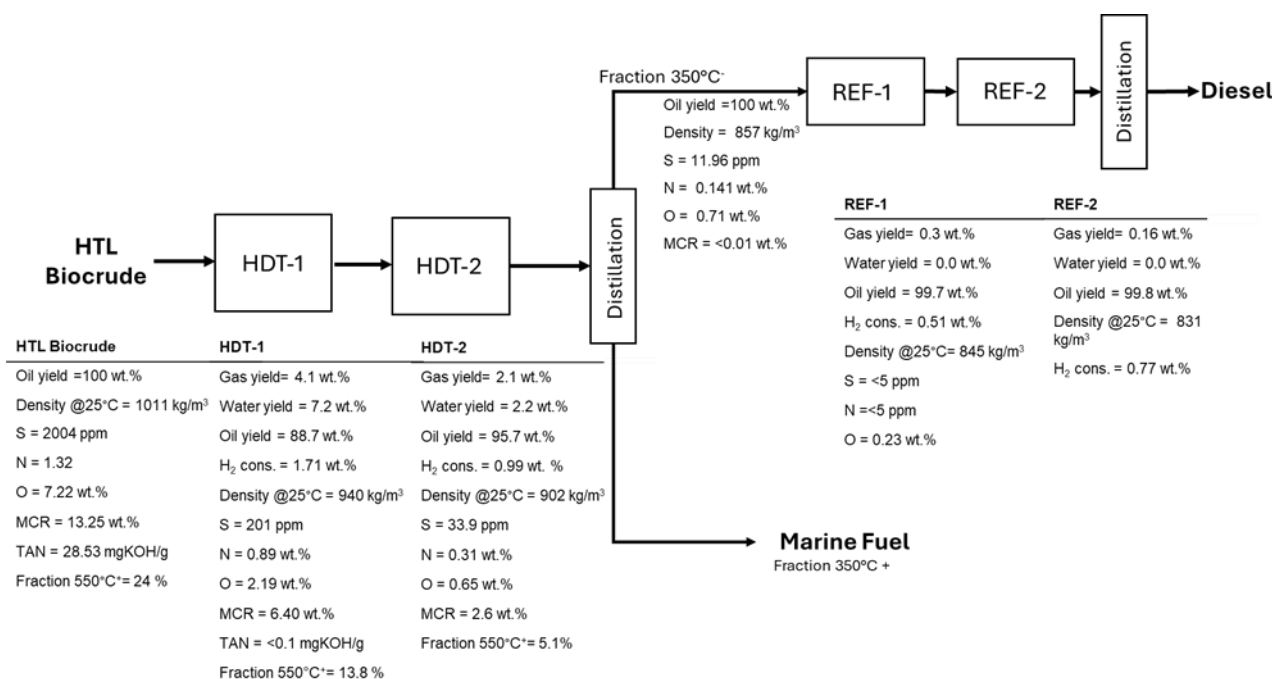


Figure 4. HTL biocrude upgrading. HDT-1: 360°C, 100 bar, 0.5h⁻¹, 1000 H₂/oil v/v; HDT-2: 400°C, 100 bar, 0.5h⁻¹, 1000 H₂/oil v/v; REF1: 320-330°C, 100 bar, 0.3-0.5h⁻¹, 1000 H₂/oil v/v; REF-2: 300°C, 100 bar, 0.3- 0.5h⁻¹, 1000 H₂/oil v/v.

The BGO research led to advances in the hydrotreating pathways for this HTL biocrude. Parametric studies were conducted at each stage of hydrotreatment to determine the optimal operating parameters. Figure 4 depicts the most outstanding outcomes for biocrude upgrading. The HTL biocrude derived from digestate fibres was hydrotreated in two continuous phases on a dual catalyst bed, including commercial NiMo-type catalysts with intermediate and high hydrotreating activity. The improved product was then separated by obtaining 350°C- and 350°C+ distillation cuts. To meet stringent diesel fuel quality standards (EN590, D975), the 350°C- distillation cut was subjected to two refining stages using a dual catalyst bed containing commercial NiMo-type catalysts aimed at decreasing nitrogen, sulphur, oxygen, phenols, and aromatics. The process was carried out for more than 1400 hours, with each step operating continuously. Stage durations were determined by the availability of feedstock: 412 hours for HDT-1, 293 hours for HDT-2, 574 hours for refining 1 and 216 hours for refining 2. No catalyst deactivation was observed in any of the tested conditions.

The hydrotreatment pathway depicted in Figure 4 illustrates a substantial improvement in the quality of the HTL biocrude after undergoing the hydrotreating stages 1 and 2 (HDT-1 and HDT-2). HDT-2 results in a significant decrease of 98% in sulphur, 91% in oxygen, and 76% in nitrogen. The microcarbon residue and the residue

fraction (550°C+) were both decreased by 80% and 79%, respectively. In addition, the density was enhanced from 1011 to 902 kg/m³, and the TAN was decreased to below the detection limit (<0.1 mgKOH/g oil). A shift in the boiling point distribution is noticed with HDT-1 and HDT-2. In particular, the percentage of distillates having a boiling point between IBP and 343°C rises from 34 to 58 weight percent.

Upon distillation of the HDT-2 products, it was noted that additional hydrotreatment was necessary to decrease the aromatic content, density, and sulphur levels of the distillates fraction (IBP-350C). This will improve the quality of the distillates and possibly produce a diesel fuel that meets the EN590 and D975 diesel specifications. Following the two refining steps (REF-1 and REF-2), the product achieves a density similar to that of commercial petroleum diesel. The sulphur content is reduced to less than 1 ppm, and the HHV increases from 44 to 46 MJ/kg.

The REF-2 products underwent vacuum distillation to assess their potential for producing diesel. Table 5 presents the characterisation of the obtained digestate fibres derived HTL diesel in comparison to the diesel specifications. This Diesel sample meets the requirements for both diesel criteria for sulphur and nitrogen concentration, viscosity, flash point, TAN, and water content. Notably, fractions with temperatures ranging from 325-360°C are deliberately excluded from fuel compositions. This is because their high density and cloud points would greatly compromise the quality of the fuel if they were included. Additional research is necessary to assess the potential extraction of aromatic compounds from the fraction 325-360°C compared to subsequent hydrotreatment. Compatibility testing has confirmed that the HTL diesel is fully soluble with regular diesel. These findings suggest the possibility of developing a renewable diesel fuel that can be used either in its pure state or as a component of a synthetic diesel mixture.

Table 5. Summary of HTL diesel characterization

Test	EN590	D975	Diesel digestate fibers
Boiling point range [°C]	max 360	max 338	150-325
Water content [wt.%]	max 0.02	max 0.05	<0.01
Ash content [wt.%]	max 0.01		<5
TAN [mg KOH/g]	max 0.08		<0.1
Density 15°C [kg/m ³]	820-845	max 900	843
Kinematic viscosity @40°C [cSt]	2-4.5	1.9-4.1	2
Sulfur [ppm]	max 10	max 15	1
Nitrogen [ppm]	max 210	max 210	31
Flash point [°C]	min 55	min 55	58
Cloud point [°C]			-30.9
HHV [MJ/kg]			45.92



Figure 5. Diesel derived from digestate fibers

Marine fuel application

The direct application of HTL biocrude derived from digestate fibres as marine fuel is constrained by its low thermal stability (as evidenced by accelerated aging studies) and low flash point (58°C). These limitations restrict the transportation, storage, and utilization of this biocrude in fuel blends. In addition, this oil possesses a greater amount of sulphur (0.2 wt.%) and a higher density (1019 kg/m³ at 15°C) compared to the low sulphur marine fuel specified in ISO 8217 (Table 5). The low compatibility between this oil and marine gasoline was

verified through spot tests conducted on blends comprising 10 wt.% HTL biocrude. Consequently, hydrotreatment is necessary before utilizing the HTL biocrude as a maritime fuel.

The study found that by subjecting the biocrude to a single hydrotreatment stage (HDT-1, Fig 4) using readily available sulphided catalysts under specific conditions (360°C, 100 bar, 0.5 h⁻¹ weight hour space velocity, and 1000 H₂/oil volumetric ratio), it is feasible to produce partially upgraded oil with a substantially reduced oxygen content (2.19 wt.%), representing a 70% reduction. Additionally, there is a 90% decrease in sulphur content (from 2004 ppm to 201 ppm) and lower density (940 kg/m³) compared to the HTL biocrude. The improved product has a higher heating value (HHV) of 42 MJ/kg and a higher hydrogen-to-carbon (H/C) ratio of 1.56. In addition, this partially upgraded oil demonstrated excellent heat resistance and compatibility with Marine fuels. The partially enhanced biocrude possesses a flash point (42°C) that falls below the minimum threshold of the ISO 8217 standard stipulated. Therefore, fractionation is necessary to achieve a flash point greater than 60°C. This can be achieved by removing the light fraction, which has a boiling point below 190°C and accounts for 10 wt.% of the partially upgraded oil.

Another feasible option involved subjecting the HTL biocrude to additional hydrotreatment. This process separated the fraction with a boiling point below 350°C for diesel production while utilizing the fraction with a boiling point above 350°C for marine fuel. The process details are depicted in Figure 4. The portion with a boiling point of 350°C and above constitutes 41 wt.% of the hydrotreated product. This fraction meets the ISO 8217 specification for marine fuel, as outlined in Table 6. Furthermore, it is entirely compatible with standard marine fuel, as demonstrated by the blending test depicted in Figure 6, which included 10 and 50% HTL marine fuel. Table 6. Summary of HTL marine fuel characterization

Test		ISO 8217	Marine Fuel from digestate fibers
Water content [wt.%]		<0.5	BDL
Ash content [wt.%]		<0.1	0.008-(82.45ppm)
MCR [wt.%]		<20	7.64
TAN [mg KOH/g]		<2.5	<0.01
Density 15°C [kg/m ³]		<991	981
Kinematic viscosity @50°C [cSt]		<380	252
Sulfur [wt.%]		<0.1 wt. %	0.003-(29 ppm)
Flash point [°C]		>60	208.5
Calcium - Ca [ppm]		<30	<5.4
Phosphorus - P [ppm]		<15	4.2
Sodium - Na [ppm]		<100	<6.5
Vanadium - V [ppm]		<450	<2.0
Zinc - Zn [ppm]		<15	<1.5
Al+Silicon [ppm]		<60	10.6

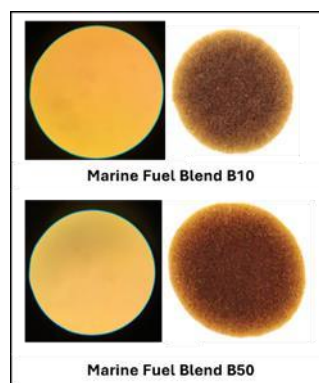


Figure 6. Marine fuel blends between 350C+ upgraded fraction with marine fuel. B10: containing 10wt.% of marine fuel and B50 containing 50% of marine fuel

Co-processing with petroleum crude oil

Investigating the possibility of co-processing HTL biocrude in existing refineries is worth considering. The preliminary blending test between HTL biocrude and crude oil showed limited compatibility. As a result, the

coprocessing tests focused on a blend containing 10 wt.% of partially upgraded HTL oil (B10), which was obtained during HDT-1. These tests aimed to evaluate the co-processing of the blend under industrial-relevant conditions for crude oil hydrotreatment. The test was conducted in three steps, beginning with a baseline investigation utilizing crude oil as the feedstock. The test was conducted for a duration of 182 hours under 380°C, 97 bar, 1 h⁻¹ weight hour space velocity, and a volumetric ratio of 800 H₂/oil. Subsequently, the feedstock was switched to blend B10 and subjected to treatment for a duration of 191 hours, with no alterations made to the reaction conditions. The third phase of the experiments involved repeating the baseline to assess the performance of the catalysts.

The results demonstrated the absence of any indication of pressure accumulation during the co-processing experiments. Nevertheless, a decline of 10% in catalyst activity was noted upon replicating the crude oil baseline. The inclusion of HTL oil in the co-processed feedstock decreased microcarbon residue reduction from 56% to 49% compared to the initial baseline. The decrease is anticipated due to the higher initial MCR content (2.7 wt.%) in the feedstock blend compared to the 2 wt.% in the crude oil. During the co-processing step, 76% of sulphur was successfully removed, with 73% of oxygen and 50% of nitrogen. Figure 7 depicts the details of the procedure. This outcome allows for the simultaneous processing of the hydrothermal liquefaction (HTL) biocrude derived from digestate fibres at industrial refineries.

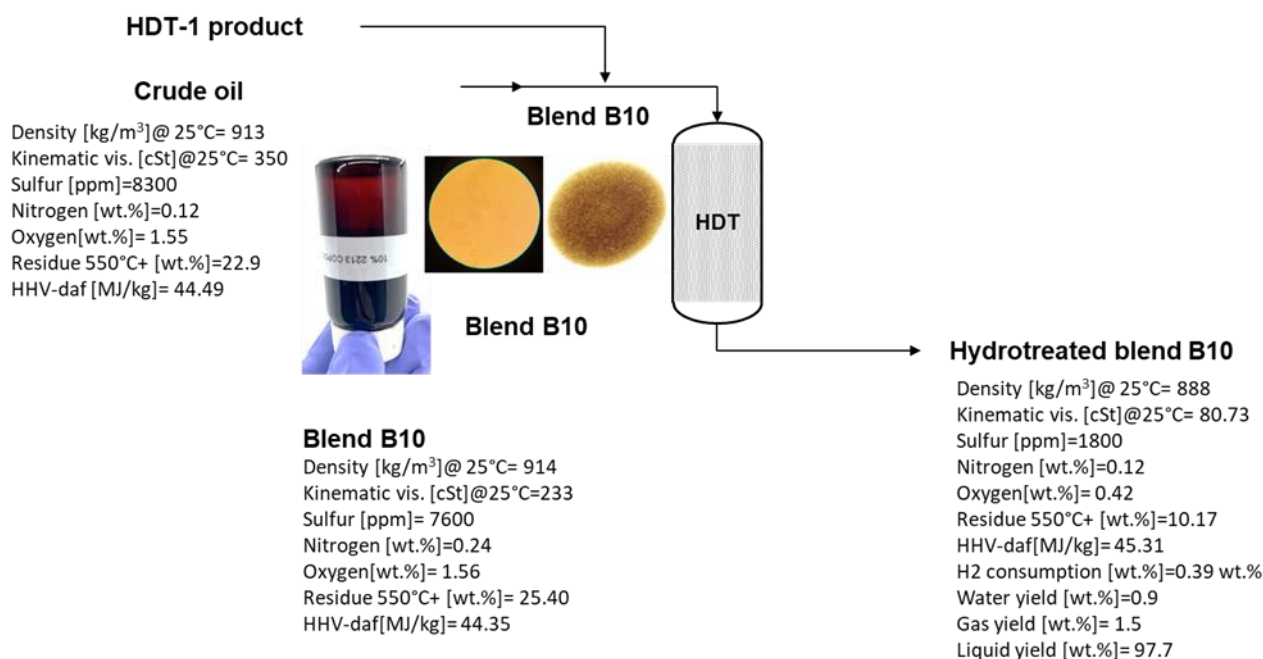


Figure 7. Summary of HTL biocrude co-processing with crude oil.

Digestate HTL solids utilization

Report on the chemical and physical characterization of the nutrient-rich byproducts

In this part, the detailed chemical and physical characterization of the nutrients-rich HTL-mineral products (biochar) was carried out. In this context, Steeper Energy produced various samples of HTL-mineral products under different parameters on a continuous bench-scale (CBS) unit (**Figure 8**). In Phase 1, AAU received two

bulk mineral products namely 2181 (HTL reactor solids) and 2179 (HTL filter solids) produced on CBS unit, which were first separated from aqueous phase using filtration bags, dried and analyzed by GC-MS and ICP techniques to measure the amount of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), nonyl phenol ethoxylates, di (2-ethyl hexyl phthalate), linear alkyl sulfonates, as well as heavy metals present to evaluate their potential to use directly as fertilizer. These mineral products were also treated with Methyl ethyl ketone (MEK) to remove organic and inorganic contaminants. The results were compared with the allowed limits of PAHs and heavy metals reported in Danish legislation (*Slambekendtgørelse*) (**Figure 9**). The total phosphorus and nitrogen content of 2179 and 2181 were also measured by ICP and elemental analyzer.

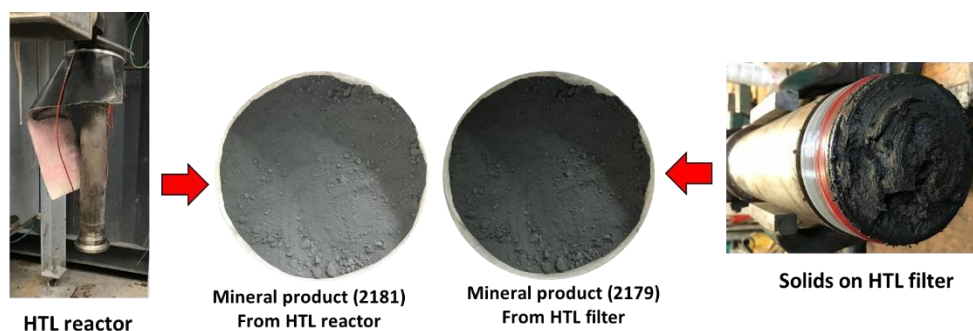


Figure 8. Pictures of HTL mineral products.

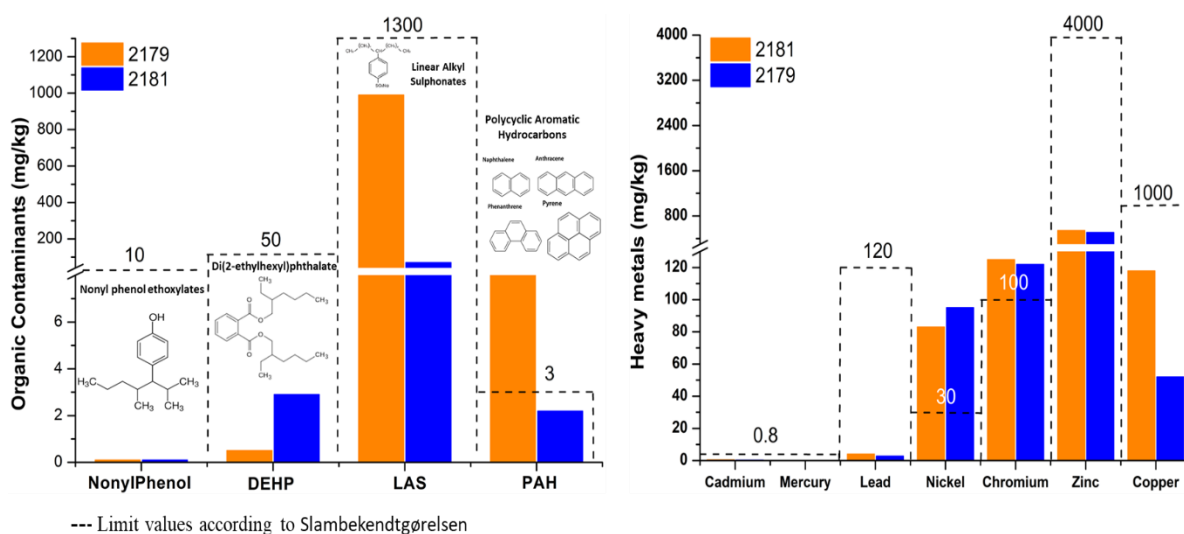


Figure 9. Organic contaminants and heavy metals content in 2181 and 2179 mineral products.

The total phosphorus content of 2181 and 2179 mineral products were measured to be 30.7 and 34.6 g/kg, respectively, whereas the nitrogen content in both the samples were around 1 wt.%. PAHs and heavy metals content in both mineral products (2181 and 2179) were found to be close to the allowed limits as reported in Slambekendtgørelse (**Figure 9**). The results show that reactor solids (2181) have all organic contaminants below the allowed limit and only Nickel and Chromium heavy metals slightly above the limit. However, PAHs in filter solids (2179) are above the allowed limit as shown in **Figure 9**. Like 2181, 2179 also contains Nickel and Chromium metals above the allowed limit according to Slambekendtgørelse. The results indicate that the mineral product obtained from the HTL filter, a primary source of HTL solids, requires treatment to remove

PAHs before it can be used as fertilizer. Additionally, avoidance and seed germination tests of 2179 and 2181 were conducted to determine the maximum permissible limits for both samples when used as fertilizer (**Figure 10**). *E. Fetida* (earthworm) species was used for the avoidance test (ISO protocol 17512-1), which is conducted at 20 °C ± 2 for approximately 48 hours with a circadian cycle of 12-16 hours of light and 8-12 hours of darkness. The concentrations of 2179 and 2181 samples used for the avoidance tests are 0% (control sample), 0.46%, 1%, 2.16%, 4.67% and 10% by weight of the soil. The results show that at 4.67% concentration of 2179, there was no *E. Fetida* remains in test soil. However, it is seen that at all concentrations (up to 10%) of 2181 at least one *E. Fetida* remains in test soil. The seed germination tests were conducted using *L. Sativa* species at 0.46%, 1.00%, 2.16%, 4.67%, 10.08% and 21.77% concentrations of both 2179 and 2181. For each concentration, three replicates are performed. EC50 values of 2179 and 2181 for *L. Sativa* were measured to be 4.75 and 21.37%, which indicate 2179 mineral product is more toxic than 2181 to seed germination for *L. Sativa* (**Figure 10**). Mineral product 2179 at all concentrations shows less germination than control experiment (only soil), however, 2181 shows positive seed growth at lower concentrations (up to 10.08%).

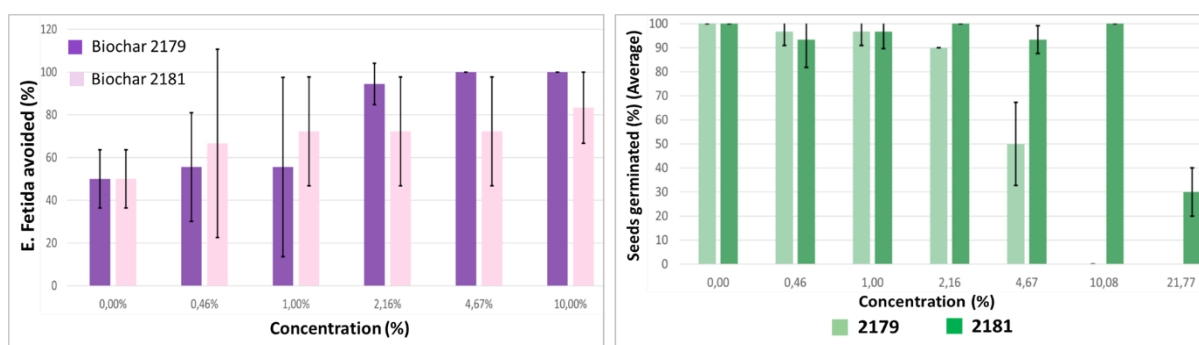


Figure 10. Effect of HTL mineral products 2181 and 2179 on avoidance and seed germination tests.

Both the solid mineral products (around 18 Kg in total) have been sent to SEGES, where the mineral products were converted into granules and used for field trials.

Parametric studies at Lab scale unit and treatment of HTL-mineral products at AAU

In this step, the effect of HTL process parameters such as temperature and catalyst on the quality of the solid mineral products produced on lab-scale unit (LSU) was determined. In this context, AAU produced four different mineral products at 380 °C without catalyst and at 360, 380 and 400 °C temperatures using K₂CO₃ as catalyst. However, the mineral products produced on LSU are suspended in the biocrude and aqueous phases, so aqueous phase was removed by centrifugation. After that, the mineral products were treated with MEK in 1:1 and 1:2 ratios followed by filtration to remove biocrude and other organic contaminants. MEK solvent was chosen for the treatment due to its common use in the HTL process for separating solids from biocrude. After that, all the mineral products were analyzed by GC-MS and ICP-OES to measure the organic contaminants and heavy metals content. As shown in Figure 11, all the organic contaminants except polycyclic aromatic hydrocarbons (PAHs) in HTL biochar are below the allowed limit as reported in Slambekendgørrelse. Among all the product samples, the mineral products generated at 380°C, under both catalytic and non-catalytic conditions, exhibited the lowest levels of PAHs. This suggests that 380°C is the optimal temperature for the HTL process to produce mineral products with the lowest levels of organic and inorganic contaminants whereas catalyst did not show significant effect on the quality of HTL solids.

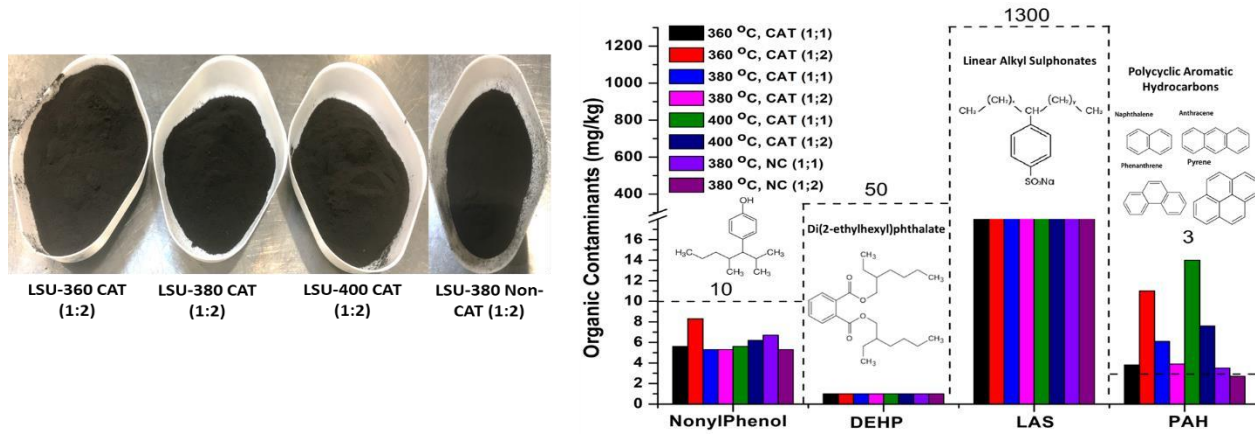


Figure 11. Effect of HTL process temperature and catalyst on the organic contaminants of mineral products.

Treatment of Continuous Bench Scale HTL-mineral products

AAU received six different mineral products, which were produced at 380 °C with different biocrude recirculation cycles (3-5 cycles) during HTL on CBS unit. These mineral products were collected from HTL filter. All these samples were first separated from aqueous phase by centrifugation and then dried at 60 °C. The total yield of all the solids was measured, which was found to be 10-11 wt.% (Figure 12). After that, the samples were treated with MEK in 1:1 to 1:2 ratios to remove organic and inorganic contaminants and analyzed by GCMS and ICP-OES techniques. The main purpose of this study is to determine the effect of recirculation cycles on mineral products' properties and quality. As shown in Figure 12, the organic contaminants in mineral products produced after 5th recirculation cycle were below the allowed limit. This indicates that biocrude recirculation cycles assist in transferring aromatic hydrocarbons (PAHs) from the solids to the biocrude phase, thereby improving the quality of the mineral products. Based on the allowable limits for organic and inorganic contaminants in the Slambekendtgørelse, HTL mineral products can be considered safe for direct use in agriculture. To test this observation, approximately 18 kg of mineral product has been sent to SEGES for field trials.

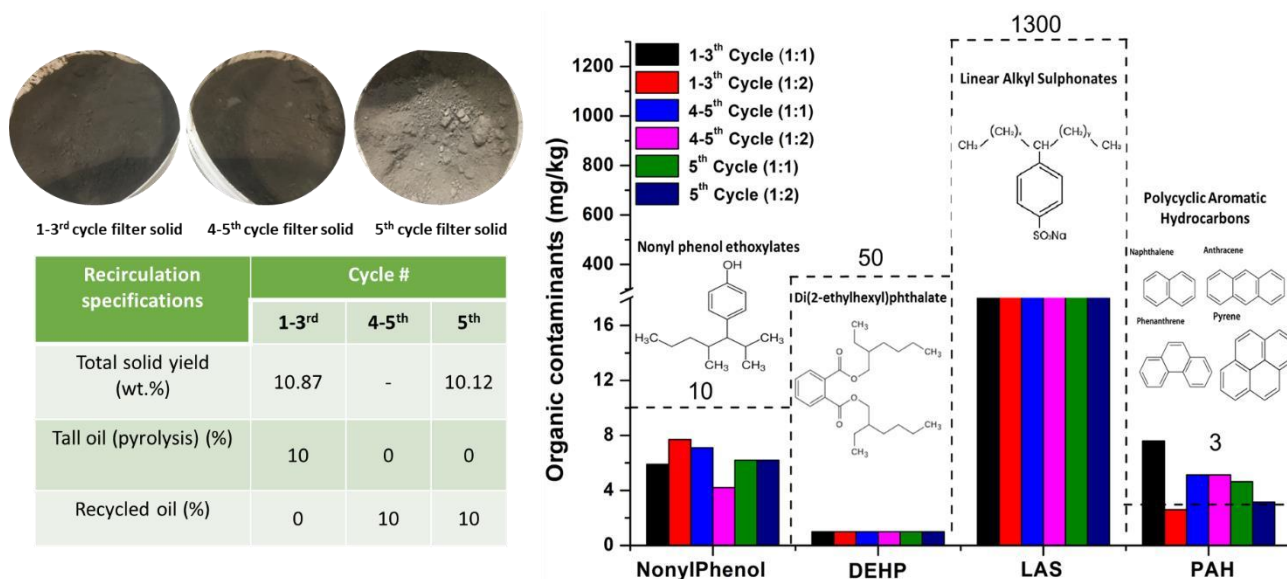


Figure 12. Total yield and organic contaminants analysis of treated mineral products.

Leaching of nutrients from the mineral product

As an alternative plan, the leaching of phosphate from mineral products was conducted to synthesize pure phosphorus containing commercial fertilizer e.g., Struvite and hydroxyapatite. In this regard, 2181 mineral product was chosen for phosphate leaching because 2181 has organic contaminants below the allowed limit. Dilute solutions (0.5-2 M) of different leaching agents like HCl, H₂SO₄, HNO₃ and NaOH were used for the extraction of phosphates from 2181 mineral product. Recovery of phosphate was measured using Hach-Lange kits (4500-P Phosphorus). All the leaching agents except NaOH showed promising results for the recovery of phosphate as shown in **Figure 13**. The highest phosphate recovery was found to be 89.86 % in case of HCl, however the phosphate recoveries with H₂SO₄, and HNO₃ were 89.15 and 88.72 %, respectively. The lowest recovery was observed with NaOH, which was found to be 22.69 %. The effect of reaction time on phosphate leaching was also studied by varying the duration from 1 to 2 hours. The recovery increased slightly with longer leaching times using HNO₃ and HCl, whereas it remained unchanged when using H₂SO₄.

Moreover, the bioavailability of phosphorus present in mineral products was checked using citric acid solution as the leaching agent. Citric acid is an organic acid and is generally non-toxic. The phosphorus leached with citric acid can be easily absorbed by the plants. Phosphorus in mineral products is bioavailable as 70 % phosphorus is soluble in citric acid.

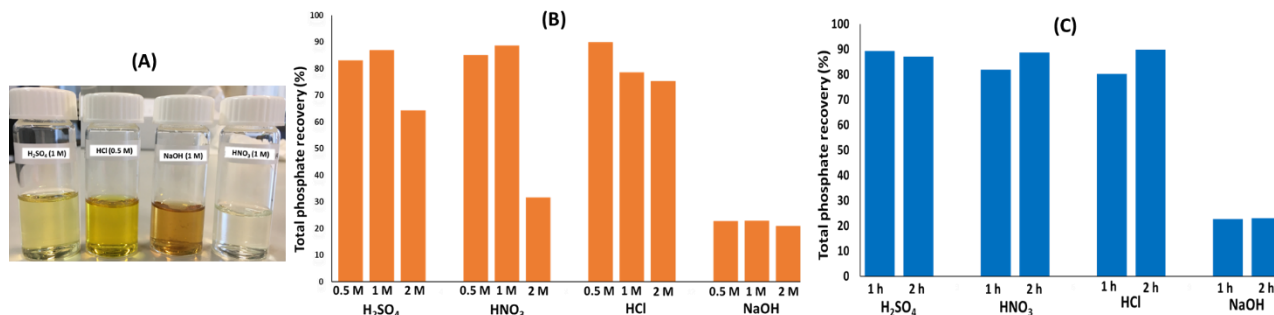


Figure 13. (A) Leached total phosphates from 2181 (B) phosphate recovery using different leaching agents at different concentrations and (C) at different recovery times.

In the next step, the extracted phosphate was converted into commercial fertilizers such as struvite and hydroxyapatite. To precipitate hydroxyapatite, the phosphate extract was mixed with calcium oxide (CaO) at pH 9. The resulting mixture was stirred for 2 hours and then filtered. For struvite production, the phosphate extract was mixed with magnesium chloride (MgCl₂) and HTL AP as a source of ammonia (NH₃). The pH of the mixture was maintained at 9 using NaOH for 2 hours with continuous stirring, after which the precipitates were filtered. Both synthesized fertilizers were analyzed using XRD spectra, which showed diffraction patterns corresponding to struvite and hydroxyapatite (Figure 14).

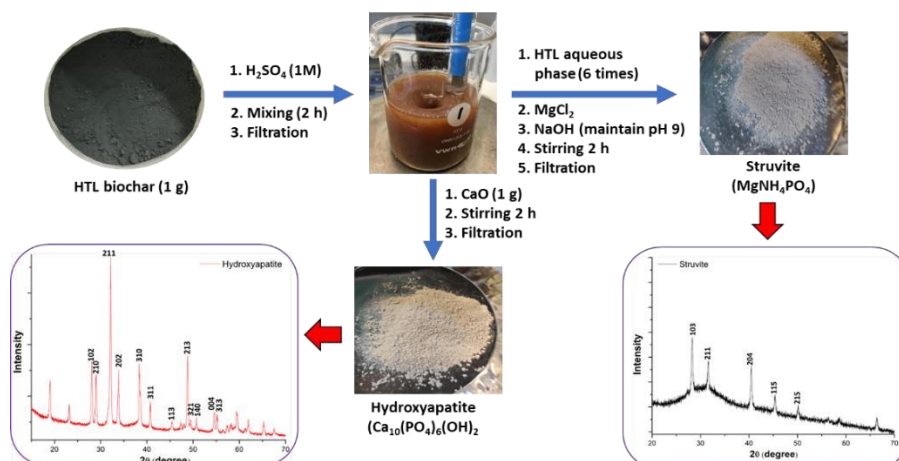


Figure 14. Precipitation of commercial fertilizers from 2181 mineral product and their XRD spectra.

Risk management of the use of carbon and field trials

The analysis of the use of carbon showed no impact on farmland from utilization of the digested fibers.

Two field trials were established in 2023. One trial was established in Northern Jutland (sandy soil) and one in Seeland (clay soil). Before spreading the mineral product was mixed with maize granular to endure even spreading in the trials. The spreading of the mixed material by hand caused no problems. Some visual effects of P-application were observed, but due to the extreme weather conditions (wet spring and dry and warm summer) phosphorus was not the limiting growth factor, and no effect on harvest yield was observed after applying phosphorus in neither mineral product nor mineral fertilizer. Details of this work were included in the Landsforsøgene 2023. Additional field trials in years with normal growth conditions are recommended.

Commercial results, Techno-economic assessment, Business case, Life cycle analysis

As determined by the experimental results and engineering evaluation, a biogas facility was identified as a potential location for a 400 bbl per day HTL plant. The agglomeration of digestate fibres from adjacent biogas plants is facilitated by the site's strategic location, which enables the collection of enough biomass to feed the HTL facility (>174 tons of dry-ash-free biomass per day).

It is necessary to integrate the current biogas infrastructure with the HTL facility in order to optimize resource utilization and reduce opex and capex costs. The integration strategies were composed of aligning feedstock supply chains, enhancing operational efficiency, and ensuring consistent biomass availability for biogas and HTL processes. Additionally, leveraging shared infrastructure like process gas and process water treatment reduces capital costs and improves overall process economics. Collaborative research and development efforts are also essential for enhancing conversion efficiencies and exploring synergies between biogas and HTL outputs, such as combined heat and power generation or biofuel production. Lastly, advocating for integrated biorefinery concepts through regulatory and policy frameworks can streamline permitting processes and incentivize investments in hybrid biogas-HTL projects, thereby advancing sustainable energy production and resource utilization.

Evaluation of the impact of capital and operating costs on future economics demonstrates that the business case is significantly impacted by the aggregation of biomass resources and the cost of an HTL facility as early indications suggest. In particular, the economic feasibility of the undertaking appears to be significantly impacted by the expenses associated with the collection and processing of wastewater from HTL. This highlights the necessity of effectively managing these costs through strategic planning and operational

optimizations to guarantee favourable financial outcomes for integrating biogas infrastructure with new Hydrothermal Liquefaction (HTL) facilities.

5.5. Dissemination activities

- A research article related to digestate Fibers utilization and fuel production is currently in progress.
- Oral presentation at the Biochar III Conference in Portugal, held from September 17-22, 2023.
- Poster presentation at 32nd EUBCE conference to be held on June 24-27, 2024.
- A research article based on the WP5 results is currently in progress as part of our dissemination activities.
- The field trials acted as a demonstration site as there was public access to the trial sites. The results of the field trials were reported in the publication *Landsforsøgene 2023*.
- In general several conferences, site visits with key stake holders, political meetings have been used to explain and disseminate the activities in the BiogasOil project. E.g. when Nature Energy and the University of Aalborg jointly had a visit from the member of the European Parliament Asger Christensen.

6. Utilisation of project results

The project's primary objective was achieved by completing a proof of concept for converting digestate fibres into fuels using Hydrofaction® technology. Additionally, the project aimed to mitigate the risks associated with critical process phases that involve the use of the HTL process for digestate fibres from biogas plants. These findings will be instrumental in Steeper Energy's future product development endeavours, particularly in optimizing the processing of digestate fibres. Furthermore, separating the mineral fraction from the output stream provides opportunities to investigate the fertilizer market and a wider range of feedstock alternatives in regions with feedstocks that have comparable high mineral content. These advancements are anticipated to be incorporated into utility operations through direct sales to biogas facilities or partnerships with established waste management technology providers.

This initiative's results were crucial in advancing research and development in hydrothermal liquefaction technologies for advanced biofuels performed at Aalborg University. These results open the opportunity to attract future projects and top-tier students, enhancing applied research and educational initiatives in the field.

How the commercial results will be utilised in the future

The initiative has illustrated that the effective conversion of digestate fibres from biogas plants through Hydrofaction® technology can generate a compelling value proposition. These fibres can be transformed into energy-dense biocrude suitable for producing marine fuel and diesel using conventional hydrotreatment strategies. Additionally, the recovery of minerals from the solid HTL stream presents market diversification opportunities for biogas and HTL technology providers. This initiative also provides an alternative fuel source that assists in the reduction of greenhouse gas emissions, thereby supporting the long-haul transportation sector. Furthermore, the initiative can potentially provide the agricultural sector with alternative sources of fertilizers.

Although the initiative has not directly increased turnover, it has already generated significant interest. A master's student from Aalborg University, who was part of the initial phases of the BioGasOil project, was recently recruited by Steeper Energy. This milestone establishes the foundation for an exciting future chapter—a follow-up project that could be focused on mitigating the risks associated with implementing the HTL technology for digestate fibers conversion at a demonstration scale.

The competitive situation in the market

The conversion of digested fibres through Hydrofaction® can be conducted either directly or in conjunction with organic waste from domestic and lignocellulosic-rich residues, resulting in a more energy- and resourceefficient solution with a reduced negative environmental impact.

Pyrolysis and gasification are technological solutions that have the potential to offer conversion options for the production of fuels and opportunities for the recovery of phosphorus in the form of biochar and residual ash. Nevertheless, both technologies result in inferior quality output products and lower carbon and energy efficiency due to the necessity for dry incoming feedstocks. This contrasts the digestate fibres' wet characteristics, which can be used without pre-treatment in Hydrofaction®, Steeper energy HTL proprietary technology.

AAUs part of the project

Efficient utilization of HTL byproducts is essential for maximizing the sustainability and economic viability of the HTL process. Aalborg university is active in hydrothermal research at global level. The project results will be used in the continued research & development of HTL technology for better separation of mineral products from the biocrude, as well as improving the properties and reducing the organic contaminants for its direct use as fertilizer. Future research and students' projects on the further utilization of HTL-derived mineral products for small pot/field trials will be attracted to explore its potential for more sustainable agricultural practices. Furthermore, the obtained results will promote ongoing advancements in applied research and engineering education in the energy sector and related fields, as well as maintain and enhance connections with leading industrial developments.

7. Project conclusion and perspective

Conclusions:

- The project has successfully achieved all of the technical objectives included in the application by:
 - Demonstrating that pumpable homogeneous slurries can be produced from digestate fibers;
 - Confirming Hydrofaction®, Steeper's proprietary technology, can convert digested fibres into biocrude without feedstock pre-drying;
 - Establishing design data for future demonstration engineered design of digestate fibres Hydrofaction® plants based on the experimental results.
 - Demonstrating and evaluating the recovery potential of phosphorous and other mineral nutrients from the solids produced during the Hydrofaction® process.
- Every 174 tons of dry-ash-free digestate fibres that are converted through the Hydrofaction® process could result in the production of 400 barrels of biocrude.
- The digestate fibers derived HTL biocrude can be upgraded through conventional hydrotreatment process into fuels that are in compliance with diesel and marine fuel standards.

Next Steps:

This project has generated a range of significant outcomes aimed at optimizing the conversion of digestate fibers into fuels, paving the way for advancements in applications, processes, and technologies. Integrating a biogas plant with a Hydrofaction® plant, a key component of this initiative, requires further technological development for commercialization. Moreover, the project's geographic focus and early technology

deployment will be guided by a thorough understanding of regulatory requirements, including new waste directives in Denmark, the European Union, and the United States.

Looking ahead, it would be interesting to deepen the understanding of the techno-economic analysis related to digestate fibers utilization initiatives, which could be next step in assessing specific business case scenarios for an initial demo project.