NEXTGEN roadfuels

NextGenRoadFuels
Turning waste into fuels

Sustainable Drop-In Transport fuels from Hydrothermal Liquefaction of Low Value Urban Feedstocks

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NextGenRoadFuels - Sustainable Drop-In Transport fuels from Hydrothermal Liquefaction of Low Value Urban Feedstocks

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Index

NextGenRoadFuels Introduction

HTL biorefinery: efficient circular use of urban waste streams for fuels, feed and fertilizer

NextGenRoadFuels (NGRF) is a four year Horizon 2020 project that started in November 2018 with the objective to prove the Hydrothermal Liquefaction pathway (HTL) as an efficient route to produce high-volume, cost-competitive, drop-in synthetic gasoline and diesel fuels, as well as other hydrocarbon compounds.
HTL processing, combined with appropriate pre- and post-treatment is the single most effective technology pathway to valorize the combination of sewage sludge, food waste and construction wood waste and to convert the carbon content of these feedstock into drop-in fuels. The process developed by NGRF is characterized by extreme resource flexibility and efficiency.

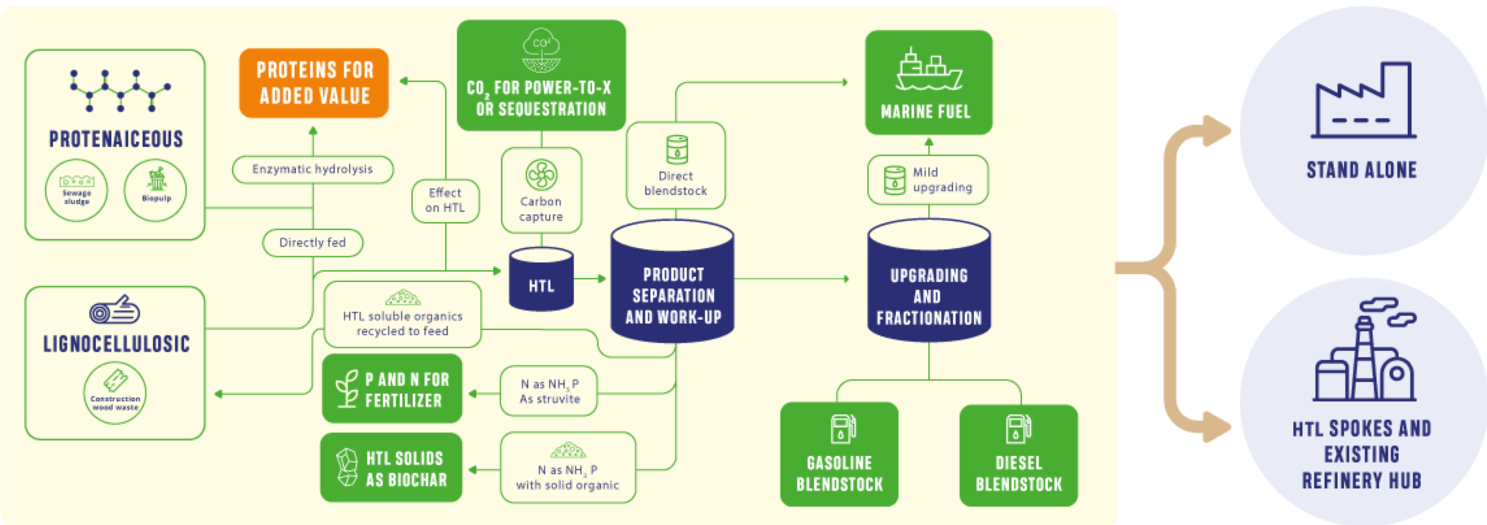


Figure 1.1: HTL Biorefinery process.

During the project the research has been driven forward with these focuses at the forefront:

1. New strategies for collecting and pre-treating urban residues, building on existing logistics infrastructure while providing a higher added value through HTL processing
2. An integrated approach along the entire value chain (at lab- and pilot-scale), to allow in-depth understanding and optimization of process parameters in a holistic approach
3. Different combinations of pre-treatment, HTL processing, upgrading and integration
4. Process simulations and associated techno-economic assessments to define future industrial-scale implementation for an increased biofuels production capacity
5. Environmental and sustainability impacts of the process
6. Efficient business strategies for the successful implementation and replication of developed value chains at European/global level
7. Full risk management strategy by considering all aspects (technology, economic, business, etc.) to ensure future implementation
8. Promotion of knowledge-sharing on HTL pathway and renewable fuels production amongst stakeholders, media and citizens.

Figure 1.2: NGRF Project partners.

The project consortium consists of an international team of eleven partners from seven countries, coordinated by Aalborg University, Denmark.

This final project publication summaries and presents the key findings from each aspect of the research:

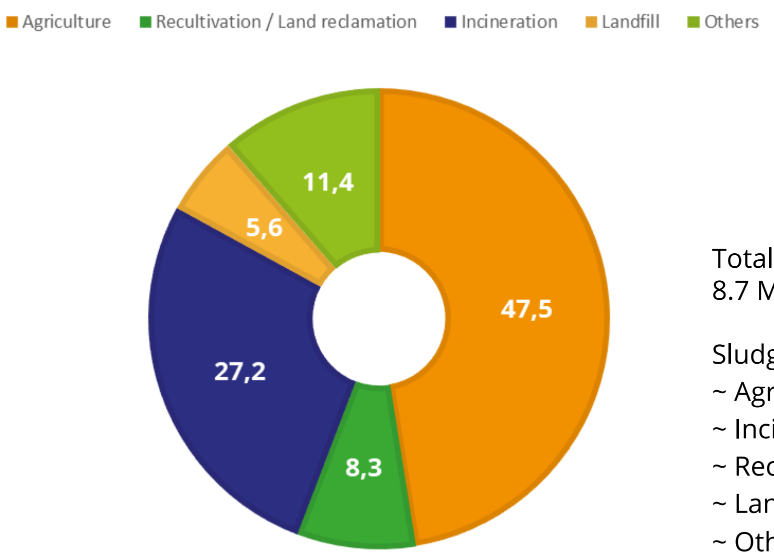
- Improving the HTL value chain from the start
- HTL as core technology for urban waste valorisation
- Turning challenging waste-derived biocrude into fuels
- The market situation for HTL
- Environmental assessment, sustainability and economics
- The future for HTL

Figure 1.3: NextGenRoadFuels KICK-Off Meeting - Aalborg University

2 . Improving the HTL value chain from the start

Sewage sludge (SS), as an end product of wastewater treatment processes, reflects the composition of the raw wastewater and therefore, the anthropogenic pollution collected in the treatment plant. This variability, which can be partially due to the anthropomorphic behaviour and the location, has an effect on the required treatment.

Data from 2017, shows that 8.7 Mt of dried SS per year is produced in Europe (EU-27 plus UK), meaning that **every one of us generates around 20-25kg of dry solids annually!!**



Total European production sludge:
8.7 Milion tonnes DS/y.

Sludge destinations:
~ Agriculture: 4.1 Mt DS/y
~ Incineration: 2.4 Mt DS/y
~ Recultivation / Land reclamation: 0.7 Mt DS/y
~ Landfill: 0.5 Mt DS/y
~ Other destinations: 1 Mt DS/y

Figure 2.1: Sludge destination in percentages according to the 2021 EurEau Survey 'Europe's Water in Figures'.

1. https://www.eureau.org/resources/briefing-notes/5629-briefing-note-on-sludge-management/file

But....Where does it go? According to EurEau[1]:
Depending on the type of municipal Wastewater Treatment Plant (WWTP) and process installation, SS is generated during the primary (physical and/or chemical), the secondary (biological) and tertiary (additional to secondary, often nutrient removal) treatment stages.
SS is a valuable fraction that can be used as a **resource for energy, nitrogen, phosphorus** and other nutrients that can be recovered and reused for valuable products pursuing the aim of a **circular economy.**

As **SS is a wet waste** product with a relatively high content of organic matter, including carbohydrates, lipids, proteins, etc., it is a **feasible feedstock** to undergo **hydrothermal liquefaction (HTL)** to produce **a renewable fuel[2] or biocrude.**

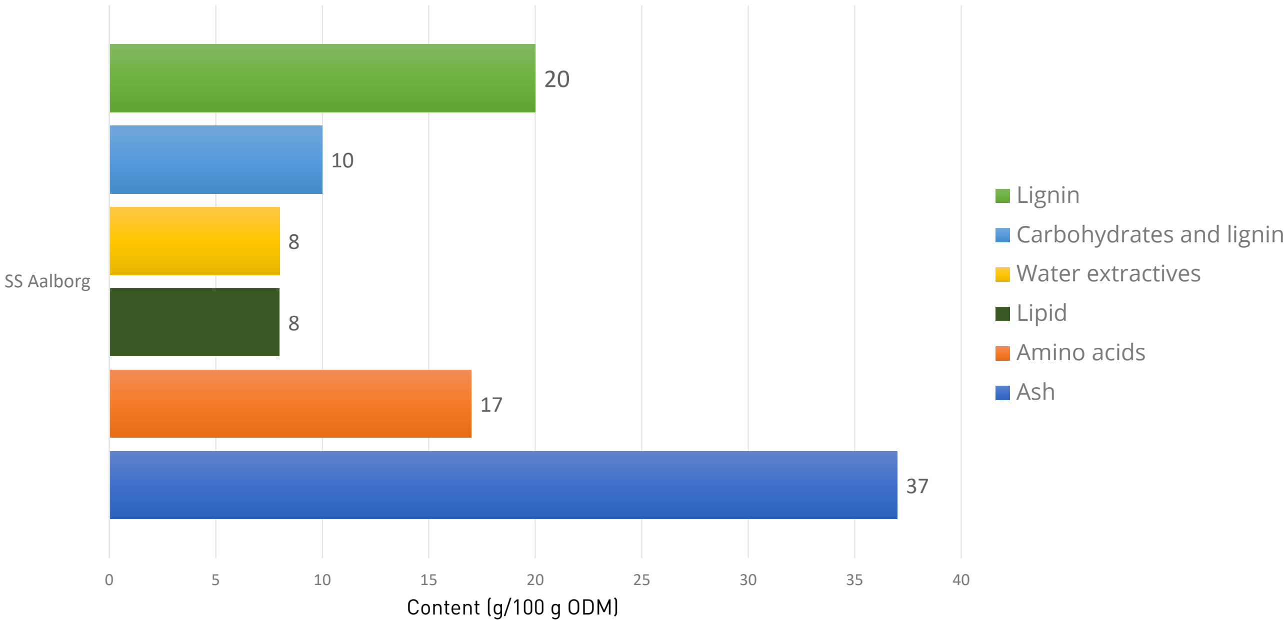


Figure 2.2: Distribution (% dry matter content by weight) of the main components of sludge.

2. A. Dimitriadis, S. Bezergianni, Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review, Renew. Sustain. Energy Rev. 68 (2017) 113–125. doi:10.1016/j.rser.2016.09.120.

Usually, traces of inorganics can be found in the biocrude[3] produced from SS, in concentrations that are often too high for the conventional catalytic upgrading process, which can result in catalyst harm. Furthermore, this biocrude presents a high nitrogen content, usually protein based, which therefore makes it largely differ from fossil crude oil[4].

The presence of these two components negatively affects the quality of the biocrude, and hinder its final upgrading. **Therefore, the aim of SS pretreatment is to remove unpleasant inorganic constituents and lower the nitrogen content in SS before entering the hydrothermal liquefaction (HTL) process.**

Sludge and its valuable organic nitrogen

The nitrogen content in SS can be classified into three different categories:

- inorganic nitrogen, mainly present as ammonia, nitrates and nitrites
- proteinaceous nitrogen, present as proteins
- non-proteinaceous nitrogen compounds, that contain nitrogen but are neither ammonia /nitrates & nitrites nor amino acids from proteins. Present as what is called prostatic components such as alkaloids, amines, phospholipids, nucleic acids and nitrogenous glycosides, peptidoglycans, etc.

The nitrogen distribution for a sample of SS from Aalborg WWTP is shown in Figure 2.3:

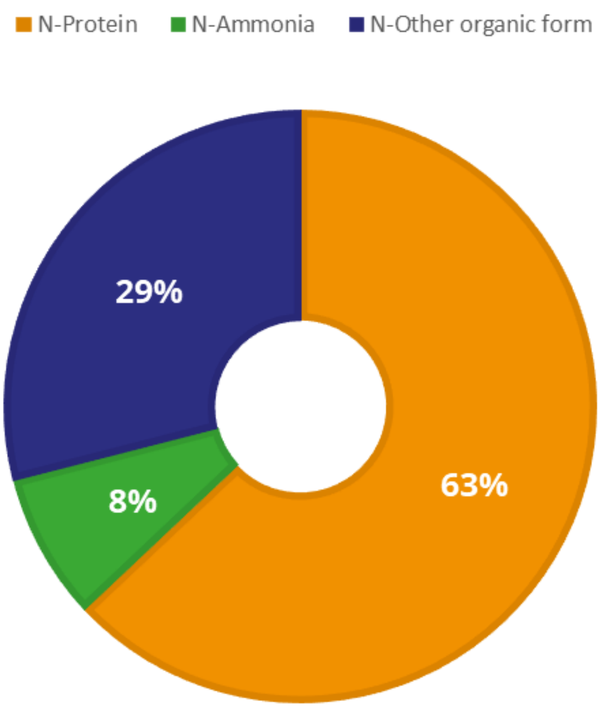


Figure 2.3: Distribution (% by weight) of the total Nitrogen content of SS from Aalborg WWTP. N-Protein: nitrogen contained as amino acids; N-Ammonia: nitrogen contained as ammonia; N-other organic form: other compounds that contain nitrogen but are neither ammonia / nitrates &nitrites nor amino acids from proteins.

3. F. Conti, S.S. Toor, T.H. Pedersen, T.H. Seehar, A.H. Nielsen, L.A. Rosendahl, Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients, Energy Convers. Manag. 216 (2020) 112925. doi:10.1016/j.enconman.2020.112925.
4. L. Leng, W. Zhang, H. Peng, H. Li, S. Jiang, H. Huang, Nitrogen in bio-oil produced from hydrothermal liquefaction of biomass: A review, Chem. Eng. J. 401 (2020) 126030. doi:10.1016/j.cej.2020.126030.

How to lower the nitrogen content in the sludge?

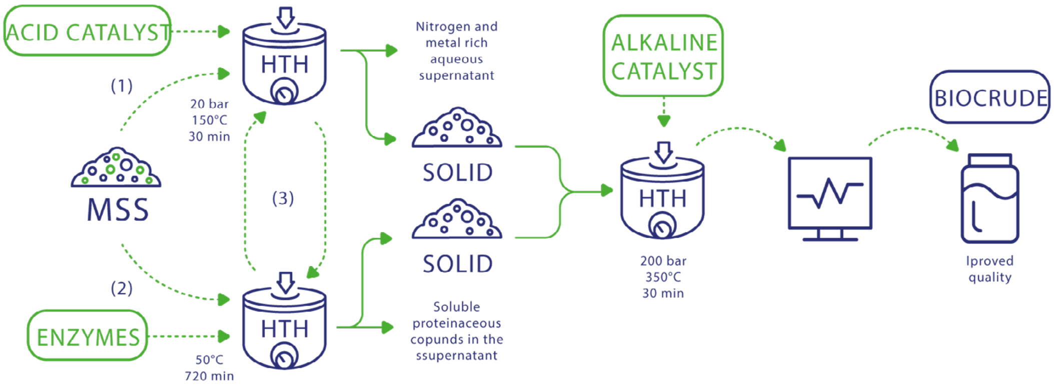


Figure 2.4: Flowchart of the strategies followed for N removal from sludge.

Due to the inconvenience of high nitrogen content in biocrude upgrading, different approaches for its removal before the HTL process were tested.
These approaches are considered either to include an acid pretreatment, an enzymatic pretreatment and/or the combination of both.

The chemical pre-treatment consisted in a hydrothermal treatment under mild acidic conditions of the sludge, as shown in Figure 2.4 (pathway (1)). The chemical treatment enhances the solubilization of more than 70% of the initial nitrogen fraction, and it also triggers the solubilisation of inorganics, such as calcium, iron, magnesium and phosphorus, reducing the ash content and thus improving the quality of the HTL feedstock.

The enzymatic pretreatment (Figure 2.4 (pathway 2)), is carried out under mild conditions in order to boost the solubilisation of protein content in SS. Enzymatic hydrolysis is considered a green chemistry process, as enzymes can be obtained from renewable sources, and are capable of catalyzing various chemical reactions, being an alternative to conventional chemical catalysts.

Even more, enzymes require moderate reaction conditions, they are biodegradable, highly selective, and generate low amounts of by-products. Under the tested conditions, enzymes are capable of solubilizing more than 60% of the proteinaceous fraction, removing more than 70% of the initial Nitrogen content. Although, this treatment requires longer residence time when compared to chemical pretreatment, it enables the released proteinaceous to be further upgraded.

In order to check all the possibilities, the combination of chemical and biochemical pretreatments were tested (Figure 2.4 (3). According to our results, the best option is to perform first the enzymatic hydrolysis, followed by the chemical treatment. This combination showed the best performance in terms of nitrogen and inorganics removal from SS.

How do these pretreatments impact on the HTL process and biocrude quality?

One of the most interesting results comes out when analysing the impact that nitrogen content reduction in SS shows on HTL biocrude yield and quality. Indeed, biocrude yield increases more than 22% on average, but also its composition is improved, as less problematic nitrogen derived compounds (such as N-heterocyclic and N-aromatics) are present. As previously stated, these compounds hinder the final biocrude upgrading regarding NOx related regulations fulfilment. Moreover, biocrude quality is also improved by aliphatic compounds (such as fatty acids) increase. On the other side, due to organic matter and organic carbon losses during the pre-treatment, the overall biocrude yield is reduced.

How can the proteinaceous fraction be upgraded?

Once the proteins are in a soluble form, they can be used as an alternative to fossil fuel derived fertilizers in order to improve the growth and nutrient content of the plants, especially when subjected to stress conditions.

The results obtained when testing the SS derived biostimulant with lettuce revealed that:

- The generated biomass is similar to the one using commercial biostimulants.
- When plants were subjected to a salinity stress, the amount of nutritional elements (**K, S, Fe, Cu, P, Zn, Ca, Mn, and Mg**) was significantly higher. Also, the bioavailability of cations in soil (**Zn, K** and **Ca**) for the plant was improved.
- Finally, the use of this product did mobilise in all cases (under saline stress or without stress conditions) more **phosphorus** in the soil.

The removal of nitrogen and inorganic components is accompanied by a solubilisation of organic matter and thus a loss of carbon. This must be taken into account and carefully evaluated techno-economically from the perspective of effective valorisation of wet side streams, such as the production of organic biostimulants or inorganic fertilisers.

Figure 2.5: Green agricultural field.
Credits: Shutterstock-CRS PHOTO.

Key points

Sludge and its valuable organic nitrogen: Sewage sludge contains valuable fractions such as nitrogen (3-5% by weight). This nitrogen is mainly in an organic form, of which 55-73% accounts for proteins.

Lowering the nitrogen content in the sludge: the removal of nitrogen prior to HTL treatment not only improves the yield of the biocrude, but also improves the quality. The formation of nitrogen species is suppressed, and may be resistant against subsequent upgrading strategies.

The impact of pretreatments on the HTL process and biocrude quality: nitrogen removal strategy prior to HTL pretreatment enhances the biocrude yields by 22% on average, but also its chemical composition is changed, improving the downstream upgrading process.

Upgrading the proteinaceous fraction: the soluble protein fraction contains nitrogen which can be used by plants as fertiliser, but actually due to its organic form (free amino acids, peptides) can have an additional effect as a biostimulant for plants.

3. HTL as core technology for urban waste valorisation

Hydrothermal liquefaction (HTL) has proven to be an energy efficient and resource agnostic technology for production of renewable refinery feedstock, Biocrude, which can be turned into future transportation fuels. **Processing urban waste biomass in HTL**, especially those having high nitrogen and inorganic contents, is still subject to several technological challenges and fundamental knowledge gaps. Through the NGRF project we have innovated and demonstrated new technology advancements, which will push HTL further towards commercialization that will bring about **a radical new way to valorise urban waste.**

Understanding the fate of nitrogen in HTL chemistry

Organic waste biomass usually consists of a mixture of lipid, lignocellulose and proteins. Proteins are of particular concern as these biopolymers are the primary source for problematic nitrogen (N) structures, generated during the process and often accumulating in the biocrude product. The generated N-compound needs to be removed by a downstream upgrading to prevent issues like NOx emissions during combustions or catalysts poisoning in refining. Certain N-species, related to an aromatic structure, are highly resistant to the common upgrading process and their extensive formation needs to be suppressed.

A first attempt is described in WP1, where sewage sludge samples were pre-treated with different techniques (enzymatic or/and mild hydrothermal hydrolysis) to remove organic N, eventually lowering the transfer into the biocrude product. The study showed two main results:

1. Pre-treatment led to an increased lipid content in the intermediate solid.
2. Biocrude produced after a pre-treatment showed significantly lower N-content and a drastically reduced content of N-heteroaromatic compounds.

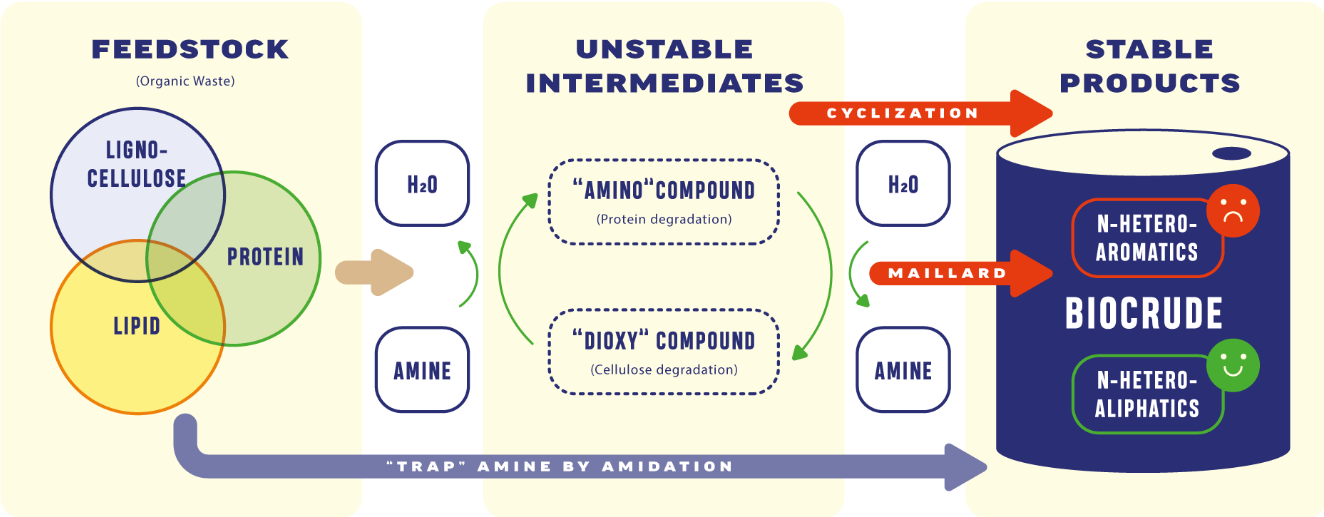


Figure 3.1: Lipid, Lignocellulose and Protein interaction and the formation of N-compounds.

A detailed view of the bio-polymers in organic waste feedstocks and their reaction products at HTL conditions identifies proteins as a primary N-source due to cyclization degradation products.
Another transfer of N into non-polar heteroaromatics and larger oligomers is often referred to as Maillard reactions with protein and sugar degradation products. If lipids are present in the biomass, their free fatty acid hydrolyzation products are likely to react with free amines from proteins to fatty acid amides which are long-chain aliphatic and less problematic in catalytic hydrotreatment.

As shown in Figure 3.1, it can be noted that the **Maillard and Amidation are two competing reaction mechanisms**, which would explain the low generation of N-heteroaromatics in the pre-treated sewage sludge biocrude.

To prove this assumption and evaluate the potential of co-liquefaction of different biowastes, a model system using a Lard oil, Bovine Albumin Serum and Cellulose is applied. Subsequently, the results are validated with real sewage sludge samples from different origins and with different compositions.

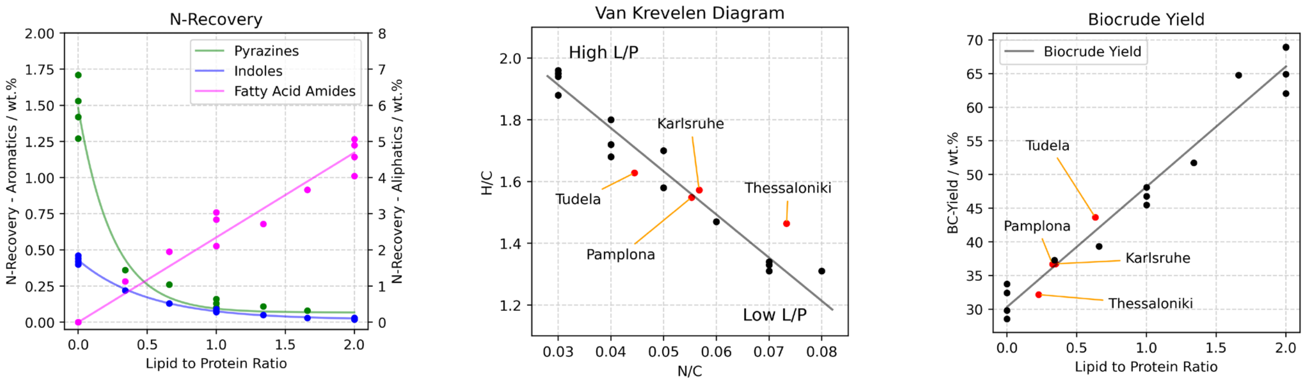


Figure 3.2: N-Recovery into Heterocompounds, Biocrude Yields and Van Krevelen Diagram.

The results are displayed in Figure 3.2. The N-recovery into heterocompounds like Pyrazines, Indoles and Fatty Acid Amides as well as the biocrude yield is given over the Lipid to Protein Ratio (L/P) in the HTL-feedstock, indicating a strong influence of Lipids on these result.

The heteroaromatics formation and therefore the **recovery of nitrogen in these species is decreasing exponentially, while the fatty acid amides and biocrude yield is increasing linearly.**

Similar observations are made for real sewage sludge samples from different European origins and changing biochemical composition. As quantification of similar N-heterocompounds with subsequent comparison would turn out to be complicated in these real biocrude samples, thus the results are displayed in a Van-Krevelen Diagram.

A high H/C and low N/C ratio indicate low aromaticity and the presence of plenty of aliphatic compounds, while a low H/C and high N/C are decisive for the presence of many N-heteroaromatics.

The real biocrude samples show a similar trend to the model samples.

HTL a terminal for problematic microplastic

The potential microplastic (MPs) degradation of the HTL process was investigated, highlighting the potential use of HTL by-products for fertilisation and soil improvement. The HTL process significantly reduced the mass of MPs by over 97 wt. % and the particle number by 76 wt. %. The mass distribution of the MPs is shown in a process block diagram in Figure 3.3. The solid residue contained the largest share of residual MPs accounting for 1.2 wt. % of input MPs and 52 wt. % of MPs in the HTL products. The most resilient residual polymers were detected to be polyolefins (PE and PP) and PU. The distillate phase held a negligible mass of MPs revealing a lower environmental risk and/or operation cost in different WWT scenarios.

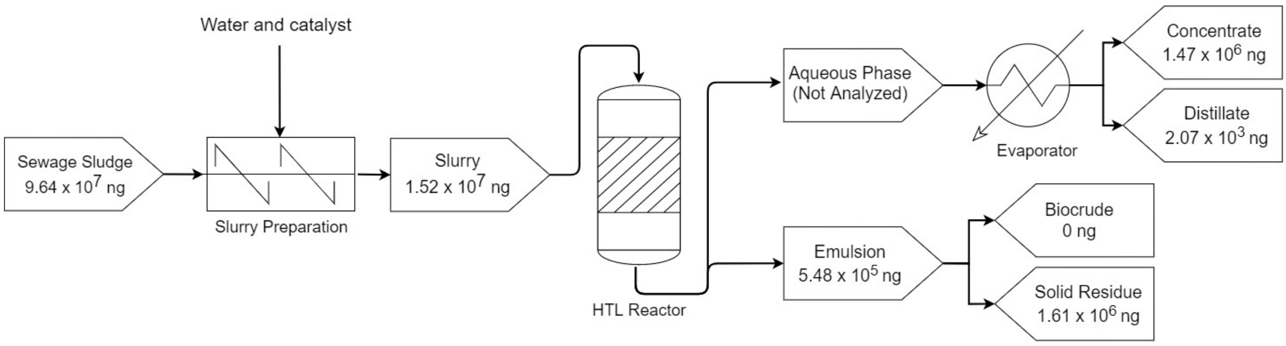


Figure 3.3: Mass distribution of MPs in sewage sludge throughout the input and outputs of the HTL process.

Significant achievements and challenges identified from continuous processing in pilot HTL unit

During the course of the project, substantial amounts of technically challenging urban waste were processed in the continuous HTL unit at Aalborg University. Figure 3.4 shows the accumulated tonnage and the disruptive effect by the global pandemic on the project activities.

Through continuous processing, we managed to obtain equally high biocrude yields similar to what was obtained by the controlled lab scale batch processing. With biocrude yields over 40 weight percent from sewage sludge and biocrude yields approaching 50 weight percent from biopulp, energy recoveries reached 80-85 %, 85 % energy recovery being one of the main KPIs of the project.

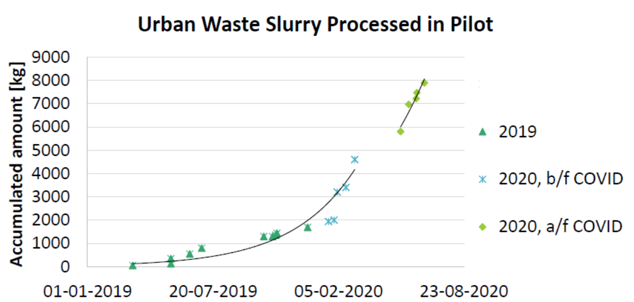


Figure 3.4: Accumulated urban waste processed in HTl pilot unit at Aalborg University. Before (b/f) and after (a/f) the COVID pandemic.

The presence of the high inorganic matter in the biofeedstock was identified as a risk factor and turned out to be a critical challenge for continuous processing. Firstly, emulsification of the process effluent products, especially biocrude and inorganic minerals, called for a whole rethinking of product separation techniques to obtain high yields of biocrude of upgradable quality, simultaneously. Being able to obtain upgradable quality biocrude is particularly essential for the entire business case. Although significant progress was made in the project and several separation techniques were tested, biocrude yield penalties were unavoidable, particularly for sewage sludge processing, when upgradable quality of the biocrude was a hard constraint in the product separation feasibility assessment. Not to stall downstream activities such as the hydroprocessing activities, we locked the separation procedure with settings, which enabled upgradable quality but with biocrude yields of about 35 % due to separation losses. At these settings, we also obtained a mineral product with a concentrated phosphorous content,

compliant or nearly compliant for the use as a fertilizer depending on the final use. The HTL aqueous could furthermore be purified to dischargeable quality. With more research and optimization we are certain that separation losses can be nearly eliminated. Secondly, the high inorganic content in the feedstock accelerated fouling and ultimately blocking in the heater section of the continuous system, which limited the on-stream time. Even though other investigators have reported continuous processing of sludge, no reports of this phenomenon has yet been published. This fouling phenomenon yet presents an unsolved challenge, which must be solved before a commercial case can be presented.
Major steps were taking to understand the fouling problem, however, remedying measures were only conceptualized but not tested in the project due to time constraints.

Innovative aqueous phase management for improved process efficiency

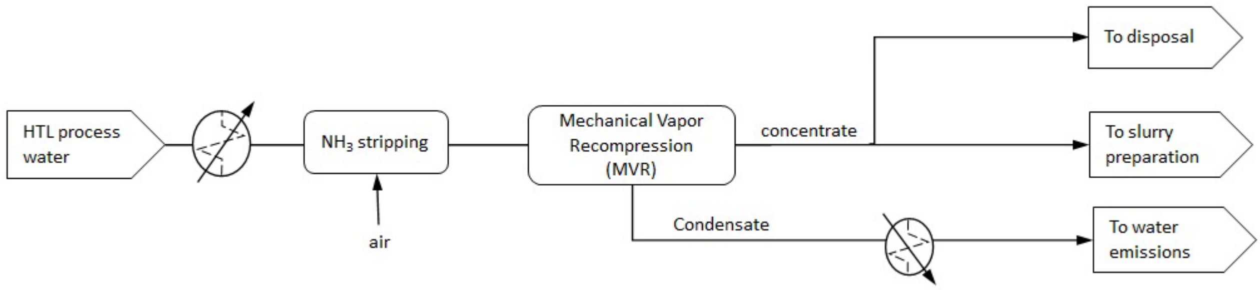


Figure 3.5: Process block diagram for the treatment of HTL water by evaporation with recycling of the concentrate for slurry preparation and condensation of evaporated water.

The evaporation of surplus water of the residual aqueous phase to form a concentrated organic fraction before recycling to the slurry preparation unit was considered as a baseline strategy in HTL process water treatment.
The process option is schematically shown in Figure 3.5.

Lab-scale experiments carried out at sub-critical HTL conditions (350 °C) were hypothesised as the proof-of-concept. Biopulp was used as the representative urban feedstock. The baseline experiment (without the addition of concentrate) yielded approximately 34 wt. % of bio-crude.

The obtained aqueous phase was evaporated until it contained the same dry matter of the biomass. The prepared slurry was loaded into the reactor, and the process was repeated for three cycles. The subsequent HTL reaction yielded 44 wt. % of the bio-crude, around 10 percent points higher than the baseline experiment. Moreover, **the energy recovery in the biocrude was significantly increased to 71%.** The concentrated aqueous phase recycling effectively increased the carbon distribution from 51.6% in the baseline bio-crude to 55.8% in the subsequent counterpart.

Further investigation of the capability of membrane technologies for HTL wastewater treatment. The treatment was done in two steps as shown in Figure 3.6:

1) **Ultrafiltration (UF)** (using (a) submerged membrane + stripping and (b) crossflow modes),
2) **Membrane distillation (MD)** (using air gap configuration).

After the treatment the main products were UF concentrate, MD concentrate and MD condensate, which represent 20%, 32% and 48% of the HTL waste water volume, respectively. Particles and oily emulsions from HTL wastewater were concentrated in the UF concentrate, while organics and salts were mainly concentrated in the MD concentrate. MD concentrate contained the major amount of the catalysts. More than 75 % of ammonium is concentrated in the MD condensate (after cross-flow UF) or in an acid trap (after submerged UF), with both solutions containing low organic impurities (e.g. phenols).

In the study of submerged UF, a hybrid system for the removal of particles and oil emulsions in addition to stripping and recovery of ammonia was introduced. To assure a long-term stable performance of the membrane, periodical backwash, relaxation cycles and sufficient air sparging rate were beneficial. Air sparging was as well efficient in rapid stripping of ammonia. The majority of stripped ammonia was recovered in an acid trap solution.

In the study of cross-flow UF, focus was given to specifying the optimal UF membrane pore size. Presence of surfactants allowed the formation of small size emulsified oil droplets (micelles) in the range of 100 nm to 10 nm, which led to rapid fouling of UF with membrane pore size > 10 nm. In addition, due to the high affinity of some surfactants to the membrane material, narrowing of the membrane pores occurred by adsorbing of surfactants on their inner walls, which played a major role in pore blockage of UF with pore size < 10 nm. As a result, 10 nm was the most adequate membrane pore size for filtration of the present HTL-WW.

Based on the findings from both UF studies, the third study demonstrates the impact of the main treatment step of membrane distillation after UF pre-treatment of HTL-WW. Here, in order to allow the recovery of ammonia in the condensate, air gap configuration was used. MD performance was stable in long term operations up to 36 days and under a wide range of feed temperatures from 30 °C up to 60 °C. With the increase of feed temperature, the filtration flux and the ammonia concentration in the condensate increased. However, higher TOC contamination in the condensate was induced by high feed temperatures. For creating a balance between both aspects, the feed temperature of 60°C was chosen. In addition, the highest possible condensate recovery was 80 %, at which non-desired wetting was unavoidable. Wetting was accelerated by the surfactant adsorption on the membrane surface. Thus, the **optimal condensate recovery is at 60%.**

In comparison with HTL-WW, the MD condensate produced has a much lower toxicity (< 99%), which was measured by applying luminous bacteria test according to DIN EN ISO 11348-2.

The presented studies show **that coupling of ultrafiltration and membrane distillation can be a successful method for HTL-WW treatment.**

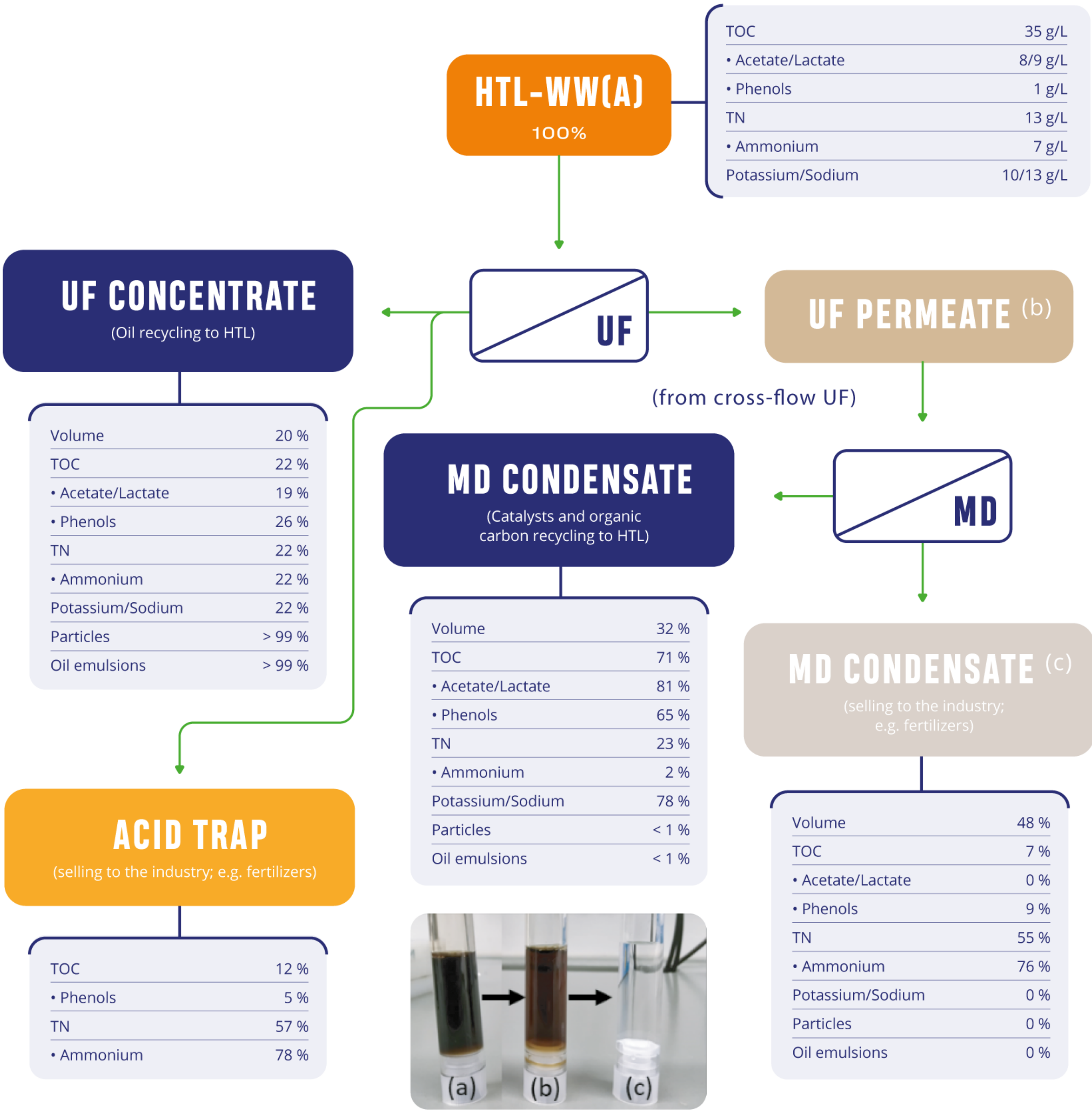


Figure 3.6: Potential process scheme of HTL-WW treatment (100 % input into UF)

Key points

Nitrogen reaction chemistry: Nitrogen occurs primarily in an organic form in proteinaceous feedstocks and reacts partly in the biocrude phase. It is crucial to know which form of nitrogen compound is formed during the process.

Suppressing the formation of N-heteroaromatics: Nitrogen bound in an aromatic ring is difficult to remove by conventional hydrotreating, therefore the formation during the HTL process should be suppressed.

Fatty Acid Amides: Fatty acid amides are reaction products from fatty acids and amines are long-chain aliphatic compounds much more suitable for hydrotreating.

Karlsruhe Institute of Technology (KIT). Credit: ETA-Florence Renewable Energies.

4. Turning challenging waste-derived biocrude into fuels

The conversion of sewage sludge with hydrothermal liquefaction (HTL) untaps a vast renewable resource for the production of green fuels. The HTL biocrude requires further upgrading to remove or recover minerals, oxygen, nitrogen, and sulphur, to produce fully finished in-spec fuels.
The Horizon2020 NGRF project, has developed a novel modular upgrading concept that allows combination of electrocatalytic and thermal catalytic upgrading of HTL oil, offering flexibility on adapting and scaling the overall process scheme and permitting an autarkic operation providing all hydrogen needed in isolated sites. The overall upgrading concept is shown in Figure 4.1.

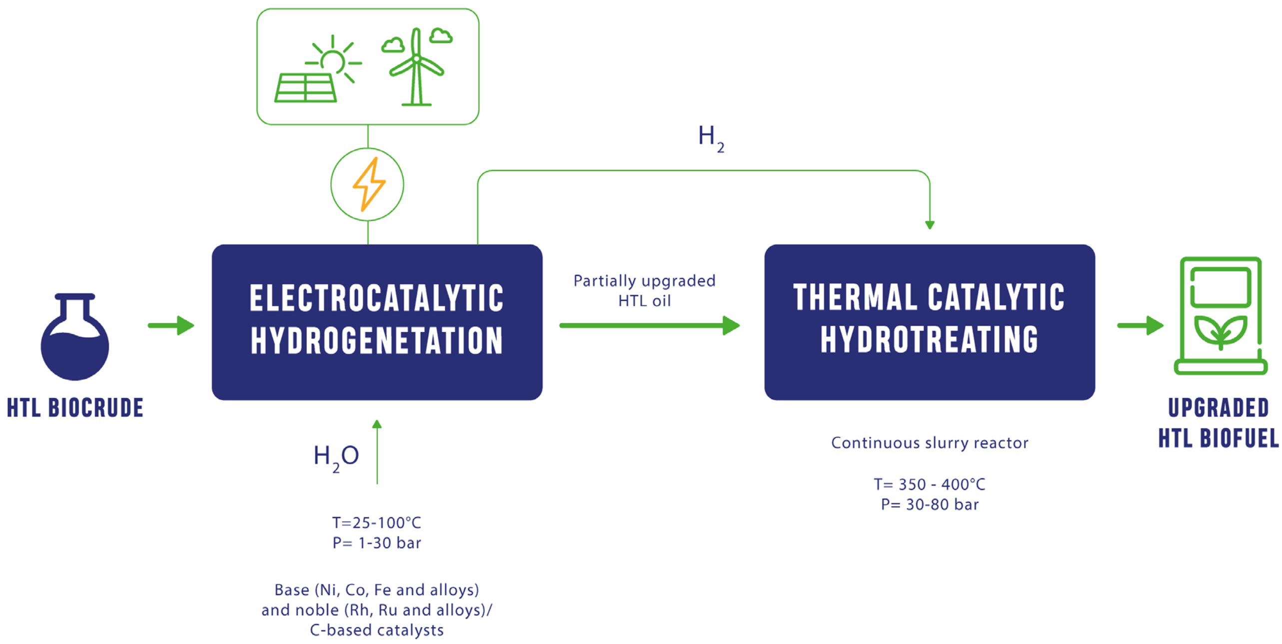


Figure 4.1: Upgrading process concept for converting HTL biocrude to high-quality biofuels.

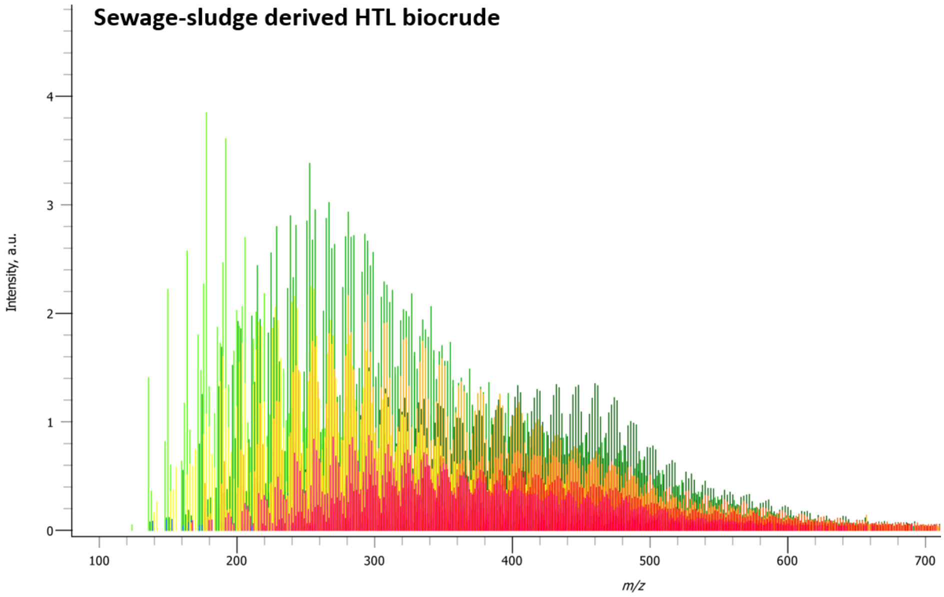


Figure 4.2: APCI+ FTICR fingerprint mass spectra of the sewage sludge-derived HTL feedstock.

Following a step-wise approach, this innovative hydrotreating technology was developed. The development of an efficient upgrading process for such complex feedstocks necessitates detailed knowledge of the molecular composition and the specific heteroatom-containing compounds to understand and optimize the hydrotreating reactions. Extensive characterization of the feedstock with advanced chromatographic techniques was performed first, such as Gas Chromatography – Mass Spectrometry (GC-MS) and Fourier Transform Ion Cyclotron Resonance - Mass Spectrometry (FTICR-MS).
The full-range positive-ion APCI-FTICR mass spectra of the HTL biocrude (Figure 4.2) show around 12,000 different mass peaks in the mass range m/z 150 - 400, confirming the complexity of the HTL oil. These analyses showed that the **HTL oil contains mainly long-chain, saturated and mono-unsaturated fatty acids, long-chain aliphatics, carbonyls (ketones) and nitrogen-containing compounds, primarily linear, saturated amides and heterocyclic nitrogenated compounds with various alkyl substitutions.**

Using this information, novel hydrotreating catalysts were synthesized and characterized based on base and noble metal carbon supported materials for the electrocatalytic hydrogenation and supported molybdenum nitrides for the thermocatalytic hydrogenation. The performance of these catalysts was first evaluated in bench-scale test units using nitrogen, nitrogen-oxygen, oxygen and aliphatic model compounds that were selected based on the advanced HTL biocrude characterization.

Catalysts for electrocatalytic conversions consist of a conductive (carbon) support and a noble or base metal component for the formation of H and the subsequent redox reactions. In a typical electrocatalytic reactor, a carbon felt is often used as a cathode. Carbon has two functionalities:

1) To stabilize the catalytically active noble metal particles, which can be anchored to the functional surface sites by impregnation methods or by depositing pre-formed metal clusters with a high and uniform dispersion.

2) Facilitate the electrical (conductive) contact from the potentiostat to the metal particles.

The carbon support can strongly affect the intrinsic catalytic activity, but also affect mass transport and catalyst utilization as well as the electric resistance (ohmic losses).

The influence of the external potential on the electrochemical hydrogenation rate of 4-methylphenol hydrogenation in a potential range between - 50 and - 275 mV, as well as the faradaic efficiency, which describes the fraction of electrons used for the (desired) hydrogenation of 4-methylphenol and side reactions (i.e., hydrogen evolution reaction), are shown in **Figure 4.3.**

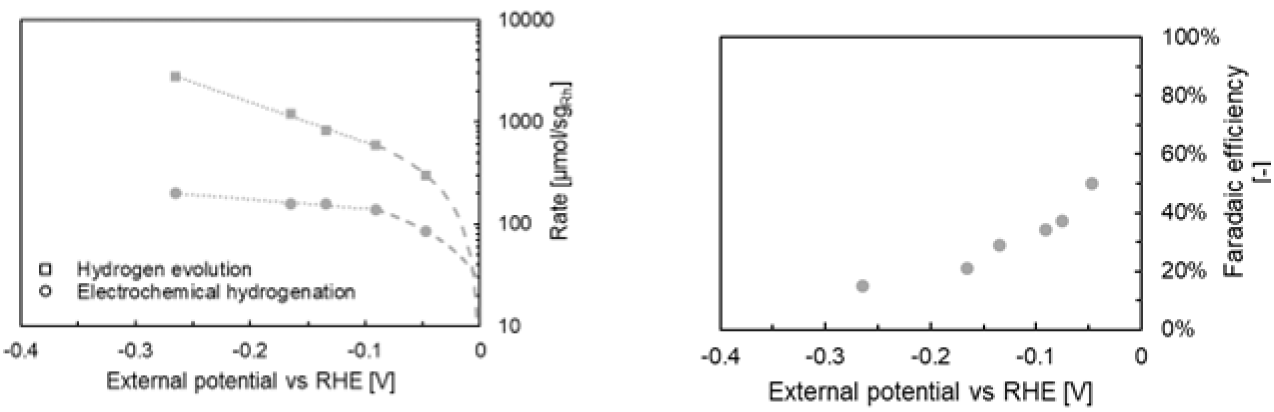


Figure 4.3: (left) Influence of external potential on the electrochemical hydrogenation of 4-methylphenol and hydrogen evolution reaction and (right) faradaic efficiency as function of applied external potential.

The ratio between the 4-methylphenol hydrogenation and hydrogen evolution reaction shifts towards the hydrogen evolution due to the high availability of electrons at higher negative external potentials. This difference in the reaction pathways is reflected in the decrease of the faradaic efficiency with increasing potential.
The electrocatalytic hydrogenation of organic molecules proceeds via hydrogen atoms formed on the catalyst surface in the electrocatalytic step (Volmer reaction), which is influenced by the anions and cations present in the electrolyte. A high ionic strength favors the formation of the methyl cyclohexanol (secondary product), whereas the faradaic efficiency was found to be independent of the ionic strength in the electrolyte (**see Figure 4.4**).

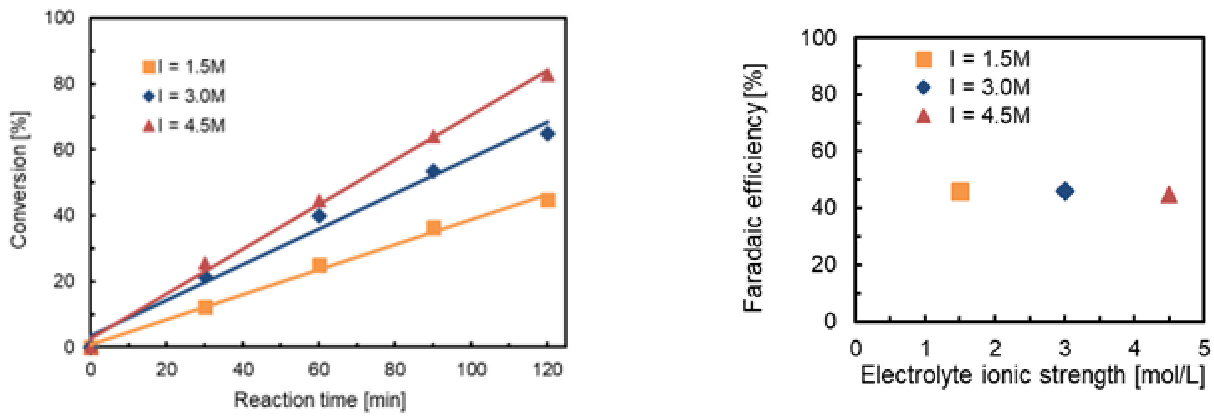


Figure 4.4: (left) 4-methylphenol hydrogenation rate and (right) faradaic efficiency as a function of ionic strength of the electrolyte.

This indicates that both, the 4-methylphenol hydrogenation, as well as the hydrogen evolution reaction, were accelerated to the same extent with the increasing ionic strength.

The effect of the chemical nature of the ions (NaNO3, KNO3 and NaCl) on the electrochemical hydrogenation reaction is shown in **Figure 4.5.**

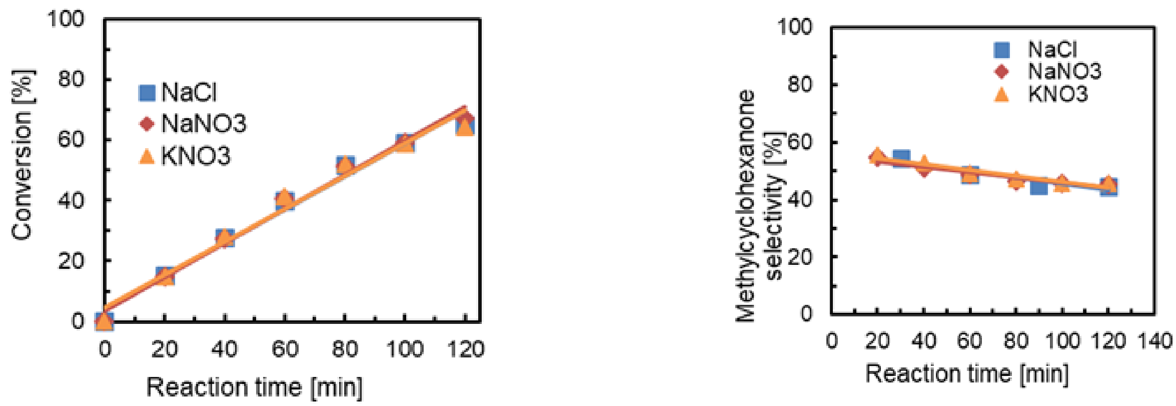


Figure 4.5. (left) hydrogenation rate of 4 methylphenol and (right) selectivity for methylcyclohexanone formation for in presence of a series of ions.

The conversion of 4-methylphenol and the selectivity were found to be independent of the type of salt added to the electrolyte, which confirms that the rates of the hydrogenation reactions were only affected by the ionic strength of the electrolyte, while the nature of anions and cations in the solution did not influence the hydrogenation activity.

For thermocatalytic hydrotreating, a series of constant loading (10.7 wt.%) Mo2N catalysts on CeO2, ZrO2, SBA-15, MCM-41 and C was synthesized and tested on small-scale batch reactors in the hydrotreating of p-cresol, pyridine, octanamide and hexadecane at 350 °C temperature and 60 bar of H_2. The nature of the support had a significant impact on the textural properties.

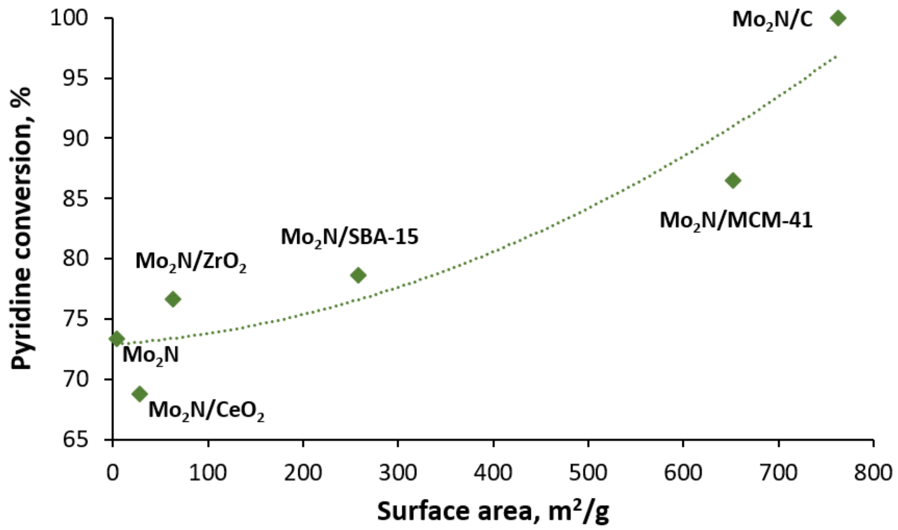


Figure 4.6: Pyridine conversion vs surface area in Mo2N-based catalysts.

The surface area of the supported catalysts was significantly higher than the bulk Mo2N phase, with substantial additional pore volume.
All catalysts were able to efficiently hydrodeoxygenate p-cresol. The bulk Mo2N catalyst appeared superior to a commercial pre-sulphided NiMo catalyst and the supported ones, as it removed the oxygen from the feed without hydrogenating the aromatic ring of the phenolic compound, producing almost exclusively toluene. The commercial catalyst was more efficient in removing nitrogen from pyridine and octanamide, achieving nitrogen removal in the range of 85 – 100%. The reactivity of the Mo2N catalysts varied depending on the support (see **Fig. 4.6**). The highest pyridine conversion was achieved with activated carbon, followed by the high surface silica-based supports (MCM-41 and SBA-15), ZrO2 and CeO_2.

Besides heteroatoms reduction (oxygen, sulphur, nitrogen), removal of inorganics (mainly iron) from the biocrude is crucial to enhance the life cycle of the catalysts bed during the upgrading process. The impact of inorganic content in the catalyst bed depends on the type of catalyst and reactor configuration used. The NGRF project demonstrated that inorganic removal could be performed in a continuous process using fix-bed or slurry reactors. The selected catalysts for these guarded stages were NiMo-based catalysts. Both approaches showed an inorganic content reduction of > 95%.

The demineralized oil was then hydrotreated using commercial NiMo-based catalysts. Parametric studies were initially performed in small-scale batch tests to assess the effect of the operating conditions and determine the optimum configuration for the upgrading tests on a continuous pilot scale. The application of a 2-stage hydrotreating, with a first mild hydrotreatment step at 250 °C to remove unstable oxygenated compounds, followed by

a more severe hydrotreatment step at 350 °C/400 °C was found to be the optimum. The upgrading process was then demonstrated in the continuous pilot-scale units at CPERI (Fig. 4.7a) and Steeper Energy (Fig. 4.7b). Optimization of the reaction conditions (temperature, pressure, space velocity), reactors configuration (fixed bed and slurry reactors) and process configurations (multi-stage) were performed.
CPERI successfully tested a 2-stage process configuration, with first processing of the sewage-sludge derived HTL oil in a fixed-bed reactor at 290 °C and further hydrotreatment in the slurry reactor at 400 °C **for more than 150 hours-on-stream.**

This configuration **efficiently removed oxygen, sulfur and nitrogen (Fig. 4.8)** and produced a light upgraded fuel, rich in **aliphatic and aromatic compounds,** with **more than 94% of its components in the gasoline- and diesel range (Fig. 4.9).**

Figure 4.7: Pilot scale units used for sewage-derived biocrude upgrading: a) High-pressure pilot test unit at CPERI; b) Steeper Energy's continuous hydrotreating units.

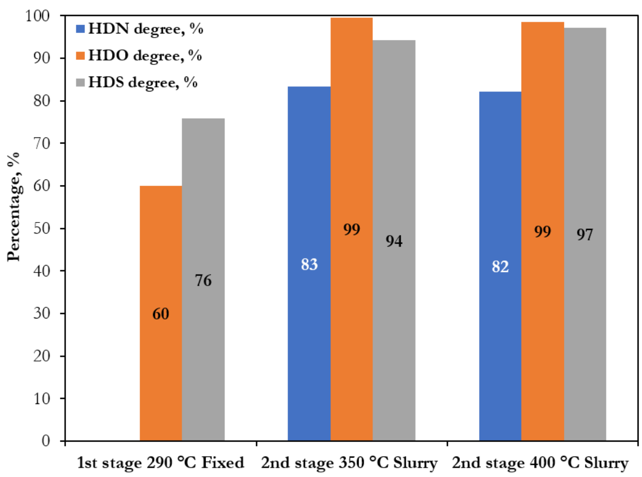


Figure 4.8: Heteroatom removal from HTL biocrude in small-scale tests.

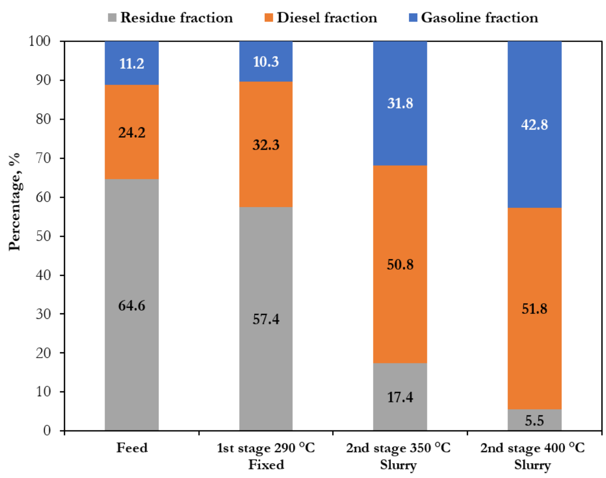


Figure 4.9: Gasoline, diesel and residue fractions in HTL biocrude and upgraded products.

Guard bed followed by a 2-stage hydrotreating process configuration using fix-bed reactors was also successfully performed at Steeper Energy. More than 150 hours of stable operation were achieved when using commercial NiMo-based catalysts. The process was carried out at temperatures between 290-360 °C, the pressure of 100-120 bar, weight hour space velocity of 0.5 h-1 and 1000 H_2 to oil ratio. Like petroleum feedstocks upgrading, sulphur and oxygen removal (96% and 94%, respectively) was more straightforward than nitrogen removal (up to 30%). However, deeper hydrotreating conditions are required to remove the resilient nitrogen.

The biocrude's properties were considerably improved after hydrotreating, achieving a viscosity reduction of 98% (632 cP (feedstock), 9.7 cP (upgraded oil) at 25 °C) and microcarbon residue reduction from 12.4 to 1.82.
Moreover, the total acid number was eliminated, and H/C ratio was increased from 1.5 to 1.8 after hydrotreating. The hydrocarbon distribution was also improved, obtaining more than double of diesel fraction (190-343 °C) while achieving a residue (550+ °C) conversion up to 88%. Simulated distillation results are included in figure 4.10.
The overall hydrogen consumption was 2.8 wt.%.

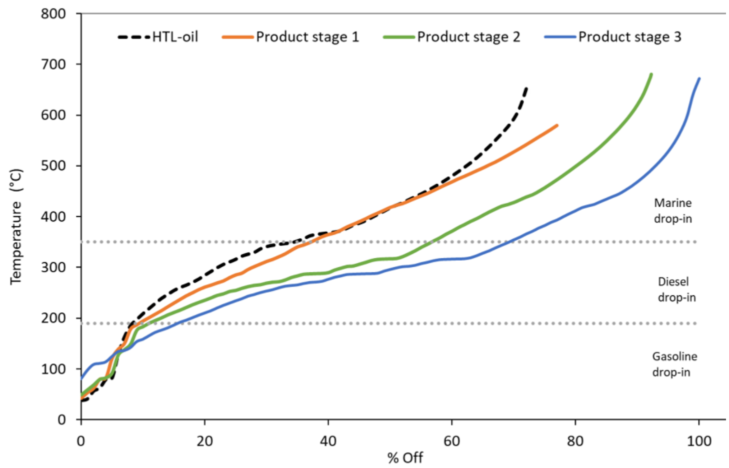


Figure 4.10: Simulated distillation of sewage-derived biocrude and upgraded products. Product guard bed stage (product stage 1), product from 2-stages hydrotreating process (production stage 2 and product stage 3).

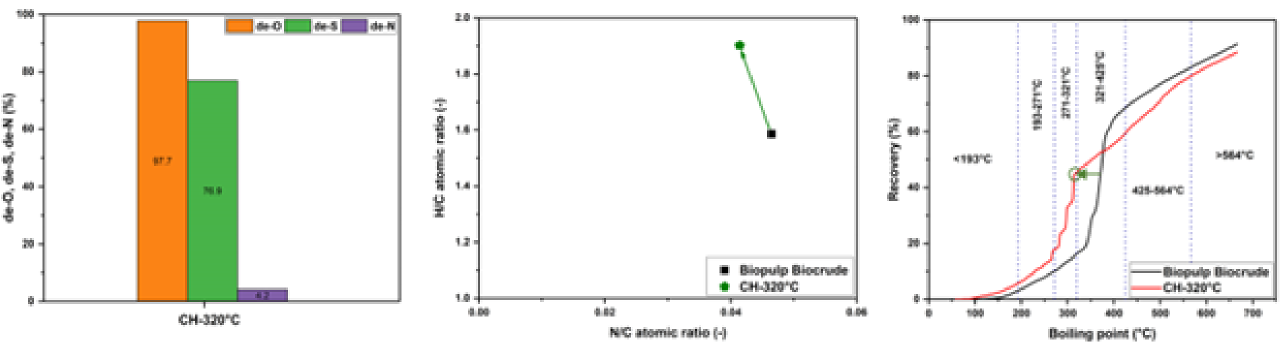


Figure 4.11: Heteroatom removal (left hand side), modified van Krevelen diagram (in middle), and simulated distillation (Sim-Dis) for boiling point distribution (right hand side) of biopulp HTL biocrude before and after continuous hydrotreatment.

Highlights on continuous upgrading of biopulp HTL oil

Continuous hydrotreating of biopulp HTL biocrude was carried out in a fixed bed hydrotreater, designed, and commissioned at AAU (Figure 4.1.2).

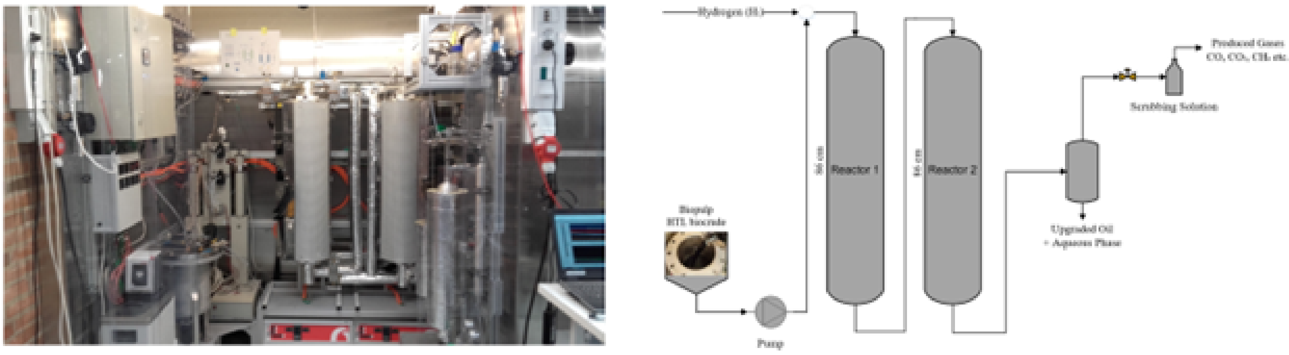


Figure 4.12:. Two-stage continuous hydrotreater at AAU (left hand side) along with simplified process scheme (right hand side).

In an experimental study, commercial hydrotreating catalysts (Mo-Al2O3 and NiMo-Al2O3) were provided by Haldor Topsøe, in the form of trilobe extrudates.

After packing Mo/NiMo-Al2O3 catalysts in both reactors (reactor 1 and reactor 2, **Figure 4.12**), in situ sulfidation was carried out with heavy gasoil (HGO) spiked with 2 wt.% of dimethyl-disulfide (DMDS).

The spiked HGO continuously flowed through the hydrotreating unit at LHSV = 2 h-1, 10.0 MPa, 350 °C, and with an H_2:oil ratio of 800. After sulfidation, the feed in the pump was changed to biopulp HTL biocrude and a steady state under desired conditions (320 °C, 10.0 MPa, 0.25 WHSV, and 1000NL/L H_2:oil ratio) was achieved within 48 hours.

After reaching the steady state, the **biopulp HTL biocrude hydrotreatment was continued for 600 hours on-stream** and thereafter the experimental activity was successfully stopped, without any sign of coking or pressure drop.

Results in **Figure 4.11** showed that mild/partial hydrotreatment (320 °C) has a significant impact on achieving hydrodeoxygenation (97.7 wt.% de-O), followed by hydrodesulfurization (76.9 wt.% de-S) and hydrodenitrogenation (4.2 wt.% de-N).

Results also suggest that severe operating conditions are possibly required to achieve higher heteroatom removal (especially, higher hydrodenitrogenation).

Modified van Krevelen diagram (in **Figure 4.11**) illustrates that **mild upgrading has a considerable effect on H/C atomic ratio**, which increased from 1.58 (before hydrotreatment) to 1.90 (after hydrotreatment).

However, N/C atomic ratio decreased slightly before (0.046) and after (0.041) hydrotreatment. Simulated distillation (SIM-DIS) results (in **Figure 4.11**) indicate that mild operation conditions result in an evident shift of boiling point distribution towards low boiling fractions. This happens because the oxygen-containing molecules have a much higher boiling point than the corresponding deoxygenated ones; therefore, significantly affecting the overall boiling point distribution.

Key points

Sewage-sludge derived hydrothermal liquefaction oil can be successfully upgraded to high quality fuels via a modular electrocatalytic-thermocatalytic upgrading process.

Mo2N-based catalysts are promising catalysts for the hydroprocessing of renewable oils.

HTL oil was processed for more than 150 hours time-on-stream in a continuous pilot-scale unit, producing a high-quality fuel.

Almost complete removal of oxygen and sulfur and more than 80% removal of nitrogen was achieved with a 2-stage hydrotreating configuration over NiMo catalysts.

Karlsruhe Institute of Technology (KIT).
Credit: ETA-Florence Renewable Energies.

5. Is the Market ready for HTL?

Reshaping the overall market focus

Initially envisioned at the early-stage rollout of HTL for urban organics to focus on food waste, sewage sludge, and wood waste derived from construction and demolition wastes. However, the European Union (EU) policy on reducing commercially generated food waste and existing industry practices for collecting construction and demolition wastes have **adjusted the initial market focus toward sewage sludge and municipal aggregated biowastes.**

Evaluated the urban feedstock market size

From an overall market perspective, the **EU generates 28 million dry-ash-free equivalent tonnes of biowaste and 8 million dry-ash-free tonnes of sewage sludge annually** which, through Hydrofaction®, can be converted to 1**6 million tonnes of renewable crude oil,** while recovering **513 thousand tonnes of phosphorus.** This directly contributes to the EU RED II commitments:

1. Up to 37% of the RED II 2030 target for all biofuels used for road and rail transport can be achieved if all EU biowaste was converted to biocrude and derivative road and rail fuels.
2. Up to 149% of the 2030 target for advanced biofuels usage in road and rail transit can be achieved.
3. Recovered phosphorus is sufficient to supply 34% of EU 27 phosphorous fertilizer consumption.

Optimized commercialization path

Industry feedback indicates that the urban waste market is highly conservative and bringing new technology into the market is challenging. In addition, projects within the sector are governed by the EU tendering process, necessitating EPC (engineering, procurement and construction) company participation.
These issues define a need to introduce HTL through a commercial demonstration project with the support of a recognized EPC company as a partner. As a commercial demonstration, such a project would be eligible for first-of-kind funding from within the EU, which would reduce its effective cost while potentially bypassing the EU tendering requirements.

Sewage sludge. Credit: AAU.

Future Markets

A Multi-Criteria Analysis (MCA) narrowed the research focus to three countries – the Netherlands, Germany, and Sweden (Fig 5.1).

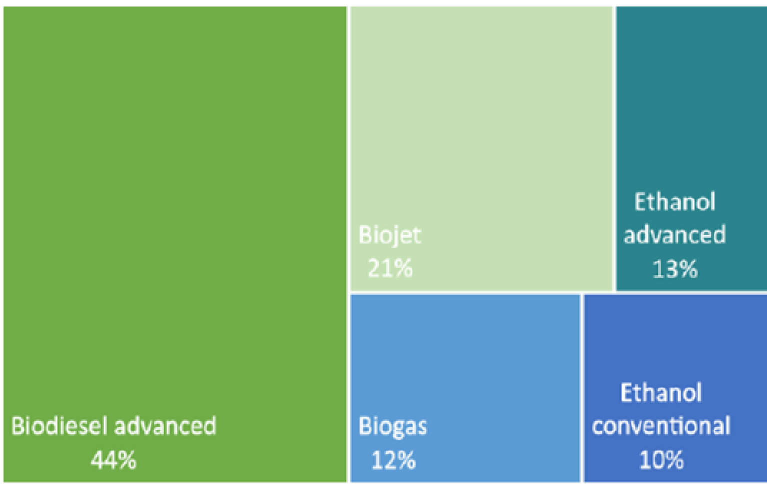
MCA	Germany	Greece	United Kingdom	The Netherlands	Denmark	Sweden	France	Weight
Market size general transport (ex marine bunker) 2020	1.00	0.13	0.88	0.25	0.09	0.14	0.89	6.0%
Market size biofuel 2020	0.50	0.37	0.42	0.33	0.84	1.00	0.60	9.0%
Market size electricity 2020	0.14	0.41	0.06	0.00	0.65	0.29	0.23	4.0%
Marine bunker market size	0.22	0.22	0.07	1.00	0.07	0.07	0.41	11.0%
Policy attractiveness	0.67	0.67	1.00	1.00	0.33	0.67	0.67	21.2%
Policy reliability	1.00	0.67	0.33	1.00	1.00	1.00	1.00	14.7%
Market size electricity 2050	0.02	0.29	0.00	0.21	0.36	0.17	0.09	5.0%
Market size biofuel 2050	0.48	0.37	0.39	0.33	0.56	1.00	0.49	15.7%
% agricultural and landfilled sludge	0.89	0.85	0.99	1.00	0.95	0.30	0.67	5.0%
Biomethane market competition	0.33	0.67	0.33	0.67	0.00	0.00	0.33	8.5%
Total	**0.57**	**0.49**	**0.50**	**0.68**	**0.49**	**0.59**	**0.59**	100.0%

Figure 5.1: Multi correspondence analysis to narrow research focus on specific eu countries.

The projection of future market size of the NGRF biofuel was based on multiple energy scenarios assessment. These scenarios show that within the EU27 plus UK transport activity will steadily increase until at least 2060. However, due to efficiency improvements, the demand for energy in transport will likewise decrease. At the same time, the share of renewable fuel will increase over time.
This combination leads to a decreased demand for fossil fuels and an increased demand for renewable fuels. Depending on the optimism of the scenario, the share of biofuels will increase more or less. Uptake of biofuels goes faster than electrification due to the drop-in/blend possibility of most biofuels.

Accelerated technological development, however, could increase the electrification of the transport sector. For biofuels, like the NGRF biofuel, the EU27 plus UK area shows a high offtake market potential. Looking globally, China and the United States show the highest demand for biofuels until 2050. The shipping and aviation sectors were not included in these scenarios as they are counted towards international bunkers. The energy demand in these international bunkers is expected to be stable or even increase. As these heavy transport modes are dependent on high energy density liquid fuels, they also show a high off-take market potential for the NGRF biofuel.

Figure 5.2: Global biofuel mix 2050.



Favourable Areas

The uptake of biofuels is, due to costs disadvantage compared to fossil fuels, dependent on governmental regulations. In this report, global regulations are assessed, and it was found that the European Union (EU) shows the most ambitious and stable regulations. For investments in hydrothermal liquefaction (HTL) facilities, stable regulations are needed. Therefore, the European Union is the most attractive area for the NGRF biofuel technology to settle. However, work needs to be done to make the EU regulations more concrete, as a specific roadmap to meet the targets is still missing. The shipping and aviation sectors show long term (2050) emission reduction targets but lack targets for the short term. This creates an uncertain situation for technology developers of renewable fuels for these transport modes.

Figure 5.3: European countries with incentive system.

Substitution Threat

The chance that the NGRF biofuel will be substituted by another fuel is low as all renewables are required to meet the GHG reduction targets. If there are substitution threats, they are dependent on the type of transport mode.

The heavy transport modes, that mainly run on diesel engines, are expected to be dependent on fuels such as the NGRF biofuel. Therefore, it is recommended to focus on these transport modes. A mixed energy matrix is most probably the future scenario for the transport sector. The allocation of the available biofuels depends on the suitability of the fuel for a specific transport mode.

Figure 5.4: Influence factors.

Factors that influence the aptness of a given fuel for a specific transport mode are:

- The energy density of the fuel
- Fuel compatibility with the existing vehicle and fuel infrastructure
- Storage, refueling and use of the fuel.

Different transport modes will share some common aspects, such as fuel compatibility. On the other hand, the energy density is a limiting criteria, for example, marine and aviation sectors. Light duty vehicles are more affected by centralized fuel production than the marine sector, impacting storage and refuelling.

Stakeholder Mapping

Three categories of stakeholders were identified for conducting interviews: feedstock suppliers, fuel users, and influencers. Primary interviewees included feedstock suppliers and oil users, such as wastewater treatment plants (WWTPs), water boards in the Netherlands, municipalities obligated to provide urban organic waste management, oil refineries, shipping companies, and ports. Influencers included research institutes, government organizations, consulting companies, industry associations, and engineering & manufacturing companies who provide suggestions or services to the feedstock suppliers and oil users mentioned above.
A total of 45 interviews were conducted between May 2019 and December 2020.

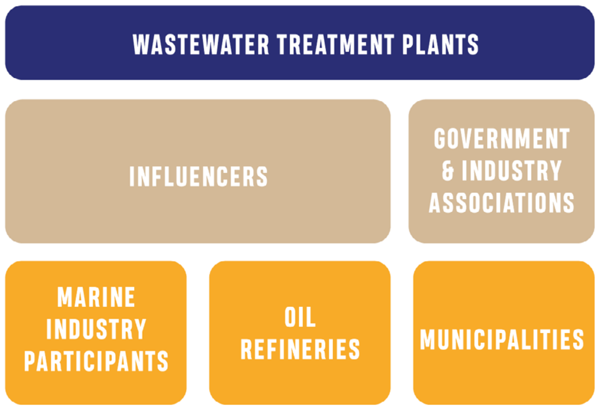


Figure 5.5: Categories of interviewees.

HTL plants accept both Sewage and Biowaste

More than half of the sewage sludge produced in the Netherlands and Germany is sent to mono- and co-incineration. There is an upward trend towards increasing mono-incineration capacity. In Sweden, sewage sludge is mostly disposed via land application on agricultural land, followed by landscaping and covering of closed landfills.

Composting and anaerobic digestion (AD) are currently the two predominant technologies for treating biowaste (e.g., kitchen waste and garden waste), with an increased focus on AD.
However, AD does not sufficiently break down the lignin from woody biomass, and plastics mixed with collected biowaste could affect fertilizer quality. Municipalities with large or growing populations appeared to be more interested in innovative technologies because the capacity of organic waste

treatment is predicted to be insufficient soon. To encourage a stable feedstock supply, HTL facilities can be designed to accept a combination of bio-waste from restaurants, caterers, and food manufacturers with municipal garden and park waste – all waste streams for which municipalities are obligated to provide treatment management.

The EU Waste Hierarchy

A challenge identified in promoting the implementation of HTL technology with food waste or bio-waste is the EU's waste hierarchy. Currently, HTL technology falls under the 'recovery' rather than the 'recycling' hierarchy. HTL technology may fall under 'recycling' hierarchy if by-products can be produced from food waste or bio-waste streams that meet the 'fertilizer' definition of the 'recycling' tier of the waste hierarchy. Alternatively, **the NGRF Consortium and other HTL technology providers may need to discuss HTL's position within the EU waste hierarchy with the European Commission**; this will require additional education and lobbying.

Potential HTL Fuel Buyers

1) Oil Refineries
Twenty-four oil refineries operate in the targeted countries, with six in the Netherlands, thirteen in Germany, and five in Sweden. **Oil refineries in the Netherlands and Sweden are more likely to be first movers, particularly the Port of Rotterdam.** Advanced biofuels are preferred, such as renewable diesel with a low carbon intensity, while biodiesel (FAME) or HVO derived from palm oil and UCO will be limited due to sustainability concerns and traceability issues associated with UCO. Germany is very heavily focused on green hydrogen. Swedish oil refineries are more open-minded to co-processing, and in Sweden, there are a few plants deriving HVO from tall oil, and more capacity is under construction and planned.

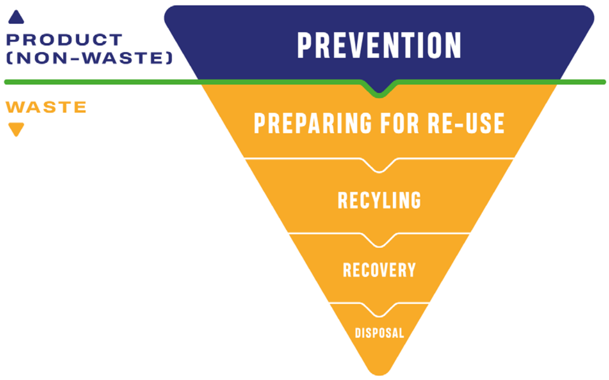


Figure 5.6: The EU waste hierarchy.

2) The Shipping Industry
Many of the world's leading shipping companies are from Europe. **Deep-sea ships are fuel flexible, and HTL oil may meet the current specifications of bunker fuels** or can be partially upgraded to lighter distillates, enabling its use for marine applications as-is. The marine sector sees that advanced biofuels likely represent the industry's most economically feasible zero-emission alternative. Some leading shipping companies have their own targets to become carbon neutral by 2050. They are **willing to pay a premium over fossil fuels.** The shipping industry believes that biofuel may account for 30% of shipping's energy use by 2030 and 10% by 2050, when other technologies reach maturities, such as

hydrogen and ammonia[5].

Ports also have an important role in promoting cleaner engines or fuels in the shipping industry.

Many incentive schemes are developed and deployed by ports globally to offer a discount on port fees and dues. HTL technology implementation and deployment would be accelerated if HTL oil is included in these incentive schemes. In addition, sustainability certification by a third party will be necessary to provide confidence to regulators and the maritime industry.

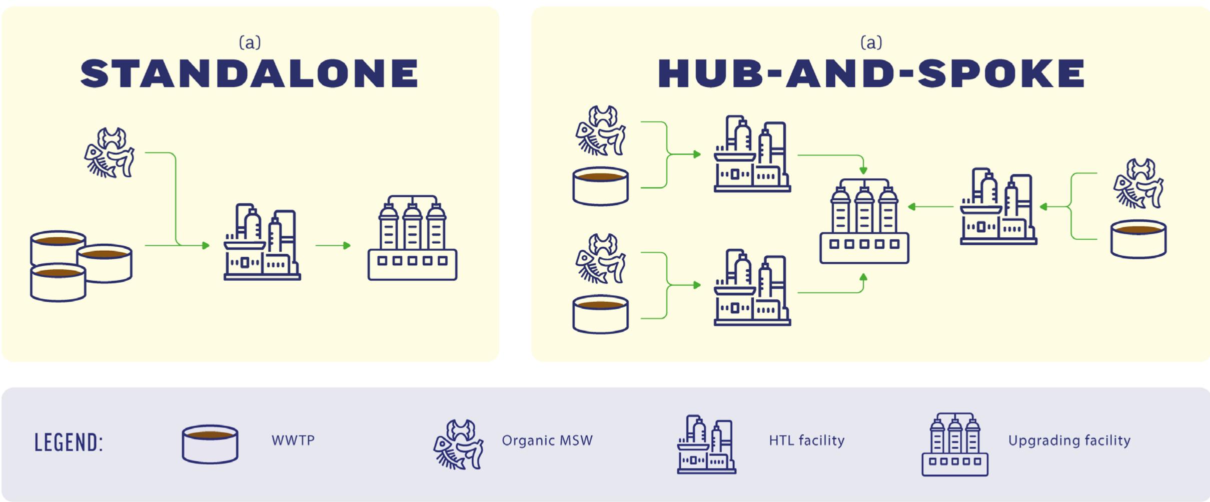


Figure 5.7: Standalone scenario & hub-and-spoke scenario.

Entry Market Options

Two EU market entry options for HTL technology are proposed:

1) Provision of HTL oil as maritime biofuels without upgrading or as a partially upgraded product;

2) Provision of a fully upgraded advanced drop-in biofuel for the road transportation, especially as a renewable diesel for heavy-duty trucks.

HTL biofuels can be produced at a central, standalone HTL upgrading unit or co-processing HTL oil with fossil crude at existing oil refineries or HVO plants. Most interviewees agreed that a centralized location for HTL biofuel production (Hub-and-Spoke scenario) could be cost-effective with a lower carbon footprint than building several small HTL upgrading units.

However, the implementation of HTL technology in the three featured countries will vary depending on the country's size, population density, the current practice and plans of urban organic waste treatment, and existing infrastructure. As sewage sludge and food waste are the focus feedstocks of the NGRF project, it is recommended that the HTL facility be located close to the feedstock.

The areas with the highest sewage sludge potential supply correspond with the highest population density; these high potential areas are mainly in central Europe, covering the Netherlands, Belgium, Germany, the UK, and Italy.

5. Sustainable Shipping Initiative (SSI). 2019. The role of sustainable biofuels in the decarbonisation of Shipping. Madrid: Sustainable Shipping Initiative.

These are also the same areas with the highest heavy-duty trucks traffic, of which the UK, Germany, and Italy are the top countries for biowaste and food waste production.

However, half of the sewage sludge produced in the Netherlands and Germany are destined for incineration.

It is important to prioritize biowaste and food waste as feedstock when implementing commercial-scale HTL facilities in these two countries.

As discussed in D6.1, second-tier cities may be suitable for co-locating HTL facilities with WWTPs aggregating sewage sludge only. However, populous towns are looking for solutions to manage large amounts of urban organic waste.

Therefore, industrial zones at, or near, urban areas with high population density are potential locations for HTL facilities and upgrading units.

Hydrofaction Demo Plant.
Credit: Steeper Energy

Key points

Feedstock market focus: The NGRF project market focus toward sewage sludge and municipal aggregated biowaste due to EU policy and existing industry practices.

Urban feedstock market size: Overall, the EU generates 28 million dry-ash-free equivalent tonnes of biowaste and 8 million dry-ash-free tonnes of sewage sludge annually which, through Hydrofaction®, can be converted to 16 million tonnes of renewable crude oil while recovering 513 thousand tonnes of phosphorus.

Optimized commercialization pathway: The urban waste market is highly conservative, and bringing new technology into the market is challenging.

Future market scenario: For biofuels, like the NGRF biofuel, the EU27 plus UK area shows a high offtake market potential. Heavy transport modes show a high off-take market potential for the NGRF biofuel.

Favorable areas for HTL implementation: European Union (EU) shows the most ambitious and stable regulations which favors deployment of new technologies.

New fuels implementation: The heavy transport modes, that mainly run on diesel engines, are expected to be dependent on fuels such as the NGRF biofuel.

6. Economic and environmental performance of HTL biofuels production from sewage sludge

The economic and environmental performance of the technology pathway developed within the NGRF project have been evaluated through detailed techno-economic and life cycle analysis.

The value chain model considered in the analysis, represented in Figure 6.1, includes a decentralized HTL plant located at the vicinity of a waste-water treatment (WWT) plant for conversion of sewage sludge to an intermediate oil-phase, so called biocrude, via hydrothermal liquefaction at supercritical water conditions, and further upgrading of the biocrude at refinery.

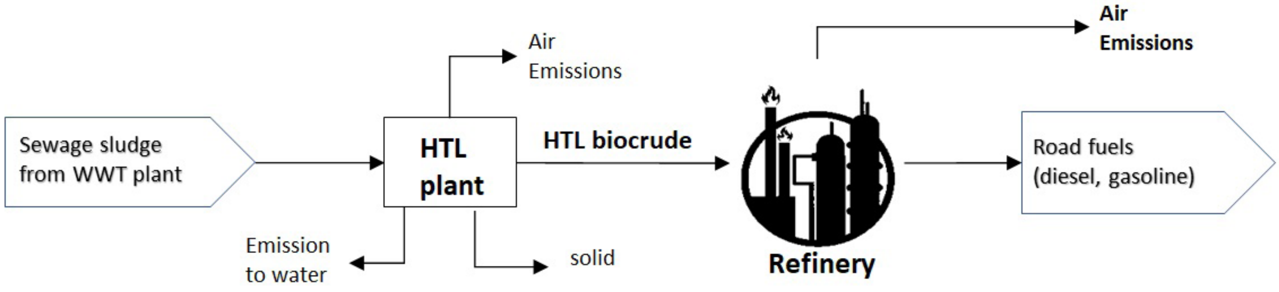


Figure 6.1: Schematic representation of the value chain model: decentralized production of biocrude at HTL plant and centralized upgrading of the biocrude at refinery.

Sewage sludge has been used in the analysis as a model urban waste feedstock, since it poses the main challenges associated to urban waste fractions for the conversion to biofuels via hydrothermal liquefaction.

The overall structure of HTL plant process, shown in Figure 6.2, consists of five differentiated systems, i.e.

1. preparation of the slurry and pumping
2. heating, liquefaction and cooling of the HTL product
3. depressurization and separation of oil, aqueous, gas and solid phases from the HTL product
4. treatment of the residual gas from HTL after phase separation for recovery of the energy content and air pollution control in compliance with air emissions limits
5. treatment of the HTL aqueous effluent to dispose the treated aqueous effluent in compliance of the water emission limits.

The process design for the upgrading of the HTL biocrude is shown in Figure 6.3. It includes:

- multi-stage catalytic hydrotreating of the biocrude for the main reduction of metals and S, N, O heteroatoms
- catalytic hydrocracking of the heavy distillate separated during fractionation of the hydrotreated oil, and
- treatment of hydrogen-rich sour gas separated after hydrotreating separation of CO_2, H_2S and NH_3 and recycling of the remaining hydrogen back to the catalytic processes.

The main products from the overall upgrading process considered here are naphtha with boiling points between 90 and 210 deg. C used for production of gasoline, and middle distillate with boiling points between 210 and 310 deg. C used as diesel. Although the processes involved in the biocrude upgrading are typically present in commercial refineries, the HTL biocrude derived from sewage sludge has however different heteroatoms composition and distillation curves than petroleum-like oils. This requires modifications and experimental testing of the catalyst and the reactors conditions particularly in the hydrotreating system to effectively reduce metals and S, N, O heteroatoms without catalyst poisoning and reactor fouling.

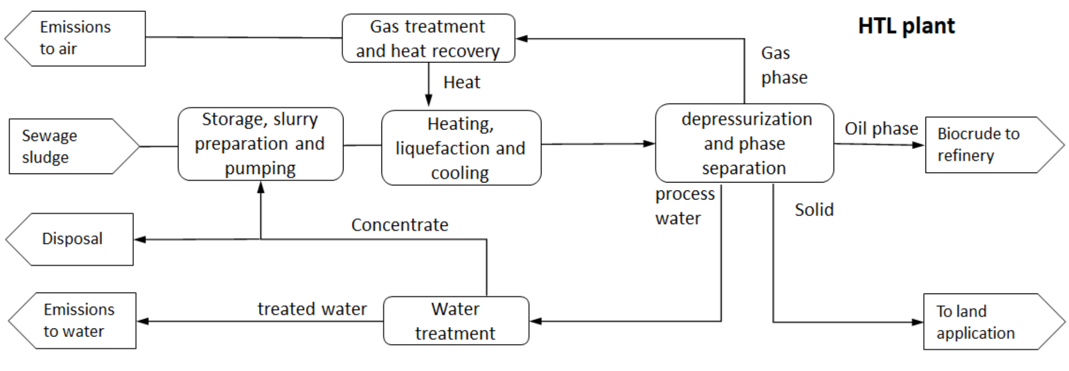


Figure 6.2: Schematic representation of the biocrude production process from sewage sludge by hydrothermal liquefaction.

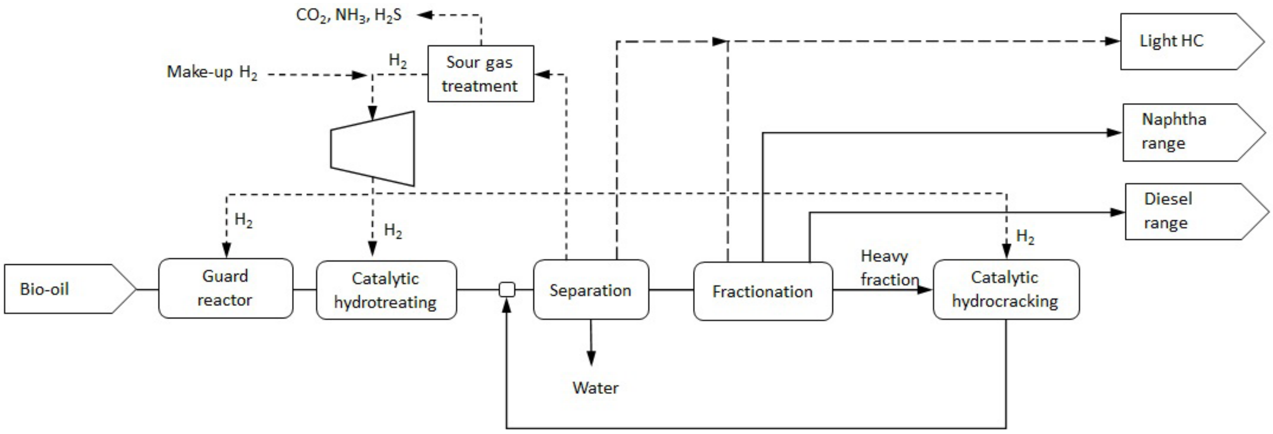


Figure 6.3: Schematic representation of the overall process design for upgrading of the HTL biocrude derived from sewage sludge to naphtha

The main material and energy flows for the conversion of sewage sludge to road fuels are shown, respectively, in Tables 1 and 2. The conversion of sewage sludge to biocrude exhibits an efficiency of 73% on energy basis and 29% on dry-mas basis. The overall mass and energy yields of combined naphtha and middle distillate from sewage sludge on dry basis is approximately 19% and 60%, where the naphtha fraction represents about 45% of the total.

Chemical energy losses during the hydrothermal liquefaction of the sewage sludge are in form of dissolved organic components in the aqueous phase, low-chain hydrocarbons in the gas phase and unconverted non-dissolved carbon in the solid residue, which represent about 17, 4.9, and 4.6% on energy basis.

Chemical energy from the biocrude which is not converted to naphtha and middle distillate is mainly in form of light hydrocarbon gases and dissolved organics on the process water after hydrotreating and hydrocracking, which represent about 11.7% and 10% of the biocrude energy.

The net heat demand in the production of biocrude represents approximately 20% of the total feedstock energy, of which 8% is covered by combustion of the HTL gas and stripped ammonia and the remaining 12% by an external source of natural gas. The overall heat demand by the complete upgrading process is 4.9 % of the chemical energy content in the biocrude, of which 1.2% is used by the hydrotreating, 1.3% by hydrocracking and 2.4% by the distillation. The total hydrogen consumed in the overall upgrading is approximately 4.0% wt. relative to the biocrude feed. The distribution of hydrogen consumption between the hydrotreating, including the guard reactor, and the hydrocracking processes is approximately the same.

HTL oil	ton	0,294
HTL aqueous phase	ton	3,961
HTL solid	ton	1,028
HTL gas	ton	0,157
Natural gas	kg	35.2
Concentrate bleed from water treatment to disposal	ton	0,281
Process water from biocrude production	ton	2.56
Emissions to water from biocrude production plant	m3	2.07
Naphtha production from upgrading	ton	0.086
Diesel production from upgrading	ton	0.100
Process water from upgrading	m3	0.031
Total H_2 consumption	kg	11.8
Solid residue from biocrude upgrading	kg	1.01

Table 1: Main material flows based on an input feed of 1 dry ton sewage sludge

Chemical energy oil product	0,734
Chemical energy aq. effluent after phase separation	0,385
Chemical energy gas after phase separation	0,049
Chemical energy solid. residue after phase separation	0,046
Heating slurry preparation	0,103
Heating slurry to HTL	0,457
Heat recovery from HTL product cooling	0,418
Heating of HTL process water before MVR	0,009
MVR condensate cooling	0,044
Natural gas consumption	0,120
Chemical energy naphtha	0.281
Chemical energy middle distillate	0.321
Chemical energy H_2 consumed	0.027

Table 2: Main energy flows (MW) based on an input feedstock chemical energy of 1 MW based on HHV

Calculations of the biocrude production cost and the minimum fuel selling price (MFSP) as a function of the conversion capacity are shown in Figure 6.4.

The results for the MFSP have considered two different scenarios, i.e., full investment in a new stand-alone upgrading unit and use of existing upgrading equipment at refinery.

In this second scenario, it is assumed that all equipment required for the upgrading of the biocrude are available at refinery and no capital investment is required, except for the initial batch of consumables, and only the annual operating costs and revenues are used for evaluating the minimum fuel selling price.

The biocrude production cost, which exhibits a monotonic decrease with the feed capacity, is in the range of 1.4 to 0.34 €/liter for plant capacities between 30 and 300 dry-ton/day. If all the capital investment in a new upgrading plant is included, **the average MFSP varies between 2.4 and 0.8 €/liter** for the range of the sewage sludge feed capacity used in the analysis. The parameters that impact the most on the MFSP are the biocrude price, the production cost of the make-up hydrogen, and the annual expenditure due to capital investment. **The analysis shows that using existing equipment at the refinery for upgrading of the biocrude leads to a small reduction in the MFSP, approximately 6 - 7% for production capacities considered.**

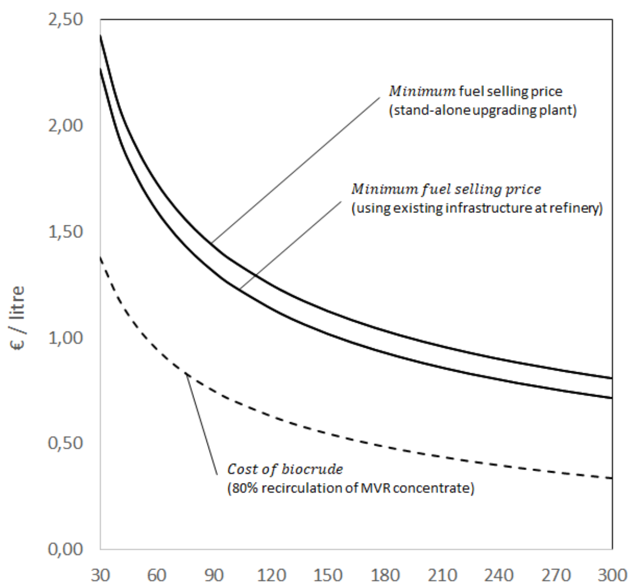


Figure 6.4: Variation as a function of the sewage sludge feed capacity of the levelized cost of biocrude production cost per liter of biocrude production (dashed line) and the minimum fuel selling price per liter (solid line) considering full investment in a new stand-alone upgrading unit and use of existing upgrading equipment at refinery.

A life cycle assessment was conducted to evaluate the environmental performance of the described value chain, which was expanded to include treatment stages for the generated wastes and recycling of nutrients from the HTL solid.

Environmental credits were assumed from the avoidance of sewage sludge treatment by incineration, and substitution of mineral fertilizers by the recovered nutrients. Regarding the latter, direct land application of the HTL solid was considered. The fate of nutrients (direct emissions) after this application was calculated from literature data.

In particular, plant nutrient uptake served to determine the amount of substituted mineral fertilizers. As a multifunctional process (naphta and diesel are simultaneously produced), allocation of impacts between the two products was required. To this end, energy allocation based on the Lower Heating Value (LHV) of naphta (42.1 MJ kg^{-1}) and diesel (39.2 MJ kg^{-1}) was applied, which resulted in 48% and 52% respectively. The selected Functional Unit (FU) was 1 MJ of produced fuel. Denmark was chosen as the preferred geographical scope. Importantly, the presented case includes recirculation of both the concentrate obtained from aqueous phase treatment and the light oil fraction from phase separation.

Indeed, recirculation is a technical point of vital importance to minimize the consumption of chemicals and improve the biocrude yield of the process.

We analyzed the following life cycle impact categories: Climate Change (CG), Cumulative Energy Demand (CED), and Mineral Fossil and Renewable Resource Depletion (MFRRD). Figure 6.5 shows the contributions to these categories. We respectively estimated -21.6g CO_{2eq} MJ^{-1}, 0.4 MJ MJ^{-1} and 0.4 mg Sb_{eq} MJ^{-1}. In particular, the CG figure represents 123% reduction when compared against the fossil fuel reference (94g MJ^{-1}) defined by the EC Renewable Energy Directive (RED II).

Overall, positive contributions are dominated by:

- CG: direct emissions from the production of biocrude, and the consumption of electricity (Danish national mix);
- CED: plant delivery of natural gas and hydrogen production (utilized in the upgrading stage);
- MFRRD: production of K_2CO_3 (HTL catalyst), production of NaOH (added in input slurry preparation), consumption of electricity, and consumption of hydrogen.

It is important to remark that what we report as direct emissions actually come from the combustion of natural gas (NG), which is utilized as a backup fuel (after the HTL gas) to cover the internal heat demand of the plant. As long as alternative heat sources (e.g. from improved waste heat integration, renewable gases, etc.) can be utilized, these particular category could be very much reduced. The same reasoning is applicable for the reduction of the contribution of NG delivery to the CED category.

5. Values indicated in parentheses are referred to Case 1.

Also, the contribution given by hydrogen production (assumed conventional refinery production) could be lowered if green hydrogen was assumed. Furthermore, we found the electricity consumption, especially in the Mechanical Vapor Recompression (MVR) package (utilized in the treatment of the aqueous phase) was high as compared to that reported by other technical sources. Emission avoidance in all cases was principally achieved by the replacement of sewage sludge incineration and the avoided production of P based (P_2O_5) mineral fertilizer. So, considering the possible improvements aforementioned, and focusing on the CG category, a figure in the range of (-40) – (-50) g CO_{2eq} MJ^{-1} produced fuel could be attained. In general, we can conclude that, under the considered assumptions, the production of fuels as proposed by the NGRF project achieves an effective reduction of the greenhouse gas emissions compared to the fossil fuel reference and preservation of resources.

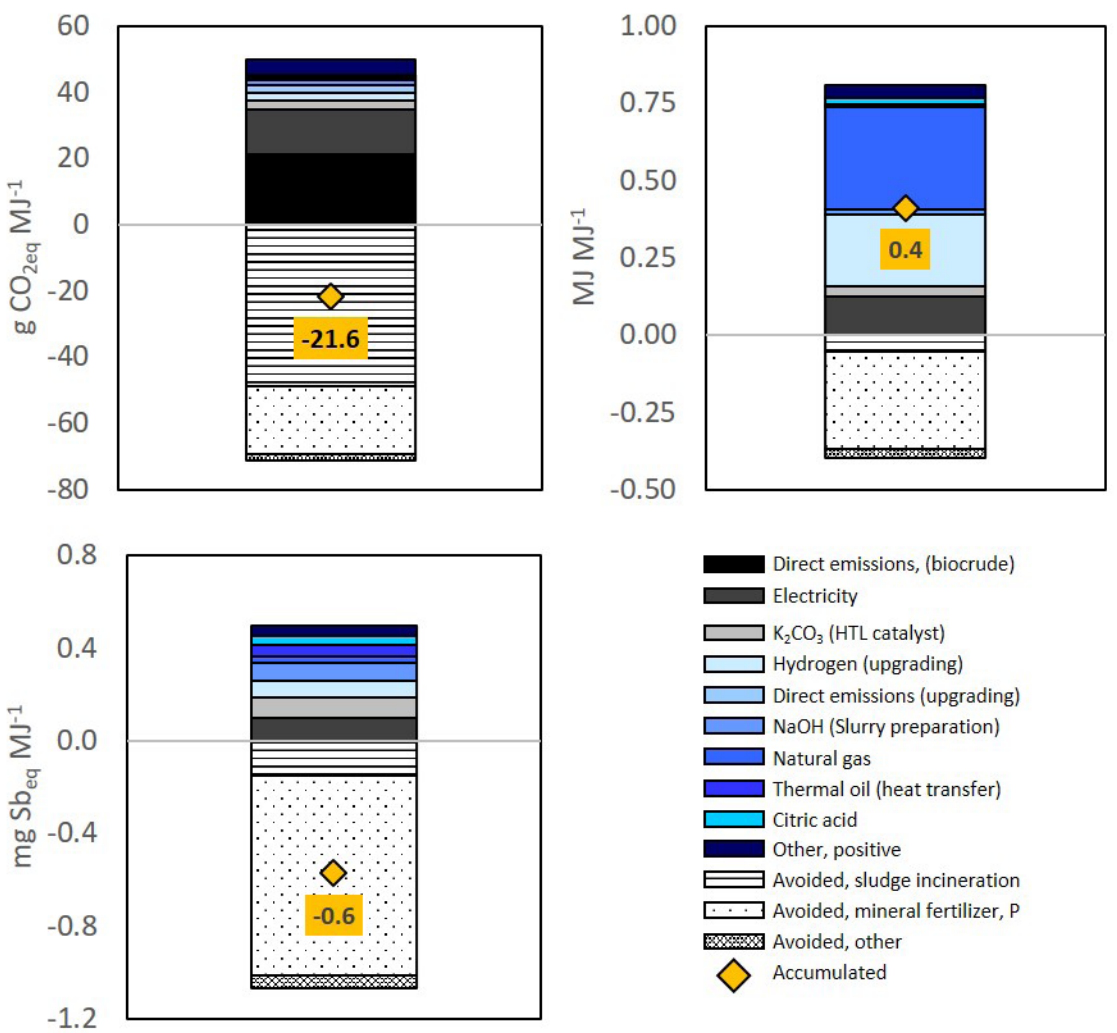


Figure 6.5: Contributions to Global Warming Potential of analyzed cases. Case 1: Fuel production with direct land application of HTL solid. Case 2: Fuel production with struvite precipitation (from HTL solid) and land application.

Key points

The overall mass and energy yields of combined naphtha and middle distillate from sewage sludge on dry basis is approximately 18.6% and 60%, where the naphtha fraction represents about 45% of the total.

The minimum fuel selling price that can be achieved for production of road fuels from sewage sludge via hydrothermal liquefaction is in the range of 2.4 and 0.8 €/liter for sewage sludge conversion capacities within 30 and 300 dry ton/day, assuming that process equipment at existing refineries can be utilized.

The estimated GHG emissions per unit fuel energy produced were of -21.6 CO_{2eq} MJ^{-1}, representing a GHG emission reduction compared to fossil-equivalent fuels of 123%. This figure may even be further reduced by further optimization of the process design.

7. The future for HTL

NextGenRoadFuels has delivered a wealth of information that can be used as building blocks for further research, knowledge sharing and even commercialisation. The project has successfully pioneered and advanced many scientific and technology areas as well as the business and market understanding.
The project has demonstrated the whole value chain from feedstock to finished fuels for two problematic Urban Waste feedstocks: Sewage Sludge and Biogenic Municipal Solid Waste ("Biopulp", "Food waste"). These feedstocks are characterized by having a high nitrogen content due to the content of proteins as well as a high inorganic content rich in phosphorus.

Using Problematic Feedstocks

The original motivation for application of hydrothermal liquefaction for such low value problematic feedstocks were driven by the opportunity to produce cost competitive, sustainable drop-in quality gasoline and diesel fuels with a lower carbon intensity due to the high oil yields and energy efficacy of HTL for such wet feedstocks. The project has demonstrated that sustainable drop-in quality road fuels can indeed be produced with attractive project economics, but that this is not the only driver for selecting HTL for these feedstocks:
Sewage sludge contains pathogens, traces of pharmaceuticals as well as microplastics and biogenic waste contains microplastics. It is undesirable to get such compounds back in the food chain e.g. by use of the land spreading. Competing technologies such as anaerobic digestion have no or low destruction efficiency for such compounds which limits the use of digestate from sewage sludge however NGRF has demonstrated high destruction efficiency for pharmaceuticals and microplastics.

Sewage sludge and biogenic household waste ("Biopulp") have a high phosphorus content (typically 2-6 wt %). The project has demonstrated that phosphorus can be concentrated and recovered with high efficacy in the solid product. Phosphorus is an essential resource that is becoming limited. Hence, both phosphorus and phosphate rock have been identified by the European Commission as critical raw materials, based on its supply risk and the economic importance for EU operators, and recovery of phosphorus constitute a key element of the EU plan for a climate-neutral, resource-efficient and circular economy. Hence, there is a growing regulatory pressure for recycling and recovery of phosphorus and more circular solutions in general which is expected to be mandatory for wastewater treatment plants in the future.
Sewage sludge and biogenic household waste ("Biopulp") also have a high nitrogen content and it has been

demonstrated that more than 2/3 of the nitrogen in the waste can be recovered from the process water as ammonia. The recovered nitrogen could be recycled to agriculture in the form as an organic fertilizer or a soil amendment product, which could position the technology as a sustainable resource efficient circular waste management technique with a low carbon footprint.

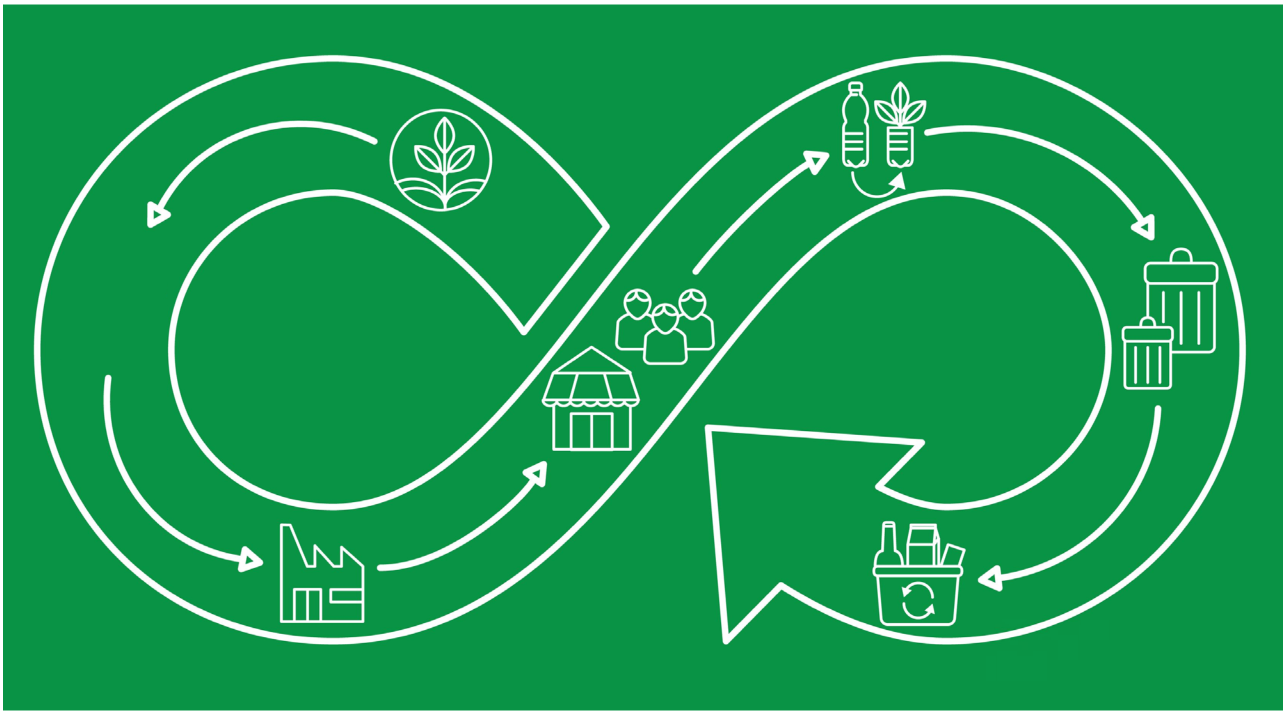


Figure 7.1: Circular economy. Credit: Shutterstock.

Technology wins

During the NGRF project extensive experimental facilities have been constructed, and with these facilities the project has pioneered a method of producing an upgradable oil from the biocrude by reducing inorganics to 10's ppm for both lignocellulosic and urban waste oils.

NGRF has significantly advanced the status quo of upgrading HTL biocrude in terms of process design and parameters, as well as catalysts. The project has brought forward a number of new technologies such as reactor types, combinations of reactors and different qualities of product to an optimum state of experimental and scientific knowledge.

As the coming RED III looks to enforce sustainability criteria on forest resources, more emphasis goes to urban wastes where the research of NGRF has been invaluable and the first activity of its kind, in either research or commercial, to highlight not only the potential of using sludge as a feedstock, but also to identify the show stopping challenge of continuous processing of sludge, due to the build up of phosphorus dominated inorganic deposits, during heating to approximately 300 degrees C.

The research has developed a new process for the upgrading of hydrothermal liquefaction oil to high quality fuels based on slurry-reactor technology in one or two stage process configuration.
The developed process can be employed for the upgrading of other heavy waste-derived oils or low-quality heavy fossil fuel oils.

Although the expected time frame of this deployment is five to eight years.
Another outcome of the project is a new co-feeding process of hydrothermal liquefaction crude oil with conventional fossil-based gas oils in existing refinery infrastructure (in existing facilities).
The developed process can be employed for the upgrading of other heavy waste-derived oils or low-quality heavy fossil fuel oils.

The process has so far been demonstrated in batch reactors. Further research development and up-scaling is required to demonstrate the continuous operation of the process.
One technology that can be used and applied immediately is a newly developed FTICR-MS characterization method for analyzing and determining the complex composition of HTL oils and similar oils and further understanding the upgrading requirements. It can be used by refineries, biofuel producers, technology developers etc.

Figure 7.2: Hydrofaction biofuel Plant. Credit: Steeper Energy

Next Generation Biofuels

The project results show the bio-blends were completely miscible and stable during storage time.
Ignoring the marginally high water, sulfur content, and cloud point, 17 wt. % of hydrotreated bio-blends can be mixed with the reference diesel, but measures to fully meet all specification have been identified.

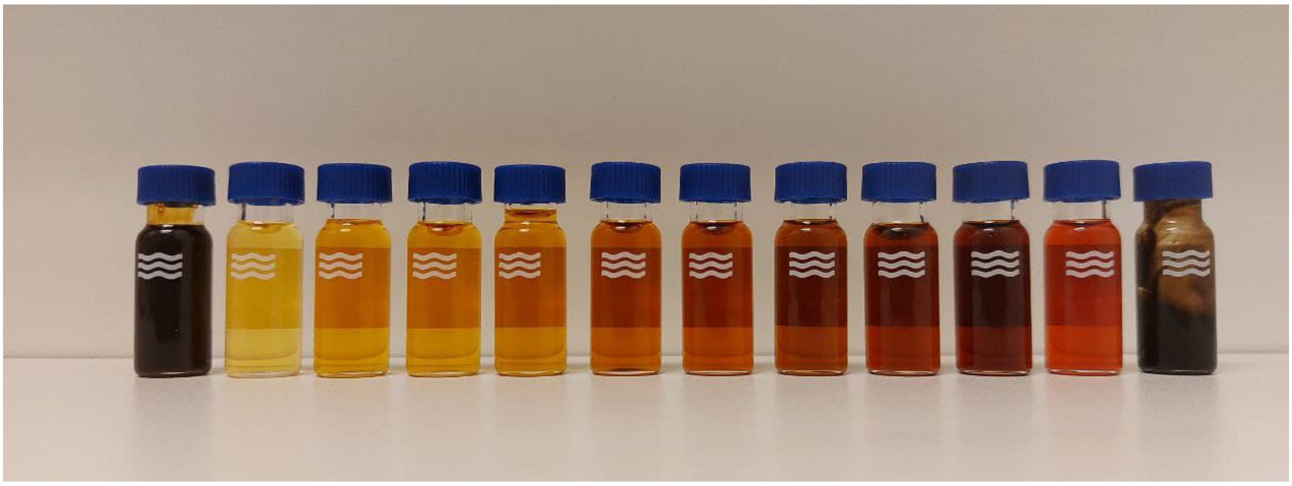


Figure 7.3: Bio-fuels blend stock. Credit: Komeil Kohansal, AAU Energy.

In summary, the early stage study revealed the viability of using upgraded HTL-driven fuel fractions as diesel blendstock and visualized a roadmap for future downstream activities. Depending on the extent of downstream processing, the fuel can be tuned for different types of engines, in this case the normal road diesel-burner engines have been studied.

Policy Change Makers

During the research various aspects have been identified that could influence adaptations to policy to incentivize HTL technology and diversify the disposal of sewage sludge. The following points are a summary of key potential policy change makers that have come to light throughout the project.

- Sewage sludge is not considered a fertilizer, but the produced biostimulants and phosphor products can be used to improve soil quality. Policy is required to back this up.

- An implementation barrier was identified in terms of the current classification of HTL as recovery rather than as waste recycling or waste disposal technology.

- HTL fuels are "electro-biofuels" if green hydrogen from electrolysis is used. It is also a key enabling technology for circular use of waste by turning the organic fraction into an energy carrier, and the inorganic fraction (phosphorous, nitrogen) into fertilizers for agriculture.

- HTL can be fitted with carbon capture, turning the CO2 produced into a feedstock for Power-to-X or carbon sequestration (BECCS, carbon negative). Thus, the value proposition for HTL is more complete than for Power-to-X, which translates into faster implementation at lower cost, thus reaching sustainability goals and security of supply faster/cheaper.

Key points

Problematic feedstocks: HTL is an efficient way to process wet feedstocks into useful molecules (fuels) while recycling valuable inorganic resources. It also promotes the destruction and recycling of persistent particles (e.g. microplastics).

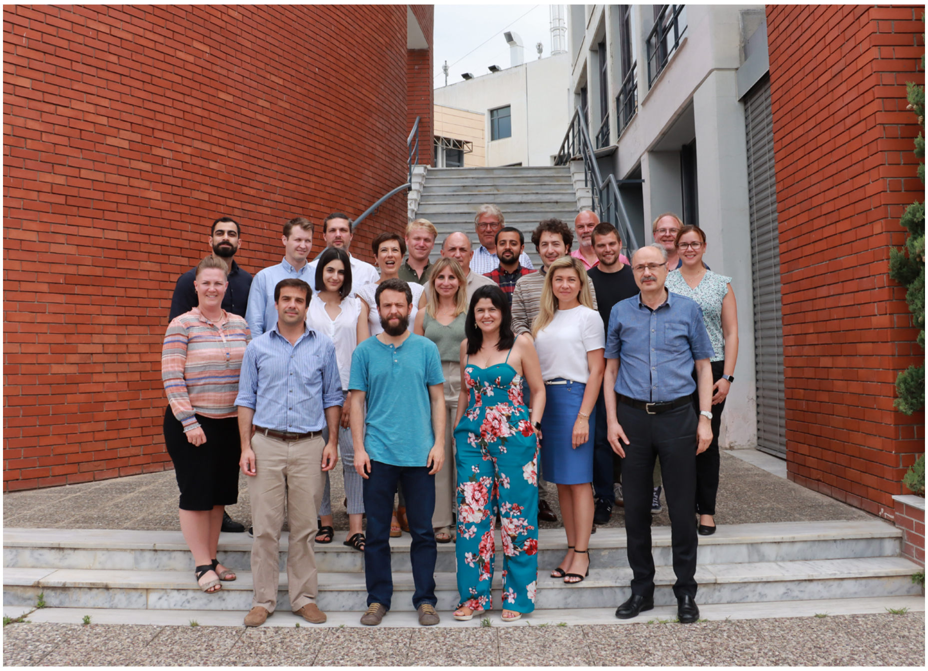
Technology wins: Pioneering research advancing the status quo of upgrading HTL biocrude in terms of process design and parameters, as well as catalysts.

Next generation biofuels: the early stage study revealed the viability of using upgraded HTL-driven fuel fractions as diesel blendstock and visualized a roadmap for future downstream activities.

Policy change makers: advancement in the technology requires policy to adjust its position in regards to classification of HTL and uses of sewage sludge.

The Project Team: Start to Finish

November 2018



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