

Please cite as: L. Moser, C. Penke, V. Batteiger, A. Roth: "Technology monitoring, application potential and market opportunities", HyFlexFuel Public Report, 2021

Public report
***Technology monitoring,
application potentials and
market opportunities***

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Project Information

Grant Agreement no.	764734
Call identifier:	H2020-LCE-2017-RES-CCS-RIA
Project full title:	Hydrothermal liquefaction: Enhanced performance and feedstock flexibility for efficient biofuel production
Project start date:	01.10.2017
Project duration:	48 months
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Public Report – Technology monitoring, application potentials and market opportunities

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Abstract:

This report provides an in depth overview of the work that has been carried out in the field of hydrothermal liquefaction and related topics. Specifically, the focus is set on technology monitoring and on the analysis of application potentials and market opportunities for HyFlexFuel products. Considering technology monitoring, state of the art as well as recently obtained results with respect to process technologies relevant for HyFlexFuel, also including results from the HyFlexFuel project, are considered. Furthermore, relevant technology gaps are identified and discussed. In addition, application potentials and market opportunities for the different HTL products, also accounting regulatory issues, are investigated. Besides the main targeted product fractions of sustainable transportation fuels, like diesel, jet fuel and gasoline, this also includes by-products such as struvite.

Submission date: 29.09.2020

Project internal reference: Deliverable D5.4, “Final report on technology monitoring, application potentials and market opportunities”

Deliverable lead beneficiary: Bauhaus Luftfahrt

This project has received funding from the European Union’s Horizon 2020 Research and Innovation Programme under grant agreement No. 764734

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Executive Summary

The present public report “Final report on technology monitoring, application potentials and market opportunities” provides an in depth overview of the work that has been carried out in the field of hydrothermal liquefaction (HTL) and related topics. The work was focused on the review of the state of the art and recent developments with respect to process technologies relevant for HyFlexFuel, which also includes results from the HyFlexFuel project. Furthermore, application potentials and market opportunities for the different HTL products are examined.

Technology monitoring

Hydrothermal liquefaction, the core conversion technology of the HyFlexFuel process chain, can be considered a “hot topic” in the field of bioenergy and biofuels that has increasingly gained attention during the past years, as reflected in the exponential growth in pertinent publications in the past years. HTL is subject to several ongoing Horizon 2020 projects. A regular exchange between HyFlexFuel and the other “HTL projects” has been established. In this context, a joint scientific workshop of all H2020 HTL projects took place on November 19, 2019, in Brussels.¹ A consensus of the possibility of HTL being commercially available within the next five years was established, fortified by statements of industrial stakeholders.

Regarding the HTL process itself, systems that can be operated in continuous mode, i.e. under industrially relevant process conditions, are increasingly gaining attention. Many associated technical challenges remain, such as effective continuous product phase separation and removal of solid products, e.g. through in-line filtration. Other issues relate to feedstock flexibility of the process, feedstock pre-treatment and the preparation of stable slurries with high dry matter content. A significant knowledge gap remains regarding yield and composition of product phases with respect to feedstock and process conditions. This is relevant for downstream process steps, particularly the upgrading and refining of biocrude.

Important research questions relate to the treatment of the aqueous product phase. This is a crucial topic for HTL as a technology that inevitably requires handling of large volumes of aqueous phase (AP) products. There are several options for AP treatment. One is recycling of the AP in the HTL process. However, the effect of AP recycling on biocrude yield and quality is not yet completely understood. Another option is application of catalytic hydrothermal gasification (cHTG) to convert organic components of the AP into energy-rich gas (mainly methane). Little is known yet about the application of cHTG for this purpose. Technical challenges are associated with the upconcentration of total organic carbon (TOC) in the AP, with catalyst lifetime and the separation of salts and sulfur-containing species from HTL AP prior to gasification. Open questions also relate to process integration with HTL: throughputs of both processes need to be aligned, and a sufficient TOC of the HTL AP is essential for economical operation of cHTG. Thus, pre-treatment of the HTL AP, e.g. membrane filtration, prior to cHTG is necessary in order to increase TOC to acceptable levels.

Anaerobic digestion (AD) can be used as alternative approach to treat and valorize the HTL AP, even though the applicability of AD has still to be demonstrated for relevant

¹ https://www.hyflexfuel.eu/wp-content/uploads/2019/03/Joint-HTL-workshop-Flyer_SMALL.pdf

process conditions. In particular, recalcitrance and even potential toxicity of certain components of the AP pose technical challenges.

The development and assessment of AP recycling, cHTG and AD as technology options for treating the HTL AP represent a central objective of HyFlexFuel. However, the technology monitoring in HyFlexFuel also includes alternative approaches reported in the scientific literature.

The upgrading and refining of biocrude into marketable products is far less developed than the HTL process itself. Consequently, many gaps in technology and knowledge remain, representing a serious hurdle for any endeavour of commercial deployment. Important issues relate to the effect of the biocrude quality on the upgrading process, the possible need for biocrude pre-treatment and tailored catalysts with long-term stability. Significant knowledge could be gained with respect to pre-treatment of biocrude from specific feedstock from batch-experiments in HyFlexFuel. This knowledge needs to be expanded on a larger variety of feedstock and on continuous mode experiments. The potential of co-refining of biocrude in conventional refineries is another important aspect that needs to be evaluated.

The recovery of inorganic nutrients entering the system with the biomass feedstock represents an additional topic that needs to be addressed and that could add value to the overall process chain. The precipitation of struvite (magnesium ammonium phosphate, $(\text{NH}_4)\text{Mg}[\text{PO}_4]\cdot 6\text{H}_2\text{O}$) offers the possibility to recover nutrients in the form of potentially marketable fertilizers. The applicability of this approach for recovering nutrients from HTL product phases has been demonstrated in the HyFlexFuel project. Nevertheless, open questions relate, i.e., challenges associated with continuous operation, completeness of recovery and purity of the precipitated struvite.

Finally, it was found that R&D activities mainly focus on individual process steps or the combination of two steps (e.g. HTL and upgrading); more research is needed addressing entire value chains, including feedstock supply, refining of biocrude to marketable products and valorizing residual process streams, particularly the AP with all its organic and inorganic compounds. Only through examining process steps in the context of complete process chains or networks it is possible to analyze issues important for and arising from process integration.

The technology gaps described above are intended to serve as guidance for future work in HyFlexFuel and further HTL developments. Future R&D efforts should endeavour to close the identified gaps in technology and knowledge in order to pave the way towards industrial implementation of HTL-based production pathways.

Application potential

This final report also describes findings from the assessment of application potentials and market opportunities for HyFlexFuel products. The main motivation for the HyFlexFuel project is the production of sustainable transportation fuels. Similar to crude oil derived fuels, upgraded HTL biocrude yields fuel in the gasoline, jet fuel and diesel range. Thus, it is important to bring the full spectrum of fuel products to the market. Among liquid transportation fuels, HyFlexFuel has a special emphasis on jet fuel production. The global jet fuel market exceeded an annual consumption of 300 Mt in 2019. In the context of the need to achieve a transition to a renewable energy basis also in the aviation sector, there is a high market potential for renewable jet fuel and, hence, also for HTL-derived jet fuel. However, for application of alternative jet fuel in civil aviation, technical approval of the specific production technology according to standard

fuel specification is required. HTL-derived jet fuel has not yet been technically approved, therefore it cannot yet be used in civil aviation. Additionally, given the current market prices of conventional jet fuel, HTL-derived jet fuel would not be economically competitive. This is a general issue in the aviation sector and true for all kinds of renewable jet fuel production pathways. Effective regulatory or market-based measures need to be installed to enable economic competitiveness and market penetration of renewable jet fuel.

Struvite is generally suitable as renewable surrogate for conventional ammonium phosphate fertilizers. There is a large market in Europe and worldwide. So far, struvite produced from biogenic sources is not certified as fertilizer according to the current European regulation framework; it is only certified at national level in several EU member states, e.g. in Germany. However, the respective EU regulatory framework is revised, and application of struvite fertilizers will become a commercial opportunity from July 2022 with the entry into force of Regulation (EU) 2019/1009.

The present public deliverable is the final report on technology monitoring, application potential and market opportunities within the HyFlexFuel project. A wide spectrum of relevant topics are discussed in depth. Specifically, this report is focused on topics related to technology monitoring and the identification of technology gaps, and the analysis of application potentials and market opportunities.

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Glossary

Abbreviation Acronym	Description
AD	Anaerobic digestion
AP	Aqueous phase
ASTM	American Society for Testing and Materials
AtJ	Alcohol-to-Jet
BtL	Biomass-to-Liquid
CHJ	Catalytic Hydrothermolysis Jet
cHTG	Catalytic hydrothermal gasification
CNG	Compressed natural gas
COD	Chemical oxygen demand
DAP	Diammonium phosphate
DCM	Dichloromethane (CH ₂ Cl ₂)
DDGS	Dried Distillers Grains with Solubles
DLD	Digestion Lysis Digestion
DM	Dry Matter
DME	Dimethyl ether
EN	European Norm
ESI	Electrospray Ionization
ETBE	Ethyl tert-butyl ether
FAME	Fatty Acid Methyl Esters
FCC	Fluid Catalytic Cracking
FT	Fischer-Tropsch
FT-SPK	Fischer-Tropsch Synthetic Paraffinic Kerosene
GHG	Greenhouse gas
HEFA	Hydroprocessed Esters and Fatty Acids
HFS-SIP	<i>Hydroprocessed Fermented Sugars to Synthetic Isoparaffins</i>
HHV	Higher Heating Value
HMF	Hydroxymethylfurfural
HTL	Hydrothermal liquefaction
HVO	Hydrotreated Vegetable Oils

IMO	International Maritime Organization
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
MON	Motor Octane Number
MTBE	Methyl tert-butyl ether
NGL	Natural Gas Liquids
OECD	Organisation for Economic Co-operation and Development
PNNL	Pacific Northwest National Laboratory
R&D	Research and Development
RED	Renewable Energy Directive
RON	Research Octane Number
TAME	tert-Amyl methyl ether
TAN	Total Acid Number
TOC	Total Organic Carbon
TRL	Technology Readiness Level
TN	Total Nitrogen

1. Introduction

The conversion of biomass into renewable fuels is a highly active field of research. Hydrothermal liquefaction (HTL), the key step in the HyFlexFuel process chain, represents a particularly promising conversion technology and has attracted considerable attention in the past decade. This has led to rapid R&D-related progress in sustainable biofuel production in general and in hydrothermal liquefaction in particular. An overview of the basic building blocks of the HyFlexFuel process chain is shown in Figure 1.

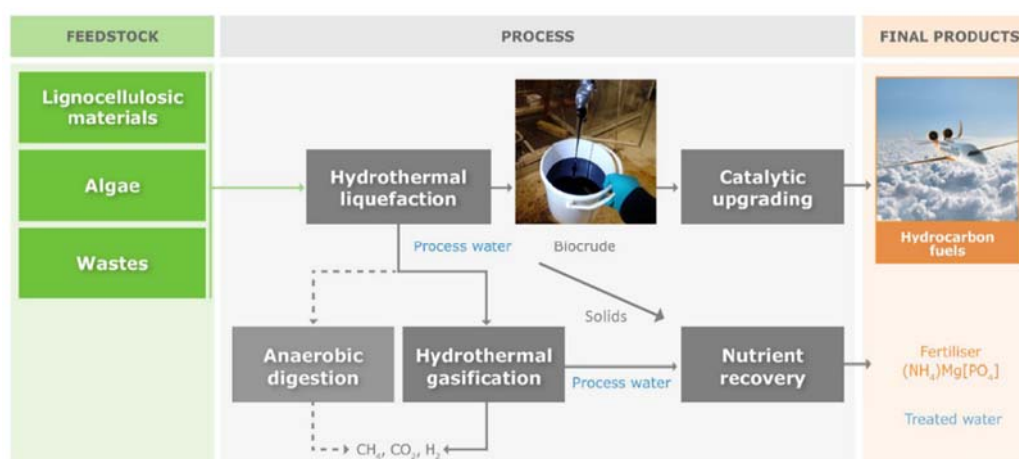


Figure 1: Basic building blocks of the HyFlexFuel process chain.

Within HyFlexFuel, various feedstocks are investigated with regard to their availability and suitability for the HTL process. Three model feedstocks, miscanthus (lignocellulosic biomass), *Spirulina* (microalgae), and sewage sludge (waste) have been chosen to demonstrate the feedstock flexibility of HTL conversion. Bulk quantities of biocrudes were produced from all model feedstocks in the pilot-scale HTL plant of Aarhus University at Foulum, Denmark. Biocrudes from two out of three model feedstocks, *Spirulina* and sewage sludge, were upgraded at Aarhus University, in close collaboration with Haldor Topsoe, via continuous hydrotreatment. The resulting hydrocarbon fuel mixtures show promising compositions for transportation fuel production. The production of combustible gases from the organic content of HTL process waters was demonstrated by the project partners OWS and PSI via anaerobic digestion and hydrothermal gasification, respectively. So far, these results stem from the pre-screening phase. Long-term cHTG and AD experiments remain as important objectives for the final project phase. Struvite, a fertilizer product, was precipitated at the University of Hohenheim, from a leachate of HTL solids. Again, these results stem from the pre-screening phase, a mini-plant for struvite precipitation was designed and it is planned to operate it during the last project phase.

The central objectives of the technology monitoring and the analyses of application potentials in HyFlexFuel are

- to monitor the state of the art and recent developments in the field of HTL-based fuel production and of biofuels in general,
- to identify important knowledge gaps or technical issues that still need to be solved (here summarized as “technology gaps”), and
- to analyse commercial potentials of main and by-products of the HyFlexFuel process chain.

The technology monitoring also includes the evaluation of technological risks associated with the individual process steps and serves the purpose of identifying technology and knowledge gaps. These gaps are intended to be used as guiding input for future R&D efforts, both within and beyond HyFlexFuel. In addition, the information collected in the course of the technology monitoring forms the basis for a high-level assessment of the HyFlexFuel process chain in comparison with alternative renewable fuel production pathways.

The technology monitoring is based on scientific literature and other publicly available sources of information, but importantly also on experimental findings from HyFlexFuel. Further experimental results and findings will be published in the upcoming public reports “Final report on feedstock analysis and characteristics”, “Final report on optimised bio-crude production campaign”, “Final report on bio-crude upgrading (parametric screening and continuous operation”, “Report on techno-economic and environmental assessment” and “Final report on production, characterization and testing of finished fuels and fuel blends”.

Next to R&D-related technical issues, knowledge of suitable markets for the targeted products is vital for any technology under development. For that purpose, an analysis of application potentials and market opportunities for HyFlexFuel products or product categories, addresses technical and/or regulatory requirements, volumes and prices of relevant markets. Relevant aspects of this report include technology monitoring of recent developments in the field of HTL as well as an overview of HTL in research and industrial projects. Different options of upgrading of the obtained biocrudes including the co-processing of biocrude with fossil crude oil in a conventional refinery is considered. A comparison of the physicochemical properties of the different fractions of the upgraded biocrudes obtained in the HyFlexFuel project with standard specifications for transportation fuels is conducted. As complementary source of revenues, the production of high value compounds, such as renewable platform chemicals, is evaluated. Furthermore, application potentials and market opportunities of the HyFlexFuel product streams are assessed. Besides the assessment of the main product upgraded biocrude, developments concerning the utilization of the aqueous phase as well as the market potential of inorganic salts (struvite) usable as fertilizers is assessed.

Technological gaps along the HTL process chain are evaluated at component and integrated system level and maturity gates for the integrated fuel production pathway are defined. Technological risks associated with the individual subcomponents and the integrated fuel production system are inferred from the technological gaps and the maturity gates and fed into the comprehensive risk assessment.

2. State of the art and recent developments in HTL conversion

This section presents a brief review of recent R&D efforts devoted to HTL-based process chains. The review is not limited to HTL itself, but also covers other important process steps, such as upgrading and refining of biocrude and treatment of residual process streams, corresponding to the scope of HyFlexFuel.

2.1 Hydrothermal liquefaction in research and industrial projects

Hydrothermal liquefaction is a “hot topic” in the field of bioenergy and biofuels that has increasingly gained attention during the past years. The risen interest becomes evident when conducting a search for the topic “hydrothermal liquefaction” on Web of Science. The search result shows exponential growth in the annual publication number, exceeding 300 per year in 2017, 2018 and 2019 (Figure 2). The search results for 2020 reflect a snapshot from June 2020.

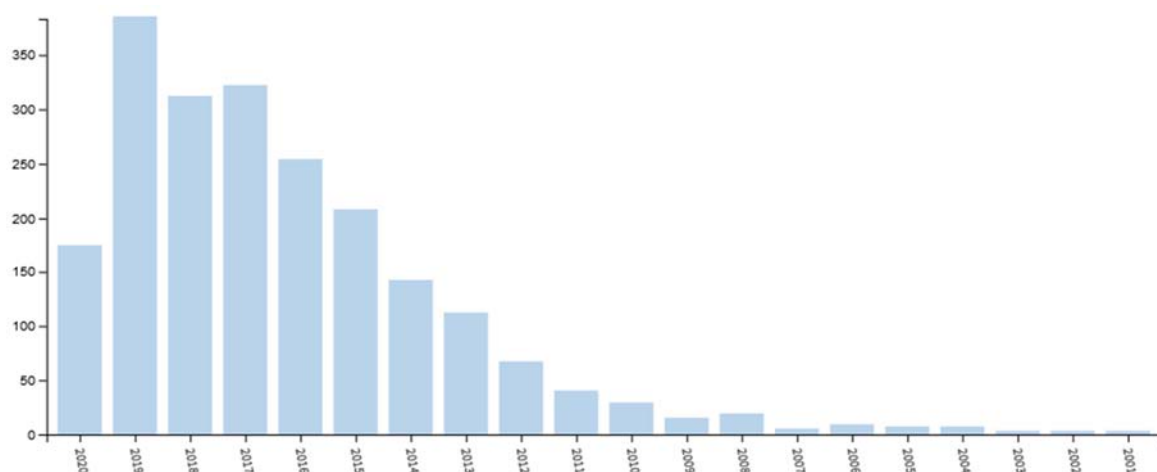


Figure 2: Temporal distribution of search results for “hydrothermal liquefaction” (in Clarivate Analytics Web of Science Core Collection; year 2001-2020)²; data recorded in June 2020.

2.1.1 HTL in current H2020 projects

HyFlexFuel is one of several ongoing EU-funded Horizon 2020 projects devoted to process chains involving HTL of biomass. These thematically related projects are briefly introduced in the following.

² The figure shows the number of publications (mainly research articles, review articles and conference proceedings paper) per year.

4REFINERY	
Scenarios for integration of bio-liquids in existing REFINERY processes	
Duration	01.05.2017 – 30.04.2021
Overall budget	5 965 473 € (100% EU contribution)
Consortium	SINTEF, CNRS, BTG, VTT, Repsol, Aalborg University, E4Tech, MOL
Website	https://cordis.europa.eu/project/rcn/209939/factsheet/en https://www.sintef.no/projectweb/4refinery/

Main objectives of 4REFINERY are

- to develop new biofuels production technology while at the same time increase understanding and control of the entire value chain and
- to scale up testing procedures and define scenarios for the best further implementation in existing refineries

HTL and fast pyrolysis are examined as primary conversion technologies in 4REFINERY. The considered feedstock are forestry residues, straw and eucalyptus. The intermediate conversion products (biocrude or biooil) are further processed through fractionation and stabilization, followed by co-processing in conventional refineries to finally yield transport-grade biofuels.

Heat-To-Fuel	
Biorefinery combining HTL and FT to convert wet and solid organic, industrial wastes into 2 nd generation biofuels with highest efficiency	
Duration	01.09.2017 – 31.08.2021
Overall budget	5 896 987 € (100% EU contribution)
Consortium	Güssing Energy Technologies, Catalonia Institute for Energy Research, RE-CORD, CEA Energy Alternatives, Johnson Matthey, Skupina Fabrika, Politecnico di Torino, TU Wien, Bioenergy 2020+, Instytut Chemicznej Przerobki Węgla, Beta Renewables, Atmosstat, Centro Ricerche FIAT, R2M Solution
Website	https://cordis.europa.eu/project/rcn/211646/factsheet/en https://www.heattofuel.eu/

Main objectives of Heat-to-Fuel are

- to deliver cost-competitive technologies achieving biofuel prices below 1 €/L through a 20% cost reduction in the biofuel production processes
- to increase the quality of the biofuel resulting in 5% life-cycle green-house gases emissions reduction
- to support local economies by generating 80-100 direct and 250 indirect jobs each time a new Heat-to-Fuel biorefinery is built, and
- to prove the technological feasibility and economic worthiness of the concept.

Heat-to-Fuel is devoted to the thermochemical conversion of wastes through a combination of gasification with subsequent Fischer-Tropsch synthesis and HTL. The project aims at enabling market readiness of the developed technology within a period of 7 years after completion of the project.

WASTE2ROAD	
Biofuels from WASTE TO ROAD transport	
Duration	01.10.2018 – 30.09.2022
Overall budget	4 996 155 € (100% EU contribution)
Consortium	SINTEF, CNRS, OMV, B.T.G. Biomass Technology Group, TU Wien, B.T.G. Bioliquids, Process Design Center, CEA Energy Alternatives, VTT Oy, Oslo Kommune, Centro Ricerche FIAT
Website	https://cordis.europa.eu/project/rcn/218229/factsheet/en https://www.sintef.no/projectweb/waste2road/

Main objectives of WASTE2ROAD are

- to develop a representative diverse and cost-effective waste supply and management system,
- to develop new biofuels production technology while increasing understanding and control of the whole value chain, and
- to scale up materials and testing procedures to define scenarios for the best exploitation through implementation of process schemes in existing refineries (achieving pilot-scale tests at TRL 5).

In WASTE2ROAD, the primary conversion technologies under investigation are fast pyrolysis and HTL. For upgrading the raw products, co-processing in existing refineries is targeted.

NextGenRoadFuels	
Sustainable Drop-In Transport fuels from Hydrothermal Liquefaction of Low Value Urban Feedstocks	
Duration	01.11.2018 – 31.10.2022
Overall budget	5 074 876 € (100% EU contribution)
Consortium	Aalborg University, Steeper Energy, Chemical Process & Energy Resources Institute, National Renewable Energy Centre of Spain, TU Munich, Karlsruhe Institute of Technology, SINTEF, Haldor Topsoe, ENI
Website	https://www.nextgenroadfuels.eu/ https://cordis.europa.eu/project/rcn/218234/factsheet/en

Main objectives of NextGenRoadFuels are

- to develop a cost-effective valorization pathway for multiple urban waste streams, such as sewage sludge, organic waste and construction wood waste, through conversion into renewable fuels, fertilizers and proteins and
- to apply different combinations of thermo-catalytic, electro-catalytic and biochemical technologies, enabling a scalable cost-competitive process that is easy to integrate into existing supply infrastructures.

NextGenRoadFuels applies HTL as primary conversion technology and considers two basic scenarios, i.e. a stand-alone model with HTL and upgrading/refining integrated in a single facility and a decentralized model with small local HTL units and a large-scale central upgrading facility.

REBOOT Generation of carbon-neutral combustibles from wastewater via hydrothermal liquefaction	
Duration	01.01.2020 – 31.12.2024
Overall budget	1 494 622 € (100% EU contribution)
Consortium	Aarhus University
Website	https://cordis.europa.eu/project/id/849841

Main objectives of REBOOT are

- to create a disruptive wet waste valorisation technology where valuable resources are re-used rather than disposed of while tackling two urgent environmental challenges: nutrient circularity and climate change
- to completely recover phosphorus from wastes while generating carbon neutral transportation fuels and a carbon sink in the form of carbon materials
- mechanistic understanding of salt behaviour in multi-phase hydrothermal systems with the aim of full recovery
- to develop tailored strategies for in-situ jet fuel synthesis
- to establish microbial electrolysis cells for in-situ hydrogen production and nutrient recovery.

CO-HTL4BIO-OIL Development of commercially viable catalytic co-hydrothermal liquefaction that converts 2G wet solid food by-products such as rye straw, shellfish, and beef tallow into a sustainable transport fuel	
Duration	01.12.2020 – 30.11.2022
Overall budget	207 312 € (100% EU contribution)
Consortium	Aalborg University
Website	https://cordis.europa.eu/project/id/895710

Main objectives of CO-HTL4BIO-OIL are

- to identify proper pretreatment prior to co-HTL for efficient removal of undesirable heteroatoms
- to validate baseline lab-scale co-HTL by determining integrated models of HTL parameters and proportions of binary/ternary mixtures
- to establish efficient catalytic upgrading to bring the HTL intermediate bio-crude oil to drop-in transport fuel
- to carry out bench-scale HTL for techno-economic assessment

BL2F	
Integrated hydrothermal liquefaction process at pulp mills to produce drop-in biofuels for aviation and shipping from black liquor.	
Duration	01.04.2020 – 31.03.2022
Overall budget	4 999 623,75 € (100% EU contribution)
Consortium	<u>Tampere Korkeakoululusaatio SR</u> , Brunel University London, Karlsruhe Institute of Technology, SINTEF, SINTEF Energi, Paul Scherrer Institut, Teknologian tutkimuskeskus VTT Oy, The Navigator Company, Valmet Technologies, Neste, Ranido, LGI Consulting
Website	https://cordis.europa.eu/project/id/884111

Main objectives of BL2F are

- drop-in biofuels production for aviation and shipping from black liquor, a side stream of chemical pulping industry
- 83 % CO₂ reduction compared to fossil fuels, and competitive production cost of 0.90 €/L for drop-in sustainable aviation fuel
- establish an integrated HTL process at pulp mills
- hydrodeoxygenation to further upgrade HTL-oil to fuel intermediate (< 5 wt% O₂), classifying as bunker-like marine fuel or feedstock for high-quality aviation and marine fuels production.

A joint scientific workshop of HyFlexFuel, the H2020 HTL projects Heat-to-Fuel, NextGenRoadFuels, 4REFINERY, WASTE2ROAD and the Norwegian National FME Centre Bio4Fuels resulted from an exchange of several H2020 projects. The workshop took place on November 19, 2019, in Brussels.³

2.1.2 Commercial HTL projects

Hydrothermal liquefaction (HTL) has not been commercially implemented yet and can therefore still be considered as emerging technology. However, there are and have been

³ A short summary, the agenda and all project presentations can be derived from: www.besustainablemagazine.com/cms2/expert-workshop-potential-of-hydrothermal-liquefaction-htl-routes-for-biofuel-production/

several projects by companies aiming industrial deployment and commercialization of HTL-based production processes. A brief description of selected examples is presented in the following (for a more comprehensive view, please refer to [1] and [2]).

Australia-based company *Licella* has developed the Cat-HTR™ (Catalytic Hydrothermal Reactor) process. *Licella* operates three separate pilot plants in Somersby, NSW, Australia. The first generation small pilot plant was built in 2009 with a capacity of 100 tonnes per annum. The second and third generation large pilot plants were built in 2011 and 2012, respectively and are able to process 1000 and 10000 t/a of organic matter, respectively. The fourth generation commercial plant was planned to be commencing in 2019 with no capacity indication yet. However, according to *Licella*, only a 2.2 scale up of the existing large pilot plant is needed to achieve the commercial level [3]. The Cat-HTR™ was originally designed to convert lignite into liquid fuels, but is now used by *Licella* to convert various types of renewable feedstock.

Muradel is another Australian company devoted to the development of HTL-based production technologies. Its Green2Black™ HTL-based technology platform is implemented in an operational demonstration plant with a capacity of about 3000 L/d feed slurry (personal communication). *Muradel* has its own microalgae cultivation test facility. Next to microalgae, the company has also applied end-of-life car tires and sewage sludge. Currently, *Muradel* is actively looking for buyers of their HTL technology and the corresponding intellectual property (personal communication).

The Danish-Canadian company *Steeper Energy* has developed, in collaboration with HyFlexFuel partner AAU, the proprietary Hydrofaction™ process. This process is unique in that it is operated at supercritical conditions [4]. The Hydrofaction™ process is the core technology of a pre-commercial demonstration plant at a former pulp mill located in Tofte, Norway [5]. The facility will use woody residues as feedstock and produce transport-grade fuels. For this project, worth EUR 50.6 M, *Steeper Energy* is partnering with Silva Green Fuel, a Norwegian-Swedish joint venture. The plant is projected to commence operation in spring 2019, after a construction phase of 18 months [6]. After a test period from 2019 to 2020, *steeper energy* is planning to build a commercial facility which will be capable of producing 100 000 tonnes of fuel per annum. The project is worth around EUR 200 M.

2.2 Research topics related to the HTL technology

2.2.1 Continuous HTL reactor concepts

The by far larger part of published studies on HTL are based on batch-mode experiments. The reason for this is mainly that such experiments are simple and quickly to conduct and do not require elaborate equipment. Batch HTL experiments allow for fast screenings of a broad range of process conditions, e.g. to identify suitable operating points for continuous systems or to analyse involved chemical reaction schemes and the impact on process conditions on the product phases. For this purpose, batch-mode parametric screenings of a range of feedstock and process conditions are carried out also in HyFlexFuel.

However, batch-mode operation of an HTL process is less suitable for industrial application, where high and efficient throughput is required to enable an economically reasonable process chain, particularly if targeting commodities like fuels as main products. For such use cases, only continuously operating HTL reactors represent

relevant systems. Therefore, it is of great importance, that continuous-mode HTL facilities are established and operated by both research institutes and companies, that enable experiments in an industrially relevant environment. A detailed review of reported continuous HTL plants can be found in a publication by HyFlexFuel partner AAU [1]. The pilot-scale HTL plant operated by HyFlexFuel partner AU which is used for all continuous HTL experiments in the project allows for an exceptionally high throughput (approximately 60-100 L/h) and enables testing at industrially relevant process conditions with integrated heat recovery.

While most of the existing continuous-mode HTL plants are operated in subcritical (often near-critical) regimes, as is also the case in HyFlexFuel, there is also significant interest in super-critical HTL systems. Important work in this field has been conducted by HyFlexFuel partner AAU [7] and Steeper Energy [5]. Supercritical HTL offers the potential of improved biocrude quality and faster kinetics, but is associated with technical challenges resulting from increased temperatures and pressures compared to subcritical conditions. While the HTL system of AU (also used in HyFlexFuel) is typically operated at 350 °C and 220 bar for example, Steeper Energy's Hydrofaction™ is operated at 390-420 °C and 300-350 bar [4].

A central challenge associated with continuous-mode operation of HTL plants is the efficient separation of product phases, particularly of biocrude as targeted product. Biocrude should contain as little water and, more importantly, inorganic salts (ash) as possible. In many laboratory-scale HTL experiments (typically conducted in batch-mode), organic solvents are added to the reaction mixture to enhance phase separation and yield biocrudes with reduced ash content. However, this is not an economically viable approach for large-scale industrial applications. A more relevant approach is based on simple gravimetric phase separation, taking advantage of the physical phase separation upon cooling of the reaction mixture, with the oil phase (biocrude) floating on top due to its lower density compared to the aqueous phase.



Figure 3: Product collection in the AU HTL pilot plant with hydro-cyclone and separation funnel.

In HyFlexFuel (at the AU HTL pilot plant), the product stream is collected under atmospheric pressure in the product collection zone (see Figure 3). The product collection zone consists of a hydro-cyclone, which separates the gaseous and liquid streams, and a 90 L separation funnel for collection and subsequent separation of the liquid products (aqueous phase and biocrude). This design has proven viable and enabled effective biocrude recovery under relevant operational conditions. However, first campaigns also showed that, in addition to effective liquid phase and gaseous phase separation, removal of solid reaction products is also crucial. Biocrude samples produced in first HTL campaigns revealed high contents of solids (primarily ash), particularly when sewage sludge was used as feedstock. The resulting biocrude contained up to 28% of ash. This amount of solids is far too much for any kind of downstream catalytic hydrotreatment. For later HTL campaigns, an in-line filter was installed to separate solid products under HTL conditions (350 °C, 220 bar) to take advantage of the reduced water solubility of inorganic salts in near-critical regimes. In an HTL run using sewage sludge as feedstock, it was found that ash content of biocrude could be strongly reduced to about 1% in the beginning of the experiment, but with increasing ash content towards longer process duration. The effective and robust in-line removal of HTL solids in continuous-mode operation is clearly an important technology gap with an impact on the quality of the yielded biocrude, but also on the recovery of inorganic nutrients: When removed from the product stream in the form of solids, recovery of inorganic salts can be achieved easier compared to cases with a high content of inorganic components in the biocrude phase.

Operation of continuous pilot-scale HTL plants, e.g. the AU HTL facility, have already yielded findings and raised questions that are highly relevant for future industrial

applications. Such applications require reliable large-scale pumps capable of pumping large volumes of slurry with high dry matter content at the required flow rate. Pumps represent crucial components in HTL systems, and failures can lead to expensive downtimes of the entire plant. Another challenge is the design of heat exchangers that enable fast heat transfer for sufficiently high heating rates of the ingoing feed stream.

2.2.2 Yields of biocrude and energy

Since biocrude is the primary target product in the HTL process, biocrude yield is often used as central metric to measure process efficiency. The biocrude yield is expressed as ratio of the obtained biocrude to the feedstock input (dry matter):

$$Y_{bc} = \frac{m_{bc}}{m_{FS,dry}}$$

However, the metric biocrude yield neglects the quality of the yielded biocrude. The biocrude quality is reflected, e.g., in its specific energy, often measured as Higher Heating Value (HHV). The energy yield Y_E combines both, biocrude yield and specific energy, and represents a more appropriate metric to assess HTL process efficiency, as also suggested by Castello et al. [1]:

$$Y_E = \frac{HHV_{bc} \cdot Y_{bc}}{HHV_{FS}}$$

The direct relation between biocrude yield and energy yield can be expressed as energy ratio r :

$$r = \frac{Y_E}{Y_{bc}}$$

For the feedstock tested to so far in HyFlexFuel by partner AU, namely miscanthus, sewage sludge, spirulina and pinewood, the achieved biocrude and energy yields as well as the energy ratio are listed in Table 1. The highest energy yield has been achieved with Spirulina und pinewood as feedstock (50.7% and 48.9%, respectively) to date in HyFlexFuel. In comparison to other reported studies on continuous HTL, HyFlexFuel results represent moderate values (Figure 4). However, it has to be kept in mind that results from HTL campaigns carried out in different facilities under different process conditions are difficult to compare. The HTL pilot-plant operated by AU has a larger throughput compared to most other plants and is thus associated with other challenges than small laboratory HTL plants.

Table 1: Results from HTL campaigns carried out by AU (γ_{bc} : biocrude yield; γ_E : energy yield; r : energy ratio) [8]

Feedstock	HHV _{FS} in MJ/kg	γ_{bc} in %	HHV _{bc} in MJ/kg	γ_E in %	r
Miscanthus	18.6	26.0	30.7	43.0	1.65
Sewage sludge	16.9	24.5	26.9	39.0	1.59
Algae (Spirulina)	21.3	32.5	33.2	50.7	1.56
Pine	20.7	31.6	32.0	48.9	1.54

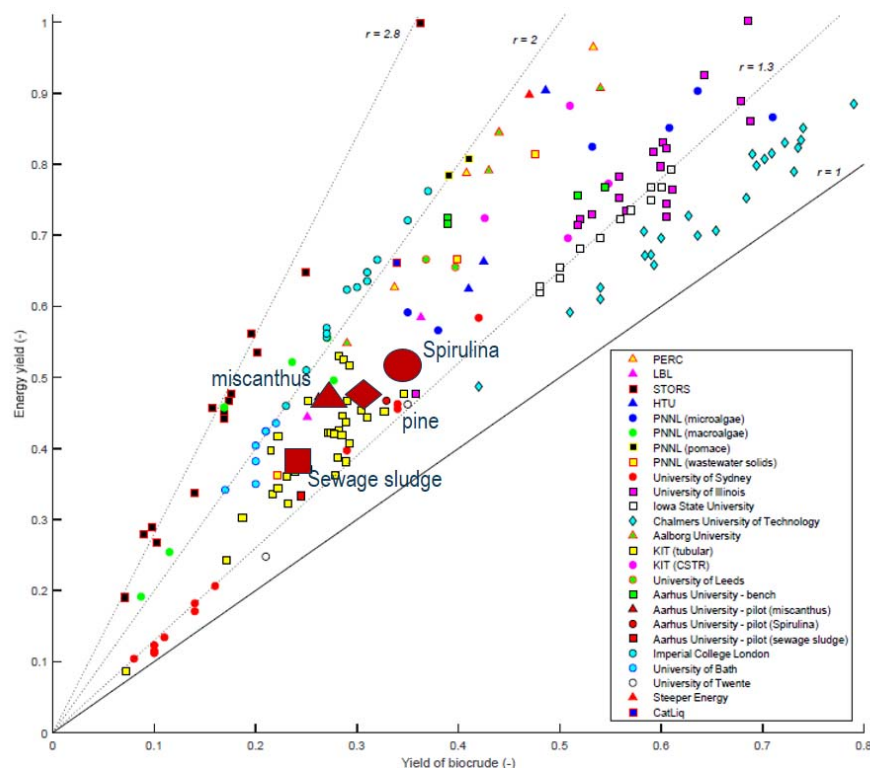


Figure 4: Energy yield from reported continuous-mode HTL campaigns on various types feedstock (Source: Castello et al. (2018) [1]). HyFlexFuel results from Table 1 included as large data points in red.

In pursuit of the obvious target to achieve high process efficiencies and improve economic performance, R&D efforts generally aim for high yields of biocrude as the desired primary product. Even though the biocrude yield alone is no sufficient metric to assess process efficiency (as described above, energy yield γ_E is a more appropriate metric), it is still an important performance indicator of HTL processes. Biocrude yields are affected by the type of feedstock and various process parameters. An important parameter in this respect is the dry matter content of the feed slurry. This relation is illustrated in Figure 5, where results from reported studies specifically on the impact of dry matter content on process yields in continuous HTL are shown.

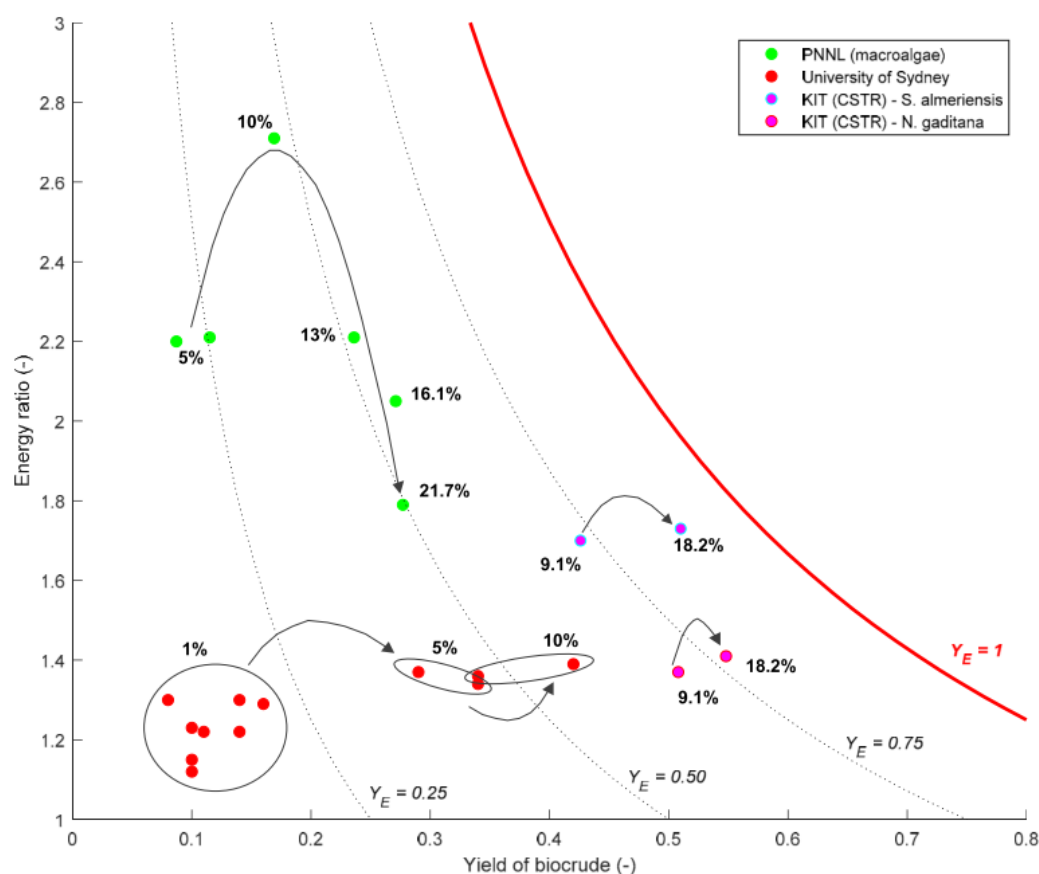


Figure 5: Impact of dry matter content (in percent values associated with the data points) on biocrude yields in continuous-mode HTL campaigns. (Source: Castello et al. (2018) [1])

It can be clearly seen that dry matter content has substantial influence on biocrude yields, while the energy ratio remains largely unaffected. As a general trend, increased dry matter content in the feed slurry leads to increased biocrude yields and, thus, process efficiency. The main reasons for this relation is that increasing dry matter content leads to an increasing volumetric ratio of biocrude to aqueous phase. This means that less material is lost to the aqueous phase through partition equilibrium between both phases. High dry matter content is also desirable for another reason: It reduces the thermal energy needed to heat the feed slurry to the HTL reaction temperature.

2.3 Upgrading and refining

The ambition of the HyFlexFuel project is to increase the technology readiness level of the key process steps along the HTL production chain, which requires in particular the validation of feasible upgrading strategies in continuous mode. Previously conducted batch-hydrotreatment experiments showed that high temperatures and pressures are necessary to achieve high levels of denitrogenation. Therefore, multi-stage strategies are suggested to reduce coke formation and to thermally stabilize the biocrudes at lower temperatures, before denitrogenation. The results of this strategy will be discussed in the following section.

2.3.1 Hydroprocessing of HTL-derived biocrude

Technologies for upgrading of biocrude are much less developed than the production of biocrude itself. In analogy to the well-established upgrading and refining of conventional crude oil, the typical approach to upgrade HTL-derived biocrude is catalytic hydroprocessing, i.e. processing under hydrogen atmosphere at elevated pressure and temperature and involving removal of heteroatoms (O, N, S), saturation of double bonds, isomerization and cracking. Typical commercial catalyst systems are based on NiMo or CoMo, which can also be pre-sulfided. On the other hand, also classical hydrogenation catalysts based on noble metals (Pt, Pd, Ir) have been used [1]. No catalyst specifically tailored for hydroprocessing HTL-derived biocrude are yet available.

A very important metric to assess the effectiveness of upgrading are the degrees of removal of oxygen and nitrogen. Removal of both sorts of heteroatoms are found to be favored at high temperatures, but denitrogenation proves to be more difficult. Complete deoxygenation is reached above 350 °C in most cases. This was also observed by the company Steeper Energy: Hydrotreating campaigns (in batch as well as continuous mode) using biocrudes derived from HTL of forestry residues resulted in complete deoxygenation and removal of acidity (TAN) at 350 °C and 370 °C, while nitrogen content was reduced down to a level of 400 ppm [4]. Interestingly, in the same study it was shown that hydrogenation of unsaturated species is favored by lower temperatures due to the exothermic nature of the reaction. Therefore, a two-zone process with a first high-temperature zone (350 °C) for removal of heteroatoms and second low-temperature zone (300 °C) for hydrogenation was examined in batch-mode, resulting in a substantially increased H/C ratio [4].

Only a limited number of studies has been devoted to upgrading of biocrude. Comprehensive reviews of research conducted in this field can be found in the literature [1,9,10]. Importantly, the majority of reported studies are based on batch-mode experiments that do not represent an industrially relevant environment, while only very few reported studies are based on upgrading in continuous mode. A team from PNNL introduced a continuous-flow mini-hydrotreater which that was used for hydroprocessing bio-oil derived from fast pyrolysis of lignocellulosic material (oak wood and switchgrass) [11]. Later, that system was also used to upgrade HTL-derived biocrude, e.g. from microalgae [12].

Another example of a study dealing with batch reactor upgrading was recently published by Haider et al. [13]. Two highly nitrogenous biocrudes obtained from primary sewage sludge and spirulina biomass were investigated therein. Due to the lack of thermal stability of the raw biocrudes at severe conditions (~400 °C) required for appropriate hydrodenitrogenation, a two-stage approach was conducted. Compared to the approach of Steeper Energy, the temperature profiles were switched. A first, low-temperature stabilization stage was used to prepare the biocrudes for a second stage of upgrading under more severe conditions. This approach yielded in complete deoxygenation and removal of 92 % of nitrogen for both biocrudes, while simultaneously reducing the coke formation from 9.1 % and 3.4 % to 1.0 % and 0.7 % for spirulina and sewage sludge, respectively [13].

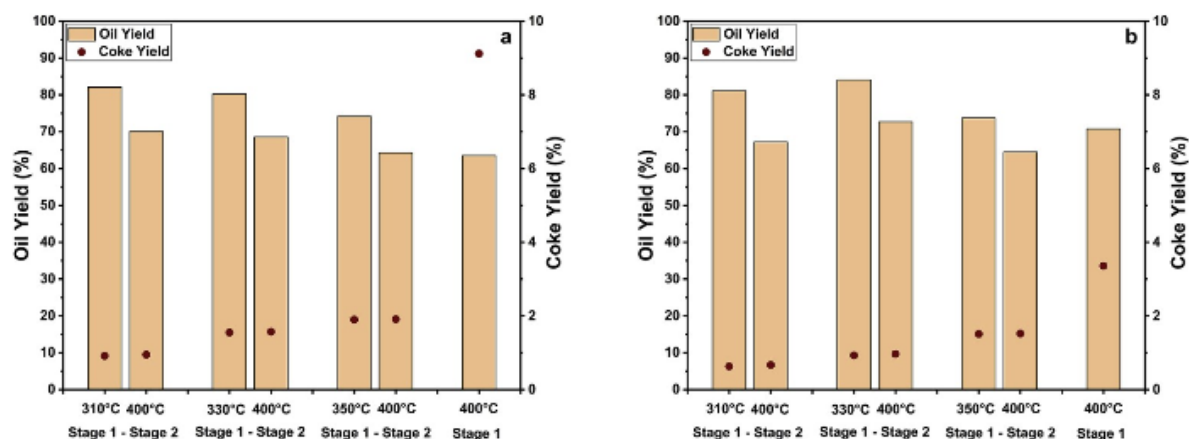


Figure 6: Comparison of oil yield and coke formation during two-stage hydrotreatment of *Spirulina* (a) and sewage sludge (b) biocrude. The results of stage 1 are shown on the left while the accumulated results of both 1st and 2nd stage (stage 2) are shown on the right, respectively [13].

Table 2 demonstrates the above outlined results of deoxygenation, denitrogenation, H/C atomic ratio and HHV. The two stage approach clearly shows the best results in all categories for both the algae, as well as the sewage sludge sample [13].

Table 2: H/C atomic ratio and HHV of the biocrude and upgraded oil samples. Both de-O and de-N were calculated based on raw biocrude), oxygen was calculated by difference [13].

Sample	de-O [%]	de-N [%]	H/C atomic ratio	HHV [MJ kg ⁻¹]
Al biocrude	-	-	1.66 ± 0.02	37.6 ± 0.2
Al 310	84.6	22.5	1.72 ± 0.01	41.9 ± 0.2
Al 310-400	100	68.6	1.83 ± 0.00	44.7 ± 0.2
Al 310	78.3	36.5	1.73 ± 0.03	42.2 ± 0.2
Al 310-400	100	76.4	1.89 ± 0.00	45.3 ± 0.2
Al 310	100	54.3	1.85 ± 0.01	44.3 ± 0.2
Al 310-400	100	92.5	2.07 ± 0.00	46.8 ± 0.2
Al 400	100	43.4	1.74 ± 0.03	43.3 ± 0.2
SS biocrude	-	-	1.71 ± 0.00	37.4 ± 0.2
SS 310	84.4	15.1	1.84 ± 0.02	43.4 ± 0.2
SS 310-400	100	74.9	2.02 ± 0.00	46.4 ± 0.2
SS 310	99.7	40.4	1.88 ± 0.01	45.0 ± 0.2
SS 310-400	100	76.5	2.02 ± 0.00	46.4 ± 0.2
SS 310	100	58.8	2.01 ± 0.00	46.0 ± 0.2
SS 310-400	100	92.1	2.16 ± 0.00	47.4 ± 0.2
SS 400	100	73.4	1.91 ± 0.03	45.8 ± 0.2

Besides the above-discussed physicochemical properties, another important property to keep in mind when discussing upgrading is the boiling point distribution. Figure 7 shows the simulated distillation curves and distillation cuts of raw and upgraded oils from *Spirulina* (a) and sewage sludge (b). As can be seen, the product spectrum obtained through upgrading is strongly dependent on the temperature. More severe conditions lead to a higher extent of cracking, which favors the formation of compounds with a lower boiling point [13].

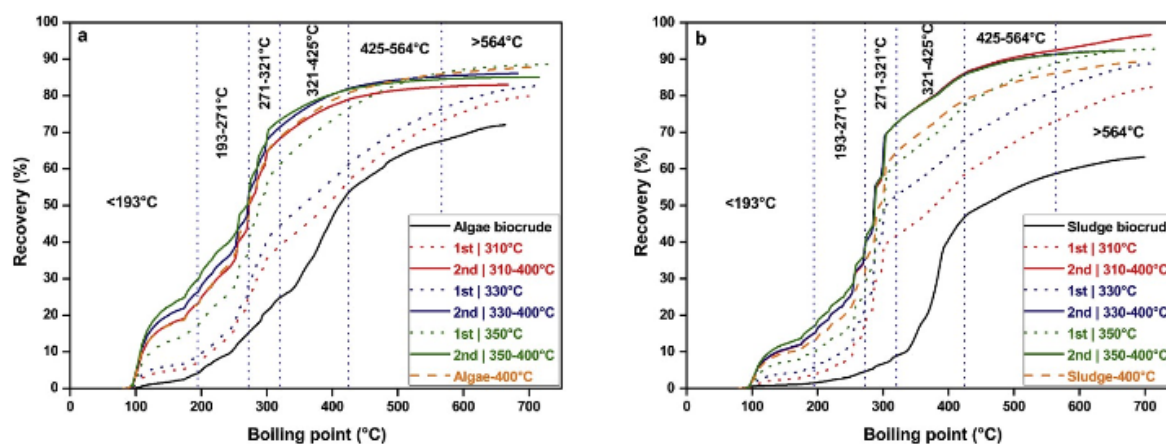


Figure 7: Simulated distillation curves and distillation cuts of raw and upgraded oils from *Spirulina* (a) and sewage sludge (b) [13].

Due to the small number of studies dealing with continuous hydrotreating experiments, there is still a large research question to be answered. Therefore, future research should deal with the implementation of successfully realized batch reactor strategies to continuous hydrotreating campaigns. Furthermore, biocrudes obtained from different feedstock might pose various different problems during upgrading. A wide variety of upgrading strategies for the diversity of possible biocrudes has to be developed.

2.3.2 Thermophysical properties vs. fuel specifications

Up to the present date, the upgraded biocrude resulting from the conversion of spirulina has been investigated in depth. In the following chapter, the different fractions are assigned to their respective transportation fuels according to their thermophysical properties, which are reported in Table 3.

Table 3: Thermophysical properties of the upgraded fractions.

No.	Boiling range (°C)		Density (kg/m ³)	HHV (MJ/kg)	Flash Point (°C)	Cloud Point (°C)	Pour Point (°C)
	From	To					
1	27.5	100	676.2	41.1 ^a	<25	<-105.0	<-105.0
2	100	150	760.9	45.3	<25	<-105.0	<-105.0
3	150	175	776.4	45.5	36	<-105.0	<-105.0
4	175	200	789.6	46.1	53	-98.5	<-105.0
5	200	225	809.4	44.9	72	-92.1	-100.5
6	225	250	828.4	45.3	91	-73.4	-77.0
7	250	275	827.8	45.6	108	-14.3	-17.3
8	275	300	806.5	45.7	131	7.7	4.7
9	300	325	815.0	44.1	143	11.0	7.9
10	325	335	828.1	46.0	156	15.1	12.1
Res.	> 335		894.4	45.0	182	n.d. ^b	-1.7

^a Value is probably underestimated, due to high sample volatility. ^b Non detectable with the used analytical instrument.

Most of the values shown in Table 3 indicate a very high potential for transportation fuel production. The measured heating values are quite high and represent those of typical hydrogen mixtures. Also, the measured densities are similar to those of hydrocarbon mixtures and are generally increasing with higher boiling points. However, a decrease from fraction no. 7 can be observed. This might be due to a change in the type of hydrocarbon species. Indeed, n-paraffins start being detected in considerable amounts as from fraction no. 7. It should be noted that the cold-flow properties (cloud and pour point) are very low up to fraction no. 6, which is a remarkable finding, especially with respect to jet fuel, since these cold-flow properties allow the utilization of the upgraded biocrude in cold conditions.

In the following, the specifications of the transportation fuels gasoline, jet fuel and diesel are shown and compared to the measured thermophysical properties above. Based on the comparison, the drop-in potential will be evaluated.

Gasoline

The main specifications for gasoline are reported in, following standard EN 228 [14] for gasoline class A.

Table 4: Gasoline specifications according to standard EN 228 [14].

Property	Unit	Spec.	Value
RON	-	min	95.0
MON	-	min	85.0
Vapor pressure	kPa	max	65-80
Density at 15 °C	kg/m ³		720-775
E70	vol. %		22-50
E100	vol. %		46-72
E150	vol. %	min	75
FBP	°C	max	210
Dist. residue	vol. %	max	2
Olefin content	vol. %	max	18.0
Aromatic content	vol. %	max	35.0
Benzene content	vol. %	max	1.0
Oxygen content	wt. %	max	3.7
Sulphur content	ppm	max	10
Oxidation stability	min	min	360
Copper strip corrosion	-		Class 1
Existent gum content	mg/100 mL	max	5

Based on the density at 15 °C, it can be observed that the fractions that qualify for gasoline production are those from no. 1 to no. 4 (see Table 3). The density values of these fractions are generally in an acceptable region, and a blend of them, made accordingly to the requirements in terms of distillation recoveries, would certainly result in the desired density value.

The chemical composition also seems promising, as the product is mostly composed of iso-paraffins and cycloalkanes, with minimal content of aromatics and olefins. On the other hand, it is important to determine octane ratings (RON, MON), in order to better qualify the product.

Jet Fuel

In Table 5, the specifications for Jet A-1 fuel are reported, following the ASTM standard D1655 [15].

In terms of distillation temperatures, the fractions from no. 4 to no. 8 can be considered. It can be observed that all these fractions present densities in an acceptable range and qualify in terms of flash point and heating value as well. As already described above, the cold-flow properties are remarkable. Cloud and pour point, which are not described in the specification, are below -70 °C up to fraction no. 6. The freezing point was not determined.

Table 5: Specifications for Jet A-1 fuel according to standard ASTM D1655 [15].

Property	Unit	Spec.	Value
Total acid number	mg KOH/g	max	0.10
T10	°C	max	205
FBP	°C	max	300
Dist. Residue	vol. %	max	1.5
Flash point	°C	min	38
Density at 15 °C	kg/m ³		775-840
Freezing point	°C	max	-47
Viscosity at -20 °C	cSt	max	8
Net heat of combustion	MJ/kg	min	42.8
Copper strip corrosion			Class 1
Existent gum content	mg/100 mL		7

Possibly even more relevant for the discussion of HTL upgraded biocrudes qualifying as drop-in jet fuel might be ASTM D7566, which defines the standard specifications for aviation turbine fuel containing synthesized hydrocarbons. In this specification, seven different fuel production pathways of synthesized hydrocarbons are specified. Some regulations, like content of heteroatoms for example, is specified more strictly in this specification than in ASTM D1655.

In ASTM D1655 the sulfur content is specified to be lower than 0.3 wt%, while the nitrogen content is not recorded as a strict number at all, but rather defined indirectly by the maximum existent gum content of 7 mg/100mL. In ASTM D7566, the sulfur content is specified to be lower than 15 ppm, while the nitrogen content has a limit of 2 ppm. These regulations are quite hard to reach with the to date developed upgrading methods. Thus, deep denitrogenation is an important aspect that requires more research.

Diesel

Table 6 shows the requirements for diesel fuel according to both European (EN590) and American (ASTM D975) standards.

The requirements regarding distillation fractions are not very strict for diesel, which is why fractions no. 6 to no. 10 qualify as diesel fuel in this regard. Concerning the densities of these fractions, the measured values are in the specified range or only slightly lower. An appropriate blending, however, would enable the use of the fractions with lower

densities. The measured flash points are in line with the specifications for all fractions between no. 6 and no. 10.

The highly paraffinic nature of the fractions leads to a sudden drop in the cold-flow properties from fraction no. 6 to no. 7, which might cause problems when applying the fuel in cold conditions. However, it might be possible to compensate for these unsuitable properties by producing blends. Moreover, the required cold-flow properties can change depending on the region of utilization, which can be considered in the preparation of the blends.

Table 6: Specifications for diesel fuel according to standards EN 590 and ASTM D975 [16,17].

Property	Unit	Spec.	EN590	D975 No. 2D
Density at 15 °C	kg/m ³		820-845	-
Viscosity at 40 °C	cSt		2.0 - 4.5	1.9 - 4.1
T90	°C	max	-	282 – 338
T95	°C	max	360	-
E250	vol. %	max	65	-
E350	vol. %	min	85	-
Flash point	°C	min	55	52
Cetane number	-	min	51.0	40.0
Cetane index	-	min	46	40
Total aromatic content	vol. %	max	-	35
Polycyclic aromatics	wt. %	max	8	-
Copper strip corrosion			Class 1	No. 3
Total acid number	mg KOH/g	max	0.08	-
Sulphur content	ppm	max	10	15

2.3.3 Co-refining of biocrude with conventional crude oil

So-called *co-refining* is an option that is currently gaining considerable attention, also in the context of other thermochemical conversion technologies, such as pyrolysis and Fischer-Tropsch (FT) synthesis based on renewable synthesis gas. The principle of co-refining is to feed biocrude (or other raw products of biomass conversion, e.g. pyrolysis oil or FT-crude) along with fossil crude oil into conventional refineries and thus take advantage of the well-established processes in such facilities that are optimized to get the highest economic value out of a given feedstock. Co-refining offers the advantage of avoiding the investment required to construct dedicated upgrading units. Reducing capital expenditure is highly attractive for capital-intensive new industrial HTL plants. For this reason, the approach of co-refining is also pursued in several H2020 projects on biofuel production, e.g. 4REFINERY and WASTE2ROAD (see Section 2.1).

However, the similarity of HTL-derived biocrude and fossil crude oil is limited, and this has implications on the application potential of biocrude as co-feed for conventional refineries. A comparison of the elemental composition of fossil crude oil and biocrude (Table 7) clearly shows that biocrudes (especially when derived from lignocellulosic feedstock) contain less carbon, but substantially more oxygen.

Depending on the feedstock, biocrudes contain also more nitrogen than fossil crude oil. A detailed analysis of the chemical composition of biocrude in comparison to fossil crude oil showed that biocrudes are mainly composed of oxygenated compounds, more

specifically of compounds that are multiply oxygenated or generally contain more than one heteroatom (O and/or N) [18], as shown in Figure 8. In contrast, fossil crude oil is dominated by pure hydrocarbons and compounds containing one nitrogen atom. In that study, it was also pointed out that biocrudes show more similarities to shale oil than to conventional crudes and that, consequently, biocrudes would “behave quite differently than crude oil in a refinery process.” Established crude oil refineries operate on specifically optimized catalysts, likewise, co-refining will require specific catalyst optimization to realize the full potential of this concept.

Table 7: Comparison of elemental composition of fossil crude oil and several biocrudes produced by AU within HyFlexFuel. (Data sources: Fossil crude oil: Ref. [19] ; Biocrudes: Ref. [20] (Miscanthus, sewage sludge, Spirulina).

Parameter	Fossil crude oil	Biocrude (Miscanthus)	Biocrude (sewage sludge)	Biocrude (Spirulina)	Biocrude (pine)
Carbon (wt%)	83-87	70.5	74.5	75.0	75.3
Hydrogen (wt%)	10-14	8.2	10.6	10.4	6.5
Oxygen (wt%)	0.05-1.5	19.6	11.0	6.9	18.6
Nitrogen (wt%)	0.1-2	1.7	3.9	7.7	0.3

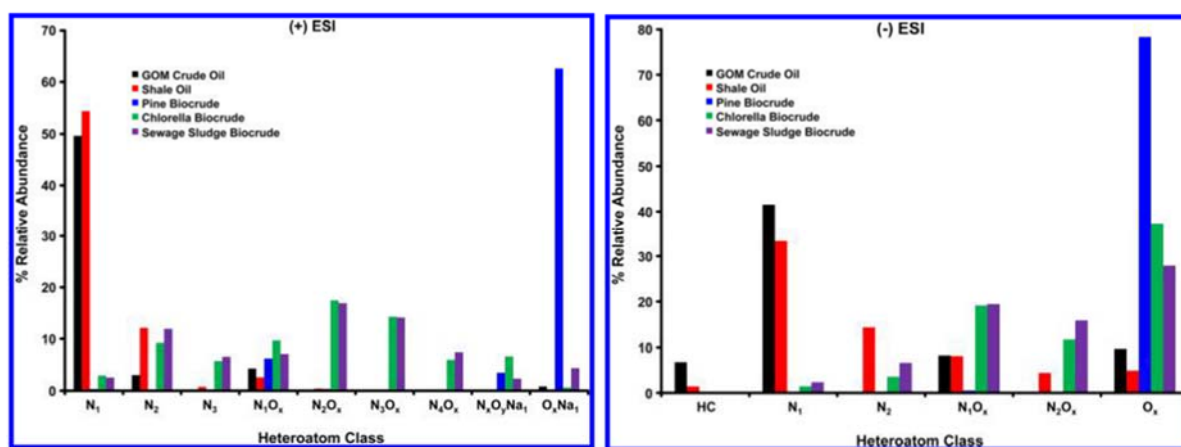


Figure 8: Distribution of heteroatom-containing species (quantified by positive (+)ESI (left) and negative (-)ESI (right) mode mass spectrometry) in HTL-derived biocrudes (from pine, microalgae Chlorella and sewage sludge), fossil crude oil and shale oil. (Source: Jarvis et al. (2017) [18])

In another joint study by Steeper Energy and HyFlexFuel partner AAU it was concluded that only a mild intermediate hydrotreatment is required to convert biocrude into a suitable feedstock for co-refining in conventional refineries [21,22]. However, this would partly abolish the principle advantage of a co-refining approach, i.e. that a dedicated unit for upgrading biocrude can be avoided. More research is needed to assess the co-refining potential of biocrudes derived from different feedstock and to identify suitable drop-in points in conventional refineries.

Evaluation of the co-processing potential

In the following, the co-processing potential of four biocrude samples derived from Spirulina, sewage sludge, pine and miscanthus produced in the HyFlexFuel project will be discussed. The biocrudes were extracted with Soxhlet using HTF as solvent and had a more liquid-like appearance, although their viscosity was still remarkable.

Nitrogen was found in relative high amounts in Spirulina and in somewhat lower content in sewage sludge. The two lignocellulosic-based biocrudes showed even lower nitrogen contents, but the highest amounts of oxygen, due to the presence of lignin and cellulose in the feedstock. Although heating values of the latter two biocrudes were lower, the lower content of nitrogen creates a higher suitability for potential co-feeding.

Sewage sludge biocrude was found to have detrimental concentrations of phosphorus in the context of hydrotreating. Furthermore, calcium was found in particular high concentrations in sewage sludge biocrude. Alkaline metals, which can be a problem in refining steps, were found in high amounts in Miscanthus and pine. Iron was found to be present in all biocrudes, with Spirulina biocrude containing the highest amount. Since the relatively high amount of inorganics represents an issue for refineries, an acid wash of the biocrudes before upgrading seems to be the only feasible option even for co-feeding or co-refining. Heavy fractions conversion processes preferably require an inorganic content of about 20 ppm and an even lower content of phosphorus is needed for fluid catalytic cracking (FCC) and hydrocracking.

The acidity levels of the biocrudes ranged between 19.5 and 87 mg KOH / g, while acidity levels of crude oils generally range from 0.1 to 2.0 mg KOH/g. Since biocrude acidity might cause corrosion of parts of the plants, it is an important metric for evaluating the co-feeding or co-refining potential. On the basis of the amount of inorganic elements and the acidity levels of the biocrudes, theoretical limits for co-feeding and co-refining can be assessed.

For the topping option, the main issue is related to the high relative acidity of some biocrudes. The TAN value of a biocrude for the topping unit of a refinery must be lower than 0.4 mg KOH/g, in order to prevent corrosion effects. Therefore, co-feeding is limited to about 1:100 with a Brent crude oil having very low acidity (TAN of about 0.1 mg KOH/g).

Main issues regarding FCC and hydrotreating are related to the inorganic content. Before these refinery units a desalter is employed. However, the desalter is not effective with an inorganic content above 200 ppm and in the removal of iron and nickel.

Considering the total amount of iron, the co-feeding limit of the biocrudes with a Brent crude oil containing 1 ppm of Fe-Ni also ranges in the low percent region.

Finally, considering the conversion processes of heavy fractions, the basic nitrogen content should preferably be less than 500 ppm in the vacuum distillate fraction. Therefore, the limit of co-feeding according to the N content of the biocrudes and of Brent crude oil (basic nitrogen content of 350 ppm)) also ranges in the low percent range, except for pine, where the biocrude fraction could be up to 10%.

Another issue associated with co-refining has to be kept in mind: During co-refining, a renewable feedstock is mixed with a fossil feed stream and various product streams contain varying shares of renewable origin. This raises a bookkeeping challenge, as potential customers would want to claim the benefits for buying a partly renewable product, e.g. to fulfil fuel quotas or emission certificates. Therefore, it has to be ensured that a traceable bookkeeping system is in place so that customers can claim their rightful “renewability benefits”, but at the same time, double-counting is prevented.

2.3.4 Alternative upgrading options

Besides hydroprocessing, there are three main other technical options that have been tested to upgrade at least parts of HTL-derived biocrude. These are solvent extraction, distillation techniques as well as esterification [23]. In the below described studies, a combination of the different techniques was performed. A comparably simple approach was studied on biocrude derived by HTL of pine wood by Australian company Licella [3]. The biocrude was distilled at “slightly above atmospheric pressure”. The distilled biocrude fraction was extracted with conventional diesel, resulting in a blend containing about 30% diesel-soluble biocrude components. The blends were tested in a diesel test engine, showing moderate combustion properties: Emissions of unburnt hydrocarbons and of nitrogen oxides (NO_x) were slightly increased, while emissions of particulate matter were reduced. The authors concluded that application of such a diesel blend in road transport would be unlikely, but application in the maritime sector or in stationary power generation would be conceivable [3].

It should be noted, that such an approach does not represent a true upgrading – it is rather a fractionation of higher value components through extraction with a hydrocarbon solvent (i.e., diesel). Thus, only the non-polar species containing low levels of heteroatoms are separated. Such a procedure leaves large parts of the biocrude behind, which is hardly acceptable from an economic perspective, and suitable ways to valorize this residue would have to be developed.

Another approach was recently reported that is also based on fractionation of biocrude (derived from HTL of wet food waste) by distillation as first step [24]. The fraction recovered in the temperature range 233-278 °C were found to mainly be composed of alkanes and alkenes, but contained also free fatty acids. Esterification with methanol was applied to strongly reduce acidity of these fractions. Combined with the distillation fraction recovered at 305 °C (used without esterification), 10 vol% and 20 vol% blends were formulated with conventional diesel. Fuel specification and engine testing showed that the blends performed comparably to pure conventional diesel with respect to cetane number, lubricity and pollutant emissions (unburnt hydrocarbons, CO, NO_x and soot [24]. However, pollutant emissions tended to be slightly increased, apart from CO emissions.

As in case of the first option (distillation combined with diesel extraction), this approach has the disadvantage of leaving a substantial part of the biocrude unused. In comparison, hydroprocessing (including cracking of heavier fractions) is a technically more demanding and more costly procedure, but offers the advantage of a) yielding products of higher quality (with total removal of heteroatoms and saturation) and of b) higher yields, as all biocrude fractions can be upgraded.

2.3.5 Relevance for HyFlexFuel

It is a central objective of HyFlexFuel to shed light on the hitherto insufficiently explored field of upgrading and refining HTL-derived biocrude into transport-grade fuels and other marketable products. As discussed above, a great deal of work on the subject of batch-mode catalytic hydroprocessing was performed [13]. Transferring the knowledge gained during these experiments on continuous-mode experiments is ongoing. Furthermore, the possibility of co-refining biocrudes or partially upgraded biocrudes in conventional refineries is explored. Combined with the comparison of upgraded biocrude properties with standard specifications of transportation fuels, these findings correlate the results from scientific experiments with the needs from a practical perspective in an early stage at low TRL.

Based on findings from chemical analysis of produced biocrudes and from hydroprocessing experiments, novel catalysts specifically for upgrading HTL-derived biocrude will be developed. The development of novel catalysts mainly deals with poisoning issues due to higher amount of contaminants in the biocrudes (metals, silicon, phosphorus) compared to fossil crude oil.

2.4 Treatment of the HTL aqueous phase

In HTL, the aqueous phase (AP) represents the by far largest product stream in terms of volume. This is a consequence of the fact that the slurry feeding the HTL process contains a large share (about 80% [25]) water. Major quantities of organic compounds formed during the HTL process as well as a range of inorganic salts are present in the AP. The organic content of the AP can sum up to 50% or even more of the organic content of the feed slurry [26]. The substantial organic and inorganic content makes the treatment or utilization of the AP a crucial aspect in the development of HTL-based value chains. There are two basic reasons for this:

- a. The high organic load poses environmental risks, in particular in case of hazardous or toxic compounds, such as phenols or ketones, which are typically present in HTL AP. Moreover, high concentrations of inorganic salts lead to eutrophication problems, when released to the environment. Consequently, HTL AP has to be treated prior to disposal.
- b. Given its large volume and considerable concentration of organic and inorganic components, HTL AP has an economic value that has to be exploited. Considering that up to 50% of the organic carbon in the feed slurry ends up in the AP, it is obvious that this share has to be valorized in order to achieve reasonable process efficiencies and an advantageous economic performance.

Therefore, treatment of the AP is required for both, environmental and economic reasons. This is not a new finding, but only very limited research efforts have been devoted to this important topic; the scope of most published studies is restricted to the HTL process itself. Nevertheless, some concepts of treating and/or utilizing the AP have been suggested and researched.

When considering options to treat the HTL AP, the dry matter content of the feedstock plays a crucial role. Comparably dry types of feedstock, mainly lignocellulosic materials, such as woody biomass or straw, require additional water to prepare pumpable slurries with a suitable dry matter content of 10-20%. In this case, it is in principle possible to recycle the AP without treatment and use it to prepare the slurry feeding the HTL process.

In case of wet feedstock, such as manures, sewage sludge and microalgae, that naturally contain more water and less dry matter than needed for HTL, i.e. that even require prior dewatering, recycling of the AP in the HTL process is not possible. Microalgae represent a special case, as the AP can in principle be recycled back as growth medium for microalgae cultivation. But in case of sewage sludge, manures and other wet feedstock, AP has to leave the system after appropriate treatment (and valorization).

The probably most frequently (but still scarcely researched) technology option for treating the HTL AP is (catalytic) hydrothermal gasification (cHTG). In this process, water-soluble organic compounds are hydrothermally converted to energy-rich gases (methane and hydrogen) and CO₂. Another option to treat the AP is anaerobic digestion (AD). AD is a well-known biological process to convert biomass into biogas, a mixture of mainly methane and CO₂. AD can also be applied to treat wastewater streams containing biodegradable organic compounds and is therefore an interesting technology option for energetic valorisation of the HTL AP through conversion of its organic components into

biogas. In the following, the above-mentioned options for treating the HTL AP as well as recent developments and findings are briefly discussed.

2.4.1 Aqueous phase recycling

Utilization of “dry” feedstock, where water has to be added in order to prepare suitable slurries for HTL processing, offers the option to recycle the AP partially or completely: The AP is thereby used for the preparation of the slurry and is fed back into the HTL process.

Adding AP instead of pure water to the feed slurry not only helps to avoid the necessity to treat and dispose of large volumes of AP, it also changes the reaction conditions of HTL. The AP contains significant quantities of organic species, mainly oxygenated species, such as aliphatic alcohols, phenols, acids and ketones [27], with Total Organic Carbon (TOC) content of some 20% or more [28] (consistent with results from HTL AP produced in HyFlexFuel). Furthermore, the AP contains a broad range of inorganic salts and elements, with major components being NH_4^+ , PO_4^{3-} and Mg^{2+} . The results of the chemical characterization of the AP from HTL of microalgae *Nanochloropsis* published by Shanmugam et al. (2017) [29] are presented in Table 8.

The dissolved organic and inorganic compounds substantially change the physical and chemical properties of the AP, such as ionic strength, pH, dissolving properties etc. Recycling the AP in HTL is therefore likely to affect reaction pathways, kinetics and, in consequence, yields and quality of the product phases. The approach of recycling the AP in HTL has been addressed only in a small number of studies. For example, recycling of the AP is applied by Steeper Energy in their Hydrofaction™ process [4]. They report a number of advantages associated with this procedure. The oxygenated organic species in the AP support the preparation of a stable and pumpable feedstock slurry. Furthermore, water soluble organics present in recycled AP can possibly “act as radical scavengers or stabilizers of intermediate products as well as hydrogen donors during heat-up and conversion, thereby inhibiting the formation of undesired char products and promoting the de-oxygenation reactions via hydrogenolysis” [4].

Table 8: Selected results from chemical characterization of the AP from HTL of microalgae *Nanochloropsis* reported by Shanmugam et al. (2017) [29].

Parameter	Value
TOC (mg/L)	28590 ± 200
TN (mg/L)	13250 ± 168
COD (mg/L)	62461 ± 437
$\text{NH}_4^+\text{-N}$ (mg/L)	5000 ± 300
PO_4^{3-} (mg/L)	3900 ± 285
Mg^{2+} (mg/L)	240 ± 20
Ca (mg/kg)	3.76 ± 0.31
Fe (mg/kg)	1.96 ± 0.14
S (mg/kg)	433.91 ± 53.60
K (mg/kg)	1510.52 ± 240.30
Na (mg/kg)	453.76 ± 21.27

As a general observation in the published studies, an increase in biocrude yields is reported as a consequence of AP recycling. However, the same studies give an inconsistent picture of the effect on the quality of the yielded biocrude. An overview of reported studies addressing AP recycling along with the respective feedstock, process conditions, sample work-up as well as impact on yield and quality (using the higher heating value (HHV) as proxy) of biocrude is presented in Table 9. This overview shows that biocrude yields were found to increase upon AP recycling, for all types of feedstock and for both, batch and continuous-mode experiments. The HHV, indicating the quality of the yielded biocrude, however does not show a consistent trend: It increases in some cases, while decreasing in others. A comparison of the reported studies is difficult, as they differ in too many aspects, such as mode of operation, feedstock and sample work-up. In particular, solvent extraction was used in most studies to separate product phases. This can have a significant effect on yield and quality of the isolated biocrude.

There are several conceivable reasons for the positive effect of AP recycling on biocrude yields:

- Concentration and saturation effects: AP recycling increases the concentration of organic and inorganic species in the AP. For example, total organic carbon (TOC) and total nitrogen (TN) were shown to strongly increase upon recycling from about 20 and 5 g L⁻¹ to more than 90 and 20 g/L⁻¹, respectively [28]. This increase could lead to “pushing” more water-soluble species into the oil phase, thus increasing biocrude yields.
- Chemical effects: Water-soluble species could further react upon recycling, forming larger and more hydrophobic compounds that move into the oil phase. This would increase biocrude yields *and* quality.

Unfortunately, the understanding of the implications of AP recycling in HTL in terms of yields and quality of biocrude is still very limited to date. It is obvious, though, that concentration/saturation effects would result in a decreased biocrude quality: Water-soluble organic species are oxygenated and/or nitrogenated (thus, polar) compounds and reduce the HHV of the resulting biocrude.

An additional study (not listed in Table 9) on the effect of AP recycling showed no significant change in biocrude yield, but a minor increase in biocrude quality [30]. However, in that study glycerol was added to the recycled AP and HTL was conducted under supercritical conditions (feedstock: aspen wood; HTL in batch-mode); it is therefore uncertain to which extent it is comparable to studies on purely aqueous systems operated at subcritical conditions.

In conclusion, it can be stated that reported studies do not convey a consistent picture of the effects of AP recycling and that suggested explanations for observations are hypothetical. More systematic experiments are required to shed light on this aspect that is highly relevant for industrial implementation of HTL-based value chains. Important research questions in this respect are:

- How does AP recycling affect biocrude *yields* under industrially relevant process conditions (i.e., continuous-mode operation, no solvent extraction)?
- How does AP recycling affect biocrude *quality*, i.e., is there a trade-off between yields and quality?
- Are the effects feedstock-dependent?
- Is a hybrid approach more viable, where the AP is recycled only in part and mixed with pure water?

Table 9: Published studies on the effect of HTL aqueous phase (AP) recycling on biocrude yields and biocrude quality in terms of heating values relative to experiments without AP recycling.

Study	Feedstock	Process conditions	Solvent extraction	Biocrude yield	Heating value
Biller et al. (2016) [28]	DDGS	Continuous (350 °C; 2x recycling) and then batch (340 °C; 8x recycles); with and without K ₂ CO ₃ catalyst	Yes (DCM); but no contact of AP with DCM; extracted biocrude contains only components soluble in DCM	Increasing	Slightly increasing (uncatalyzed); Decreasing (catalyzed)
Pederson et al. (2016) [30]	Aspen wood	Continuous (400 °C; 300 bar; 4x recycling)	Yes (glycerol)	Increasing	Increasing
Klemmer et al. (2016) [31]	DDGS	Continuous (350 °C; 250 bar; 2x recycling)	No	Increasing	Decreasing
Hu et al. (2017) [32]	Microalgae (Chlorella vulgaris)	Batch (275 °C, 50 min; 4x recycling); with and without Na ₂ CO ₃ catalyst	Yes (formic acid)	Increasing	No change
Ramos-Tercero et al. (2015) [33]	Microalgae	Batch (220/240/265 °C, 30 min; 6x recycling)	Yes (DCM); but no contact of AP with DCM; extracted biocrude contains only components soluble in DCM	Increasing	Decreasing (slightly)
Déniel et al. (2016) [34]	Blackcurrant pomace	Batch (310 °C; 10 min; 5x recycling)	Yes (ethyl acetate); no contact with AP; extracted biocrude contain only components soluble in ethyl acetate	Increasing	Increasing
Zhu et al. (2015) [35]	Barley straw	Batch (300 °C; 15 min; 3x recycling)	Yes (acetone); no contact of AP with acetone; extracted biocrude contains only components soluble in acetone	Increasing	Increasing (slightly)
Parsa et. al (2018) [36]	Macroalgae	Batch (350 °C; 15 min; 2x recycling)	Yes (DCM)	Increasing	Not analyzed

2.4.2 Catalytic hydrothermal gasification (cHTG)

The HTL aqueous phase (AP) still contains significant amounts of organic compounds. Energetically utilizing the organic components dissolved in the AP is an obvious option in order to improve the overall process efficiency.

In order to convert the organic components of the AP into usable products, (catalytic) hydrothermal gasification is a promising option. At temperatures beyond 400°C, various homogeneous and heterogeneous catalysts can be used to convert organic compounds into the basic components methane, hydrogen, carbon dioxide and carbon monoxide. Watson et al. [37] identified the reaction pathways for the gasification of HTL AP and presented them as a reaction diagram (Figure 9).

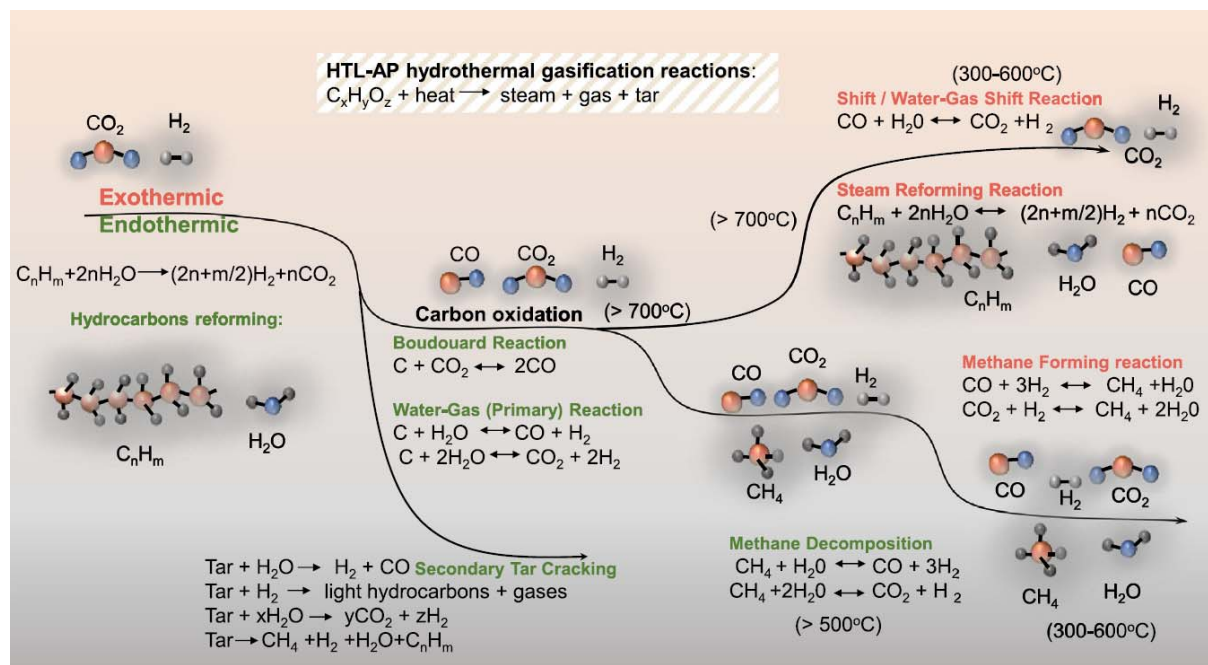


Figure 9: Reaction diagram of the reactions occurring during AP gasification (Source: Watson et al. (2020) [37]).

Gasification in supercritical water, which can be assisted by heterogeneous catalysts, has proven to be a suitable process for the production of a high-energy gas. The applicability of catalytic hydrothermal gasification (cHTG) for the conversion of different types of biomass feedstock, such as wood sawdust, algae, fermentation residues and waste glycerol, has been demonstrated in several studies [38]. The organic content of the feed streams has found to be almost completely (up to 99%) gasified through cHTG, yielding a highly energetic product gas stream (54 vol% CH₄, 42 vol% CO₂, 4 vol% H₂ and < 0.1 vol% CO) [39].

The applicability of cHTG for the conversion of the organic components of HTL AP has been demonstrated by PNNL [40]. An organic carbon conversion efficiency of about 99% was achieved for HTL AP produced from woody biomass, algae and sewage sludge [41]. Energy-rich gases could be generated in the process. For example the product gas for the conversion of sewage sludge AP is composed as follows: 74 wt% CH₄, 22 wt% CO₂ and 1 wt% H₂ [40].

Ru/C has proven to be particularly suitable as catalyst in cHTG, furthermore Raney-nickel and carbon have a catalyzing effect on hydrothermal gasification of HTL process water [42,43]. To avoid poisoning of the precious catalyst by sulfur-containing compounds, it is important that an effective trapping of sulfur-containing species and salt separation upstream of the catalyst is performed [42]. Such a sulfur trap, typically based on transition metals like zinc, is also installed in HyFlexFuel partner PSI's cHTG plant Konti-C to protect the Ru/C catalyst [42,44]. In the treatment of the aqueous HTL phase via cHTG, several studies have been carried out in recent years with the aim of integrating these two process steps. The efforts of process integration are described in more detail in Section 2.6.

Another challenge regarding the application of cHTG for treating HTL AP is the thermal efficiency. If the organic carbon concentration of the inputs for the cHTG is below 50 g/L, the process has a negative energy balance as more energy is required to maintain the gasification reaction than is harvested in the form of methane. Therefore, the applicability of cHTG for treating HTL AP is only reasonable with high organic loads of the water phase. As essential parts for stable continuous-mode operation of the cHTG unit under relevant conditions, salt separator and sulfur trap are subject to permanent efforts of development and optimization at PSI. According to Watson et al, there are three main factors that affect the performance of AP gasification: Reaction temperature, residence time and catalyst selection [37].

2.4.3 Anaerobic digestion

An alternative approach to energetically valorize aqueous HTL phase is anaerobic digestion (AD), a process in which microorganisms break down biodegradable material into biogas.

The digestate generated as by-product contains the majority of inorganic nutrients and can be used as fertilizer. The technique of AD is frequently utilized in wastewater treatment plants, but only a few studies devoted to the application of AD for treating the HTL aqueous phase have been reported to date. One of those studies included an economic assessment that indicates that AD is economically more favourable compared to cHTG for energy valorization of the HTL AP [45].

A challenge in the biological conversion of AP by AD are inhibitors, which can lead to low conversion efficiencies. A suitable pretreatment can improve the efficiency of AD by removing inhibitors or converting them into readily biodegradable compounds. The main pretreatment methods are partial oxidation, adsorption and extraction and are described in Table 10.

Table 10: Pretreatment methods for anaerobic digestion of HTL AP. (Source: [37])

Pretreatment	Main process	Benefits
Partial oxidation	Incorporation of ozone, UV, and H ₂ O ₂ in order to oxidize the aromatic ring structures and N-heterocyclic compounds	Recalcitrant compounds are converted into more biodegradable products
Adsorption	Adsorb organics and inorganics using activated carbon and zeolite	The potential inhibitors for biological conversion are adsorbed, including N-heterocyclic compounds, aromatic compounds, and ammonia
Extraction	Extraction of organics and inorganics through organic solvents, resins, nanofiltration, and struvite formation	The potential inhibitors for biological treatment are extracted from HTL-AP, including aromatic, nitrogen-containing organics, and ammonia

Shanmugam et al. [29] have investigated the possibility of nutrient recovery from microalgae used as HTL feed in the form of struvite and subsequent biogas production via anaerobic digestions. They concluded that the methane yield of AD can be up to 3.5 times higher than without previous struvite precipitation. Tommaso et al. performed biomethane potential tests on HTL water from microalgae and found a biodegradability of 35-84% [46]. In comparison to these studies, in HyFlexFuel it is aimed to examine the possibility of anaerobic digestion with *subsequent* struvite precipitation.

The fact that the efficiency of AD in treating the HTL AP is uncertain and little knowledge exists on the sensitivity of microorganisms to potentially recalcitrant or even toxic organic compounds in the HTL AP calls for further studies. Future work in this context should also focus on possibilities to integrate continuous AD into an HTL plant of industrial scale and under relevant conditions.

Other aspects to be considered with respect to application of AD relate to the behavior of microorganisms at low concentrations of organic compounds in the HTL AP and the adaptivity of the AD process to varying compositions of feed stream. Overall, more research is needed to close the knowledge gaps regarding the application of AD in the context of HTL-based process chains.

2.4.4 Alternative approaches for treatment of the HTL aqueous phase

Besides hydrothermal gasification and anaerobic digestion, a few other technology options to valorise the AP are discussed in the scientific community.

In a recent article, application of *membrane distillation* has been suggested as such a technology option [47]. Membrane distillation is a well-known technique to treat various aqueous streams. It is based on a vapour pressure gradient across a hydrophobic membrane driving the transport of water vapour or other volatile compounds through the membrane, while the liquid phase with all dissolved non-volatile species is hindered by the hydrophobic membrane from passing. The vapour pressure gradient is induced by temperature difference. The conceptual idea is to apply membrane distillation to the hot HTL AP and let pure water (vapour) pass through the membrane into a colder permeate stream. This water could then, theoretically, be safely disposed or used for other purposes. The remaining retentate stream contains high concentrations of inorganic salts and non-volatile organic compounds and is thought to be useful for fertilizer applications.

However, first experiments indicate that several issues associated to this approach [47]:

- Volatile organic compounds pass through the membrane, rendering treatment of the permeate stream necessary before disposal.
- Membrane fouling: The membrane revealed increasing permeability for non-volatile organic compounds.
- The raw concentrated retentate stream is not directly applicable as fertilizer for two reasons. 1) Not all inorganic salts are desirable as fertilizers. 2) Non-volatile organic compounds could be hazardous, e.g. phenols, and need to be removed first.
- Treatment of the concentrated retentate stream is also required for economic reasons: The organic compounds need to be energetically valorised, otherwise an economically viable operation of the overall process is hardly conceivable.

In another article the application of *microbial electrolysis* for treatment of HTL AP from conversion of swine manure is reported [48]. A schematic illustration of the applied microbial electrolysis cell is presented in Figure 10. The cell consists of an anode made of activated carbon and is colonized by a consortium of anaerobic bacteria. The bacteria anaerobically digest organic substrate compounds that are adsorbed at the porous anode material. The resulting electric current is used at the cathode, made from nickel foam, to evolve hydrogen.

This microbial electrolysis set-up was found to achieve high COD removal of 90-98% and performance stability [48]. A serious drawback of this technology could be an insufficient energy yield in the form of hydrogen. The reported efficiencies (ratio of yielded chemical energy as hydrogen to external electric energy input) ranged from below 100% (net energy consumption) to 120%, depending on experimental conditions. A detailed mass and energy balance based on findings from experiments under relevant operational conditions is required to assess the economic viability of the suggested approach. The high reported COD removal and performance stability but comparably low efficiencies found in first laboratory experiments indicate that microbial electrolysis could be an effective technology for HTL AP treatment, enabling the disposal of the treated water, but not for efficient energetic valorization. However, both aspects, effective treatment (removal of hazardous organic compounds) and energetic valorization, are important for an economically viable process design.

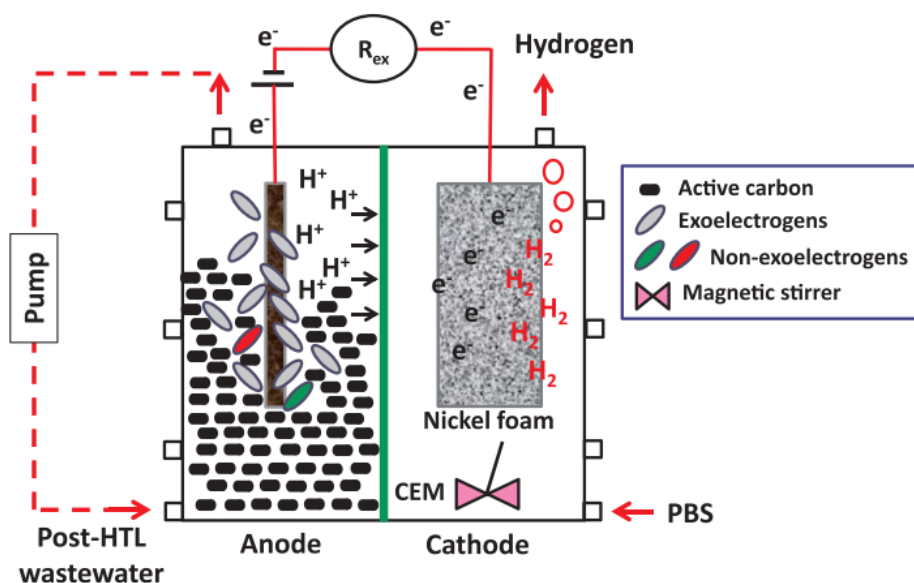


Figure 10: Schematic representation of the applied microbial electrolysis cell. (Source: [48])

2.4.5 Separation of marketable chemicals

Organic compounds in HTL AP have a broad variety of applications ranging from liquid fuels to the extraction of high quality chemicals. Possible technical applications and market opportunities for substances and chemicals that can be obtained from the HTL AP are shown in Table 11.

Table 11: Chemical components present in the HTL AP with possible applications. (Sources: [37,49–54])

Chemical component in AP	Possible Application	Reference
Acetamide	Heat storage material in solar systems	[49]
Acidic acid	Manufacturing of polyethylene terephthalate (PET)	[50]
Amides	Fuel additives	[51,52]
Glycolic acid	Cosmetics	[50]
N-organics	Pharmaceuticals, agrochemicals, solvents	[53,55]
Phenol	Input for petrochemical processes (dyes, antioxidants)	[54]
Pyrazines	Perfumes, pharmaceuticals, and agricultural chemicals	[53]

The separation and concentration of chemicals from the HTL AP is a major challenge for a value-added chemical extraction and has already been studied in several previous studies. Zhang et al. report that they extracted carboxylic acids from a model solution of HTL-AP [56]. Chen et al. carried out the extraction of phenolic compounds from rice straw HTL-AP and achieved a phenolic compound content of 78% in the aqueous solution [57]. Lyu et al. separated the HTL AP from straw by a two-stage nanofiltration into a glucose, a monophenol and a cyclopentenone concentrate as well as acetic acid permeate [58].

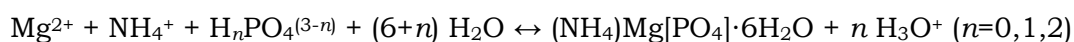
On the one hand, high profits can be achieved by the separation of high-value chemicals from the AP. On the other hand, a complex separation technique is associated with high costs and requires more work in R&D. Therefore, the economic efficiency and sustainability of the HTL-AP separation technology for the recovery of high-value chemicals should be evaluated in the context of the entire HTL process chain on an industrial scale.

2.5 Recovery of inorganic nutrients

The closure of nutrient cycles represents an important aspect of a future circular economy. The growing need to cultivate biomass to meet the global demand for food, feed, fuels, materials and chemicals corresponds to growing demand for fertilizers. In the light of conventional fertilizer production through energy-intensive processes (ammonia) or from mineral (depletable) geological reserves (phosphate), it is of great importance to close nutrient loops and enable a renewable supply of fertilizers. From an ecological and economic point of view, recycling of nutrients, particularly phosphorus, is therefore generally desirable wherever process streams rich in phosphorus occur. This surely applies for HTL-based production chains. In recent years, a number of techniques that

enable the recovery of inorganic nutrients, such as phosphorus, have been developed. An overview of the proposed techniques is presented in Table 12.

In principle, phosphorus recovery in wastewater treatment plants is possible either by precipitation from the digested sludge or the supernatant liquor or from the sludge ash. In full-scale plants, where phosphorus is recovered through precipitation of struvite from digested sludge or supernatant liquor, a maximum recovery rate of 40% is currently possible (see Table 12). The process is limited to the extent that only a certain proportion of phosphorus can be dissolved from the solids. The formation of struvite can be described as follows.



In the subsequent struvite precipitation, at least stoichiometric quantities of magnesium and ammonium salts have to be present in the aqueous phase to enable an effective phosphorus recovery. Depending on the HTL feedstock and its specific inorganic nutrient content, adjustment of the concentrations of Mg^{2+} (e.g. in form of $\text{Mg}(\text{OH})_2$) and ammonium salts might be necessary to enable high recovery rates [59].

In case of ash from sludge incineration being used as starting material, phosphorus can also be recovered in the form of phosphoric acid (H_3PO_4), or as CaNaPO_4 . However, these technologies are not yet mature and still under development. Presently in Europe, sewage sludge is mainly incinerated in wastewater treatment plants (e.g. approximately 65% in Germany [60]) which makes nutrient recovery from sludge ash attractive.

Table 12: Overview of processes for phosphorus recovery in waste water treatment. (Source: [61])

Starting point	Term/process	Product	Development status	Recovery rate
Precipitation in digested sludge	1. Without forced dissolution, e.g. Airprex	Struvite	Full-scale	5-15%
	2. Lysogest	Struvite	Full-scale	5-15%
	3. With Pondus hydrolysis of excess sludge	Struvite	Full-scale	5-15%
Precipitation in supernatant liquor	4. Without forced dissolution, e. g. Pearl, NuReSys, Phospaqa	Struvite	Full-scale	5-25%
	5. With excess sludge pre-treatment via Wasstrip	Struvite	Full-scale	10-40%
	6. With Haarslev hydrolysis	Struvite	Piloting, full-scale in construction	15-35%
	7. With mixed sludge pre-treatment via Wasstrip and digested sludge hydrolysis via Lysotherm	Struvite	Full-scale	15-40%

	8. Stuttgart Process	Struvite	Piloting	Up to 50%
	9. EcoPhos H ₃ PO ₄	H ₃ PO ₄	Piloting	>90%
	10. TetraPhos	H ₃ PO ₄	Piloting, full-scale in construction	>80%
Sludge ash	11. Direct reuse of sewage sludge ash in conventional fertilizer industry	-	Large-scale campaigns	Up to 100%
	12. AshDec	-	Piloting	>90%

The product phases of HTL, particularly the solids and the aqueous phase, offer potentials for the recovery of inorganic nutrients, particularly macronutrients, such as phosphorus, potassium and nitrogen. Some results from current research on this subject are summarized in the following.

Ovsyannikova et al. [62] recently published a paper dealing with the distribution of nutrients throughout the different phases of continuous pilot-plant scale HTL experiments with *Spirulina* and primary sewage sludge as feedstock. On the basis of nutrient distribution, strategies for nutrient extraction and recovery were identified. It was found that the distribution of phosphorus strongly depends on the abundance of multivalent cations, such as Ca²⁺, Mg²⁺, Al³⁺ and Fe^{2+/3+}. A high abundance of these cations may lead to a higher extent of precipitation of phosphate salts. In consequence, this leads to the solid phase being the main reserve of phosphate. In the study, this behavior could be observed for sewage sludge (19.3 wt% ash). On the other hand, phosphates from *Spirulina* (5.8 wt% ash) were found both in the solid phase, as well as in the aqueous phase. In contrast to the above-mentioned multivalent cations, which showed the tendency of precipitation and were found mostly in the solid phase, monovalent cations (K⁺, Na⁺) mostly remained dissolved in the aqueous phase. The estimated elemental balance for the HTL runs of the two feedstocks sewage sludge (A) and *Spirulina* (B) are shown in Figure 11.

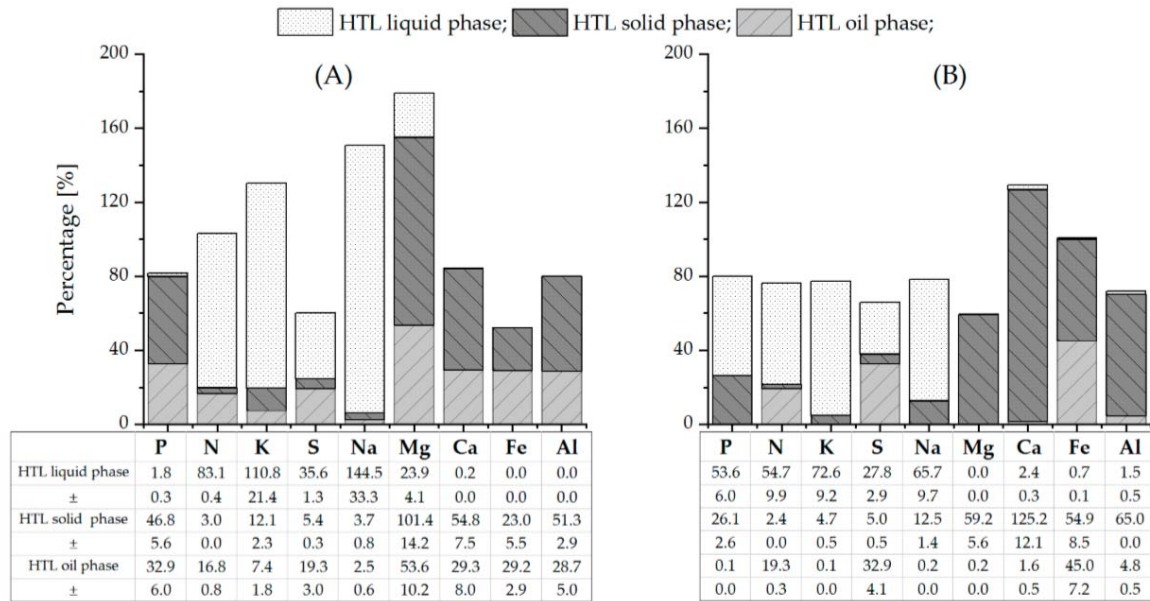


Figure 11: Estimated elemental balance for HTL runs of sewage sludge (A) and *Spirulina* (B) [62].

Considering nutrient recovery in the form of fertilizers, such as struvite, also the nitrogen distribution has to be taken into account. Nitrogen is mostly found in the aqueous phase (sewage sludge: ~80 %; *Spirulina*: ~75%), while the remaining nitrogen is almost exclusively found in the oil phase. Despite the discrepancies in the elemental balance, several general trends can be observed. Furthermore, strategies for nutrient extraction and recovery can be identified. The phosphorus part of the solid phase was found to consist mostly of inorganic phosphate, while the organic phosphate amounted to less than 1% in both cases.

The crop-available form of phosphate was quite low (1% for sewage sludge, 31% for *Spirulina*). Therefore, it was concluded that no direct use of the solid phase is feasible and phosphates have to be enriched in a fertilizer. Considering the elemental balance, two promising strategies for nutrient recovery can be considered:

1. Leaching phosphates from the solid phase and mixing them with ammonia from the aqueous phase to precipitate struvite (both sewage sludge and *Spirulina*)
2. Direct precipitation of struvite from the aqueous phase (*Spirulina*)

Concerning the optimal leaching conditions, it was found that the pH value of the leachate should be lower than 2 in order to prevent precipitation of secondary Al- and Fe-phosphates after leaching the primary Ca-phosphates, which are most abundant in the solid phase (in the form of apatite). It was found that leaching with 0.5M sulfuric acid showed the best experimental results. Recovery rates of phosphorus of 99% and 66% could be realized for sewage sludge and *Spirulina*, respectively. The smaller amount of recovered phosphorus in the case of *Spirulina* can be explained by the lower amount of available magnesium. Thus, an additional Mg^{2+} source would be necessary in order to realize higher recovery rates. However, in the context of an optimal design, a compromise between performance and expenses for additional resources has to be made. In the case of *Spirulina*, more than 50% of phosphorus was found in the aqueous phase. Therefore, direct precipitation of struvite from the aqueous phase was investigated. A recovery rate of phosphorus of 99.9% could be achieved.

Another study by Conti et al. has investigated HTL of four different waste streams, namely swine manure, cattle manure, fish sludge and sewage sludge. In terms of nutrient distribution, mostly similar results were concluded. Multivalent cations are found in the solids in high quantities (<70%) for all feedstock. Sodium and potassium show a higher appearance in the aqueous phase for swine manure and cattle manure but are present in higher quantities in the solid phase for FS and SS. It was also found that Ca and P are primarily present as apatite and hydroxyapatite, as was concluded in [62] as well.

Shanmugan et al. [29] investigated the struvite precipitation from the HTL aqueous phase under variation of pH, temperature and reaction time. More than 99% of the phosphorus and up to 100% of the nitrogen could be removed from the aqueous phase. The authors estimate that about 69.5 kg struvite can be obtained per metric ton of microalgae (dry matter) processed via HTL [29].

Alternatively, and instead of isolating nutrients as defined chemical compounds, such as struvite, the HTL aqueous phase (or the process water from catalytic hydrothermal gasification) with all dissolved components can directly be used as growth medium, e.g., for the cultivation of microalgae [63]. This also closes the nutrient cycle without the need to implement a chemical precipitation step. It was shown that microalgae *Chlorella vulgaris* and *Nanochloropsis gaditana* can grow without restriction in a cultivation medium where 75% of the required nutrients were supplied through recycling of HTL AP, thus strongly reducing external fertilizer input. Another, more recently published study [64] showed the successful semi-continuous growth of *Tetraselmis* sp. with a 50 % support of nutrients by an appropriate dilution of the aqueous phase. Growth rates and biomass yields were found to be equal or higher compared to the control cultures.

However, this approach does not use the solid phase for nutrient recovery. In the case of algae used as HTL feedstock, a combination of precipitation (solid and aqueous phase) and use as growth medium (aqueous phase) could be considered. Regarding an optimal design, it has to be evaluated, if the amount of phosphorus in the solids is worth the chemical expenses for leaching.

There are also other processes, like HTC of sewage sludge, where phosphate can be leached from a solid product [65]. Some of the knowledge gained from these experiences can also be transferred to the HTL process.

It should be noted that an effective separation of the different HTL phases (solids, aqueous phase and biocrude) is of great importance for the fuel quality, but also in terms of nutrient recovery. As described above, accumulation of inorganics in the solid phase facilitates their recovery. Inorganics appearing in the biocrude however are highly undesired for two reasons. Firstly, metals can lead to the deactivation of the catalyst during the upgrading process and secondly, inorganics can have a negative influence on fuel properties [66]. Application of in-line filtering in the HTL reactor system, thus taking advantage of the reduced water solubility of inorganic salts in near-critical regimes, not only reduces the ash content of biocrude (see Section 2.2.1, it also supports phosphate recovery from the separated solids that could otherwise mix with the oil phase (biocrude).

As can be seen from the above shown results, different feedstocks show a great variety of nutrients and nutrient distributions after HTL. It is therefore a particular challenge to adapt the process design for nutrient recovery accordingly and to ensure dynamic process control.

Another important issue to consider in nutrient recovery through struvite precipitation is purity of the product. As described in Section 4.2.6, the fertilizer produced must meet the nitrogen and phosphorus content requirements as a fertilizer. Furthermore, it must be excluded that toxic components such as cadmium are present in the fertilizer produced.

In this context, it should also be noted that the recovery of inorganic nutrients in HTL-based value chains does not only serve the purpose of generating a value-adding product stream; another important purpose is to purify the HTL process water so that it can safely be disposed of without further processing. Although the topic of nutrient recovery has gained more attention lately, many questions still remain unanswered, which leads to large knowledge gaps.

2.6 Integrated HTL-based process chains

Most R&D efforts related to HTL-based production pathways have been limited to individual process steps. As described in the previous sections, most studies have been dedicated to the HTL process as primary conversion step itself, while comparably little research has been done on upgrading techniques to refine biocrude into marketable products, and even less is yet known about technology options for treating or valorizing the HTL aqueous phase. The lack of studies and knowledge is even more apparent for integrated process configurations, i.e. process chains including HTL, upgrading and AP treatment. Specific challenges arise from process integration. For example, the high thermal energy required in HTL and cHTG to heat large volumes of aqueous slurries and solutions will require a high level of integration to enable efficient thermal management and heat recovery. Scale, throughput and reaction time of process steps have to be designed to enable smooth operation, temporal storage of intermediate products might be required and more issues need to be considered. Such considerations are crucial for industrial implementation of HTL-based value chains, as any industrial facility would have to include technology options for AP treatment for economic and environmental reasons. An upgrading unit would not necessarily have to be integrated, as biocrude production and upgrading/refining can occur at different locations, e.g. if co-refining is chosen or in case of decentralized HTL plants combined with a central large-scale upgrading unit. However, there are only few studies based on system-modelling approaches devoted to integrated HTL-based process chains that also include AP treatment [45–48]. For example, a research group of PNNL developed an integrated process covering HTL, a gasification of the AP and an upgrading for the application of microalgae [67]. The PNNL researchers can take advantage of the fact that they have in-house experimental experience on various process steps, from HTL [41] over biocrude upgrading [18] and hydrothermal gasification [68] to anaerobic digestion [69].

The cultivation of algae using the effluent from anaerobic digestion of different feedstocks has been studied by several research groups. The studies report that the integration of AD and algae cultivation is feasible and leads to reduced GHG emissions [24,70]. Toxic compounds such as phenols, N-heterocycles and furanics could be partly degraded by application of AD.

The special character of HyFlexFuel is to address the entire value chain in a single project, particularly the treatment and valorization of the AP and also the recovery of inorganic nutrients as marketable fertilizers. All process steps are examined in experiments under relevant operational conditions. However, experiments in HyFlexFuel are not conducted on an integrated plant: The process steps are investigated at separate locations. Aspects of plant integration are covered by an integrated work plan with close communication and feedback loops between partners. Furthermore, the project includes a comprehensive techno-economic assessment of the entire integrated process chain, based on the experimental results and in-depth process modelling.

3. Technology gaps

From the review of the state of the art of process technologies relevant for HTL-based fuel production, combined with conclusions from experimental work carried out in HyFlexFuel, a set of technology gaps are identified. These technology gaps are intended to serve as guidance for future work in (but also beyond) HyFlexFuel. The technology gaps are listed in the following tables. The tables will be updated, as new findings arise from within the project or are reported in the scientific literature.

Feedstock supply

Technology gap	Possible impact
Sustainable (local) feedstock availability	Economic viability; determines potential scale of production plant
Competing (possibly traditional) use of specific feedstock; accessibility of feedstock could also be impeded by local legislative framework supporting other use	Economic viability; determines potential scale of production plant; could induce social and/or economic pressure on other sectors

Hydrothermal liquefaction

Technology gap	Possible impact
Feedstock-flexible operation: Use of feedstock mixtures or alternating types of feedstock	Flexible operation, increased production potential, increased supply security, increased economic viability; operational challenges
Feedstock pre-treatment and feeding - Concentration of wet feedstock to sufficient dry matter content - Pre-treatment of solid feedstock; stabilization of slurries, particularly with high dry matter content - High-pressure pumping of highly concentrated feedstock slurries	Strongly affects thermal efficiency of HTL and biocrude yields; impact on operability and system lifetime (e.g. of pumps)
Reactor design: Cost-efficient steel alloys that are resilient to corrosion under hydrothermal conditions and at high salt concentrations to enable long lifetime of components	Strongly affects system lifetime and economic performance.
Scale-up: Availability of suitable pumps and heat exchangers matching requirements of continuous operation in large-scale HTL systems	Strongly affects system design and scale; reliable pumps crucial for sufficient load factor (failure of pumps results in downtime); heat exchangers have to enable fast heat transfer for high heating rates

Water phase recycling in HTL	Relevant for dry feedstock (woody, straw, etc.); possibly reduced need for supply of freshwater and costly disposal of waste water; inconsistent picture in literature: impact on biocrude yield and quality not certain
Continuous separation of HTL product phases	Essential for commercial operation; high water content in biocrude or organics in water phase would affect downstream processes and increase cost
In-line filtration of HTL mixture to remove solids (inorganics, ash)	Important for bio-crude quality (ash content); impact on catalytic upgrading and economic performance; effective in-line filtration also important for phosphorus recovery: isolation of P in HTL solids would enable efficient recovery
HTL reaction model: Understanding of - HTL reaction pathways - Impact of feedstock properties and process conditions (e.g. reaction temperature, heating rate, solid loading, reaction time) on yields and quality of product phases	Ability to adapt applied feedstock (combination of feedstock) and process conditions to optimize yields (qualitatively and quantitatively)

Catalytic upgrading of biocrude

Technology gap	Possible impact
Bio-crude quality (e.g. ash content) insufficient for direct catalytic upgrading	Pre-treatment required, economically disadvantageous
Effect of biocrude composition and quality (aromatics, aliphatics, O and N content etc.) as function of biomass feedstock and HTL conditions on process requirements in upgrading and on final product spectrum and quality; for example, high oxygen content in biocrude is likely to result in an increasingly exothermic character of hydrotreatment. Required flexibility of upgrading unit to cope with varying composition of biocrude upon switching HTL feedstock	Varying product spectrum and quality could affect the value of product streams. Unconventional process design (i.e. differing from conventional refining techniques) might be required. Needed flexibility of upgrading unit could make a more complex process design necessary and result in higher cost.
Continuous operation in relevant environment with stable catalyst and effective removal of oxygen and nitrogen	Essential for commercial operation; risk of insufficient product quality, e.g. reduced drop-in capability and value as fuel
Tailored catalyst with long-term stability for upgrading of bio-crude	Yields and quality of products, hydrogen consumption, catalyst lifetime; economic performance

Potential of co-refining biocrude in conventional refineries as technology option to yield marketable products	Potential economic advantage, as no dedicated upgrading unit would be required
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Catalytic hydrothermal gasification (cHTG) of HTL aqueous phase

Technology gap	Possible impact
Separation of salts and sulfur-containing species from HTL AP prior to gasification	Catalyst lifetime and, thus, economic viability (expensive catalyst)
Catalyst lifetime (e.g. affected by Ru leaching or sulfur poisoning) and long-term operability of cHTG process under relevant conditions (continuous mode; stability of sulfur trap and salt separator)	Economic viability (expensive catalyst)
Process integration with HTL: matching of throughput and of concentration of organics, heat recovery/thermal energy management; HTL AP might require pre-treatment to increase concentration of organics to minimum level	Economic viability: positive energy balance needed

Anaerobic digestion of HTL aqueous phase

Technology gap	Possible impact
Toxicity/degradability of organic content of HTL aqueous phase; Effectiveness of AD: potential degree of COD and TOC removal	Applicability of AD for HTL AP treatment; potential need for post-treatment or pre-treatment; or for blending with other substrates to dilute problematic components of HTL AP; economic viability
Continuous-mode operation: Adaption of microbial community specifically to HTL AP (and potentially toxic or recalcitrant organic components)	Affects practical applicability of AD to treat HTL AP
Continuous-mode operation: Impact of low COD of HTL AP and degradability of organic content on required scale of AD reactors and residence time	Affects economic viability; blending with other substrates possibly needed to increase COD and dilute problematic compounds

Nutrient recovery

Technology gap	Possible impact
Separation of phosphorus species as part of HTL solids from liquid HTL product phases through effective in-line filtering.	Concentration of Phosphorus in HTL solids would make recovery easier compared to even distribution of Phosphorus over several product phases; affects economic viability
Struvite precipitation: pH adjustment, stoichiometry (adapting concentrations of Mg^{2+} , NH_4^+ , and PO_4^{3-} to required ratios), continuous operation, completeness of recovery, purity of struvite	Incomplete recovery: reduced economic potential and high salt concentration in wastewater (direct disposal possible? Post-treatment required?); affects economic viability

Fully integrated process chain

Technology gap	Possible impact
Technical approval/certification of fuel products; fuel testing	Crucial step on the way to industrial deployment
Process integration (feedstock supply and treatment, HTL, upgrading and refining, treatment of water phase etc.): Matching of scale, throughput, etc.; heat recovery and thermal energy management	Crucial for economic viability

4. Application potentials and market opportunities for HyFlexFuel products

This chapter addresses market potential of the main products of the HyFlexFuel process chain. Next to targeted liquid hydrocarbon fuel products gasoline, jet fuel and diesel, additional opportunities for products and by-products that could add value to the overall process chain are analyzed. Further commodity products include marine fuels, biocrudes or partially upgraded biocrudes for co-processing in refineries, and naphtha as a substitute feedstock for the chemical industry. Combustible gasses from various streams along the HyFlexFuel process chain represent an important by-product that may e.g. be used as a fuel to produce electricity and heat for local energy networks. HyFlexFuel furthermore investigates the recovery of a marketable fertilizer product (struvite) from nutrient rich HTL product streams. Finally, the extraction of high-value by-products is discussed.

Arguably, the thermal treatment of waste streams can also be seen as a product, which can generate significant revenue⁴. In the context of this report, waste management services are not understood as a product that results from the process. However, HyFlexFuel will consider the economic and environmental benefits of embedding HTL plants in waste management system in an upcoming public report⁵, at hand of the example of sewage sludge.

4.1 Product spectrum of the HyFlexFuel process

The central target aimed for in HyFlexFuel is the production of sustainable liquid fuels: Liquid fuels are yielded at the end of HyFlexFuel's central process pathway, from hydrothermal liquefaction of biomass over hydrotreating of biocrude and final fractionation. Additional products are yielded from valorization of residual process streams, particularly of the HTL aqueous phase.

4.1.1 Targeted products

The main targeted products of the HyFlexFuel process are sustainable liquid fuels for the transport sector:

- Gasoline
- Jet fuel (kerosene)
- Diesel
- Marine fuels

HyFlexFuel has a special focus on jet fuel, therefore the project puts strong emphasis on the upgrading of HTL biocrudes to on-specification jet fuel blend components. It is important to understand that the upgraded HTL biocrudes contain a mix of hydrocarbon molecules, which are distributed over a broad product range. Therefore, it is very important to identify market opportunities, not only for jet fuel as a single target product, but for a basket of liquid hydrocarbon fuels. Gasoline and diesel can be produced

⁴ Waste incineration plants usually derive more revenue from the thermal treatment waste streams, than from the provision of power and heat. Consequently, an appropriate regulatory framework is required to ensure thermal waste treatment in incineration plants, which are otherwise not commercially viable.

⁵ This report is scheduled for Q1/2021

alongside with jet fuel, but they may represent the target products by themselves. HTL is also frequently discussed as a prime option to produce marine fuels. In this case, less stringent specifications and therefore less stringent requirements for biocrude upgrading apply. Another pathway towards the target fuel products is co-processing of a HTL biocrude or partially upgraded HTL biocrude in refineries. In analogy with current crude oil refining a certain fraction of the product may also be used as a feedstock for petrochemical processes.

Important by-products from the HyFlexFuel production chain are:

- Combustible gasses (mainly methane)
- Struvite

Methane is produced as additional marketable energy carrier mainly from the treatment of the HTL aqueous phase, either through catalytic hydrothermal gasification or anaerobic digestion. The produced biogas, which contains mainly methane but also significant amounts of CO₂ will mainly be used for on-site electricity and heat generation. Initial process modeling results indicate that a substantial excess of biogas remains, after the process energy demand of the plant is covered, the excess electricity and heat or the excess biogas can be sold on the market. Struvite (magnesium ammonium phosphate, (NH₄)Mg[PO₄]·6H₂O) represents the targeted product of nutrient recovery from residual process streams.

4.1.2 Other potential products

In addition to the targeted main products of the HyFlexFuel process, other compounds, such as platform chemicals or compound classes might be yielded from the output phases and could add value to the overall process as potentially marketable products.

In this context, especially lignocellulosic materials have to be mentioned. Under specific hydrothermal conditions, lignocellulosic materials are readily destructed into cellulose and hemicellulose. Via hydrolysis and oxygen removal, initial platform chemicals can be formed. Platform chemicals from lignocellulosic material include i.e., ethanol [74], 3-hydroxypropionic acid, isoprene, succinic, lactic and levulinic, furfural, and 5-hydroxymethylfurfural (5-HMF) and polyols, e.g. sorbitol and xylitol [74–76]. It should be noted, that glycerol is another polyol, which, however, does not stem from a lignocellulosic feed, but rather from the transesterification of fats [75,77].

However, most literature contributions in this context are not related directly to HTL, but rather to other conversion technologies, like microwave-assisted processes [75] or biorefineries [77]. Nevertheless, a small portion of literature deals with the topic of platform chemicals derivable from HTL. One example is the investigation of co-hydrothermal treatment of agro wastes to produce 5-HMF [76]. Shamsul et al. showed a significant increase in 5-HMF production of 39 % in the biocrude by co-hydrothermal treatment of a mixture of different agro wastes compared to previous single HTL experiments with empty fruit bunches palm [78], sugarcane bagasse [79] and giant reed [80]. It should be noted, however, that this study explicitly was focused on producing 5-HMF as main product.

For example, in 2015, a method was reported to isolate phenolic compounds from the HTL aqueous phase based on liquid chromatography using specifically modified adsorption resins [57]. The resin is loaded with aqueous phase and the products are eluted with ethanol/water mixtures. Light carbonic acids and other oxygenates are eluted first at lower ethanol/water ratios (higher polarity), while targeted phenolic compounds are eluted with mixtures of higher ethanol concentrations. Phenols are of great interest

for the chemical industry, so the isolation of such compounds could be of commercial interest for the HyFlexFuel process.

In 2017, the same research group, Chen et al., also described another resin, a cation exchange resin, with which they were able to separate organic acids and phenolic compounds from the aqueous phase of an HTL experiment performed at 300 °C with rice straw as feedstock via ion exchange chromatography [81].

Although some work on the topic of using platform chemicals as and from HTL by-products has been done, the answer to the research question still remains as a gap and has to be investigated in more detail in the future in order to further optimize the HTL process.

4.2 Market opportunities

In this section, market opportunities for the HyFlexFuel products or product categories are analyzed. The analysis addresses background information as well as technical and/or regulatory requirements with respect to potential products and markets. It also includes relevant market volumes and prices and evaluates the relevance of products and markets for the HyFlexFuel process.

4.2.1 Conventional transportation fuels from crude oil

The majority of the global energy demand is still met by fossil resources. In transportation, coal was historically used as a fuel for steam engines, currently it is indirectly used via electricity generation or as a feedstock for synthetic fuel production via coal-to-liquids processes. In contrast, the direct use of natural gas as a transportation fuel (CNG, LNG)⁶, is increasing mainly due to the competitive pricing compared to crude oil in many markets. In addition, short-chained hydrocarbons, which result as a by-product of natural gas production and processing (NGL), are used for transportation fuel production. Nevertheless, the great majority of transportation fuels are currently derived from crude oils. Furthermore, the main products of crude oil refining are transportation fuels⁷. This strong link between crude oil and transportation fuels is illustrated in Figure 12. Crude oil is a mixture, which mainly consists of liquid hydrocarbons of various chain length. Most of the crude oil products encode product fractions with certain boiling temperature ranges the result from distillation. The individual fractions correspond to mixtures of hydrocarbons, where the number of carbon atoms in the hydrocarbon molecules typically increases with the boiling temperature⁸. Ethane and LPG (C2-C4) are gaseous hydrocarbons, which result from crude oil production and processing. Naphtha and gasoline are liquid hydrocarbon mixtures with low boiling temperatures (C5-C10). Naphtha is typically used as a feedstock for the petrochemical industry, while gasoline is a highly refined transportation fuel (see Section 4.2.1). Jet Fuel (C8-C15) and Diesel (C11-

⁶ CNG: Compressed natural gas, LNG: Liquefied Natural Gas, NGL: Natural gas liquids

⁷ Crude oil was historically used in all energy sectors. Over the past decades, significant price premiums per unit energy compared to coal and more recently also compared to natural gas and renewables, shifted crude oil use increasingly towards the production of transportation fuels and petrochemicals.

⁸ For straight hydrocarbon molecules (n-alkanes) the boiling temperature strictly increases with chain length. The presences of branched molecules (isomers), cycloalkanes and aromatic species introduces deviations, but the general trend of increasing boiling temperature with increasing number of C-Atoms usually persists.

C20) are highly valued transportation fuels from the middle distillate boiling range. While higher boiling range distillates and the distillation residue is usually marketed at a discount in form of fuel oil, which is e.g. used as a marine fuel. The basket of crude oil products indicates that transportation fuel use co-evolved in line with the availability and pricing of crude oil derived refinery products. Likewise, the refinery design, which can shift the product spectrum of a petroleum refinery, evolved with respect to the development of transportation fuel demand.

Similar to crude oil, HTL biocrudes as well as hydrotreated HTL biocrudes contain molecules of various chain length. In analogy to the current trends in crude oil refining, it can be expected that an HTL biocrude upgrading facility will produce a similar spectrum of hydrocarbon products that need to be marketed in form of various transportation fuels or as feedstock to the petrochemical industry.

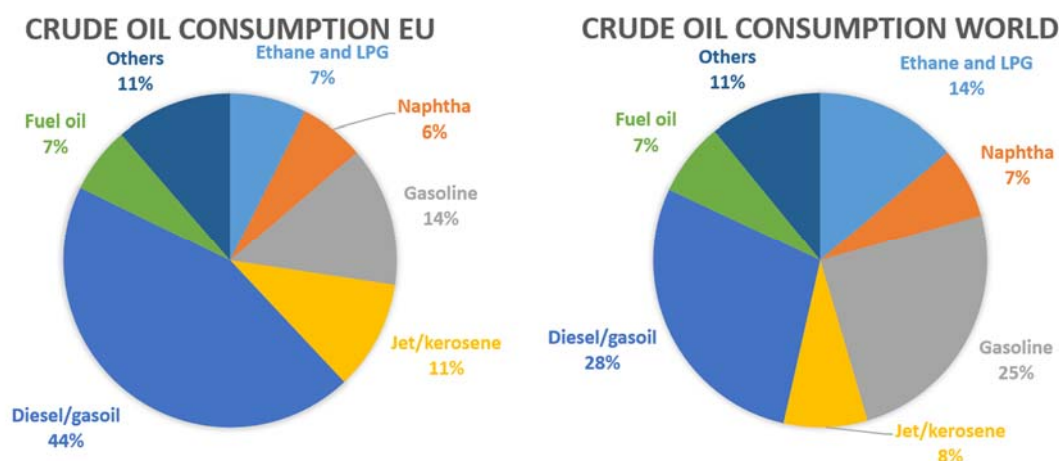


Figure 12: Consumption of crude oil product in the European Union (left) and worldwide (right). Transportation fuels dominate crude oil consumption, middle distillate fuels (diesel, jet fuel) are dominating in Europe, while gasoline is used more widespread worldwide. Data based on BP Statistical Review of World Energy 2020.

4.2.2 Motor gasoline

The main motivation of the HyFlexFuel project is the sustainable production of middle distillate fuels, to assist the future decarbonization of aviation (jet fuel) and heavy-duty road transportation (diesel). The production of jet fuel and diesel (C9-C20) from HTL biocrudes also yields a hydrocarbon fuel product in the naphtha range (C5-C11). The naphtha range fraction can be used to produce a renewable blend component to motor gasoline, as an additional contribution to the decarbonization of the transportation sector. Alternatively, naphtha can serve as feedstock for the production of renewable platform chemicals for the petrochemical industry (see Section 4.2.1).

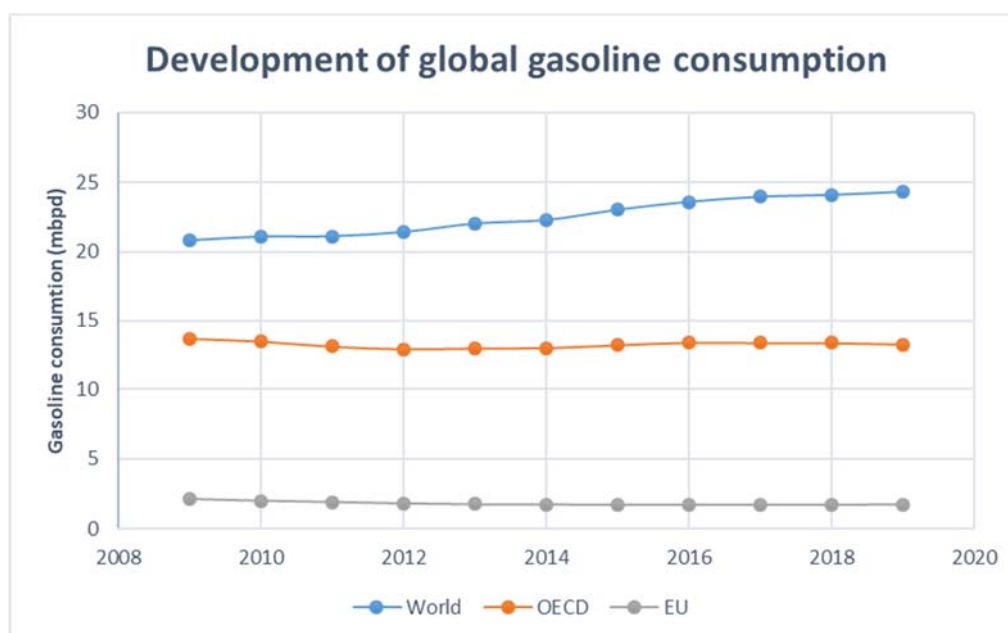


Figure 13: Development of global gasoline consumption. The global demand is increasing at a rate of about 1.5% per year; OECD demand is almost flat, the EU gasoline demand declines. Data based on BP Statistical Review of World Energy 2020.

Current and future demand

Motor gasoline is mainly used as fuel for passenger vehicles⁹. The global gasoline demand amounts to 25% of the global crude oil consumption (see Figure 12). The demand in OECD countries evolved almost flat during the last years, while the global demand increased mainly due to strong growth in the Asia Pacific Region, especially in China (see Figure 13). The relative share of gasoline use in the European Union is lower compared to the global average (13.6% in 2019, due to the above average share of diesel fueled passenger vehicles). Based on the current global consumption levels, gasoline may be the most important transportation fuel product of HTL plants. However, many observers expect a decline of gasoline demand over the next decades due to mandated fuel efficiency improvements and a growing share of passenger cars with alternative drivetrains¹⁰. Battery electric vehicles, and potentially hydrogen/fuel cell drivetrains, are expected to play a major role in the decarbonization of road transportation. As of today, despite of a rapidly growing share of electrified passenger vehicles sales¹¹, the great majority of new cars is still powered by conventional drivetrains. Due to fleet dynamics, only a small decline in global gasoline demand is expected over the next decade, while a major reduction of European gasoline demand seems inevitable to achieve the European Green Deal target of 90% emission reduction in the transportation sector. Apart from a reduced total gasoline demand, by a switch to alternative and more efficient drivetrains, an increasing share of the remaining gasoline demand should be covered by renewable fuels to achieve the emission reduction targets. During a potential scale-up of HTL fuel production, it can be expected that the naphtha range fraction of the upgraded HTL fuel

⁹ To lesser extent, aviation gasoline is used in small aircraft with spark ignition engines. The great majority of aviation fuel is combusted in gas turbines (jet fuel).

¹⁰ See e.g. <https://about.bnef.com/blog/three-drivers-curbing-oil-demand-road-transport/> and www.mckinsey.com/industries/oil-and-gas/how-we-help-clients/energy-insights/global-oil-supply-demand-outlook-to-2035

¹¹ Europe, June 2020: 8.4% plug-in share (4% hybrid electric, 4.4% battery electric) <http://ev-sales.blogspot.com/>

can be blended into the gasoline pool (upon appropriate refining steps) at least for the next two decades. For the longer-term future, the development of gasoline demand can be reassessed and the market potentials may shift to alternative valorization options for short-chained liquid hydrocarbons.

Regulatory issues

The European specifications for motor gasoline are defined in EN 228 (see Table 4). The specifications are in many aspects less stringent than jet fuel specifications, e.g. significant shares of olefin, aromatic and oxygenates are allowed. Different grades of gasoline are distinguished based on their octane numbers (RON and MON), which is a measure of the compressibility of the fuel without unwanted ignition. A high octane number is important for efficient spark-ignition engines to ensure an optimized cycle. Typically, regular gasoline has a minimum RON of 95¹² within Europe. An octane number of 100 is assigned to an isomer of octane (2,2,4-Trimethylpentane), while zero is assigned to unbranched n-heptane. Unbranched n-alkanes show generally low octane numbers, isomers are more beneficial, and aromatic components tend towards high octane numbers. Furthermore, additional fuel components such as alcohols and ethers (MTBE, TAME, ETBE) are added to adjust the octane number to values approaching or exceeding a RON of 100. Gasoline is a major product of crude oil refineries, generally the gasoline range distillation products (naphtha) need to be refined¹³ to contribute to the gasoline blending pool. Similarly, it can be expected that upgraded HTL biocrudes can contribute to the gasoline blending pool. Similar to crude oil refining, it is likely that further refining steps are required to increase the octane rating of the naphtha range fraction of hydrotreated HTL bio-crudes.

Many adaptations to motor gasoline specifications and regulation were motivated by environmental considerations. The concentration of benzene, which was historically a major component of gasoline is limited to 1% by EN 228, tetraethyl lead as an additive to increase the octane rating was globally banned. Sulphur content is limited to 10 ppm and the aromatic content was reduced from 42% to 35% (EN 228). More recently, the GHG emissions that result from the production and combustion of gasoline fuels are increasingly regulated. As a result, it can be expected that the use of HTL products in the gasoline pool is increasingly incentivized by GHG regulations. On the other hand, future regulations are also expected to increasingly induce a transition from liquid hydrocarbons towards electrification and gaseous fuels due to air quality considerations.

Current feedstock supply and alternative fuel use

Today, motor gasoline is mainly produced via crude oil refining. Furthermore, synthetic gasoline is produced from natural gas or coal, via Fischer-Tropsch or Methanol-to-gasoline pathways. Compared to jet fuel and diesel, there is also a larger variety of alternative fuels that qualify as substitute or blend components to gasoline. Spark ignition engines and fuel systems can be adapted to use gaseous fuels (CNG, LNG, LPG). For conventional gasoline, ethanol is currently the most important renewable blend component. Within Europe, it is common to use ethanol up to a blending ratio of 10% (E10) while much higher blending ratios are possible¹⁴. In addition, higher alcohols, such as butanol, and synthetic gasoline from renewable feedstocks may find more frequent use as blendstock for the gasoline pool in the future. As indicated above, battery electric and

¹² Premium fuels typically show a minimum RON of 98, high performance fuels with RON > 100 are available

¹³ Hydrotreatment, isomerization of light naphtha, catalytic reforming of heavy naphtha, cracking of heavier fractions, alkylation of alkenes resulting from cracking procedures etc.

¹⁴ Slightly higher blending ratios are possible with minor adaptations (E15-E30), Flexible Fuel Vehicles which are common in Brazil, but also in European countries e.g. Sweden, are designed for high blending ratios (E85).

fuel cell vehicles are expected to substitute a significant share of the current gasoline consumption. The multitude of renewable energy alternatives for light-duty vehicles is the reason why the development of production pathways towards renewable liquid hydrocarbons is mainly motivated by middle distillate fuels. Air quality considerations are another important motivation to prioritize electrification and hydrogen in road transportation.

Market prices

Similar to jet fuel and diesel the market prices of gasoline are strongly linked to the oil price. A market indicator for the difference between the price of a refinery product and the price of the crude oil feedstock is the so-called crack spread. Crack spreads are fluctuating and can significantly differ in between regions, but also with respect to the quality of the crude oil feedstock. The US Gulf Coast gasoline crack spread was typically about 10 \$/bbl (15 \$/bbl¹⁵), which shows that the production cost of gasoline at a refinery is dominated by the price of the crude oil feedstock (about 40 \$/bbl, 30-70 \$/bbl over the past five years). Gasoline was traded below a price level of 0.50 €/L over the last years¹⁶. In the absence of regulations, it will be difficult to achieve a profitable margin for HTL derived gasoline unless the oil price increases significantly.

For the time being, the market price for the leading renewable alternative fuel may be a more meaningful comparator. The price of ethanol fluctuated between 0.25/L and 0.4 €/L over the past five years¹⁷, which corresponds to a gasoline equivalent of 0.4-0.6 €/L adjusting for the lower energy density of ethanol. This price level indicates that ethanol can be produced at near-competitive cost, the price premium compared to conventional gasoline furthermore indicates the presence of effective regulatory measures in many countries. In the European Union, the Renewable Energy Directive sets a framework for the regulations in the individual Member States. The revised Renewable Energy Directive (EU 2018/2001) requires that 14% of the energy that is consumed on the transportation sector is provided by renewable energy in the year 2030. The policy measures in the individual member states shall ensure that the EU target and the targets of the individual member states are met. According to Eurostat, the renewable energy share in transport was 8% in 2018, Sweden (29.3%) and Finland (14.1%) significantly exceed the average share¹⁸. Both countries have strong policies in place that support the use of biofuel in the transportation sector. The Swedish support system is mainly based on taxation, significant energy and a carbon tax applies to conventional gasoline, while tax exceptions apply to biofuels¹⁹. With respect to the renewable energy share, the Swedish support scheme proved to be the most effective biofuel policy in Europe. In contrast, the Finnish system is mainly based on quota obligations for biofuels in transportation. A quota of 20% in 2020 (double counting applies for advanced biofuels) will increase to 30% in 2020 (without double-counting), in addition a 10% subquota for advanced biofuels is planned. Within the Finnish system, and similar supporting schemes in other Member States, HTL fuels produced from advanced feedstock can compete at a significantly higher market price than conventional gasoline and ethanol produced from food crops.

¹⁵ For a chart see e.g. www.eia.gov/todayinenergy/detail.php?id=38552

¹⁶ For a chart see e.g. www.finanzen.net/rohstoffe/rbob-gasoline

¹⁷ For a chart see e.g. www.finanzen.net/rohstoffe/ethanolpreis

¹⁸ <https://ec.europa.eu/eurostat/web/products-eurostat-news/-/DDN-20200123-2?inheritRedirect=true>

¹⁹ The carbon tax of 1190 SEK/t_{CO2} alone amounts to about 30 ct/L gasoline: www.government.se/government-policy/taxes-and-tariffs/swedens-carbon-tax/

4.2.3 Jet fuel

In conventional refining jet fuel is derived from a relatively narrow fraction of the middle distillate (C8-C15). In many cases jet fuel is also used to adjust the production of the main refinery products gasoline (C5-C11) and diesel (C9-C20) according to market conditions. The jet fuel specifications are relatively easy to meet in crude oil refineries, in many cases jet fuel is directly derived from the distillation column, without the need for excessive additional refining steps. However, in the case of HTL biocrude upgrading it is more challenging to meet jet fuel specifications due to the necessity to remove oxygen and nitrogen compounds from the biocrudes. Although the current market share of jet fuel is much smaller than the current market share of gasoline and diesel, jet fuel is a prime target for long-term oriented biofuel research and development projects, as aviation fuel cannot readily be replaced by electrification and hydrogen.

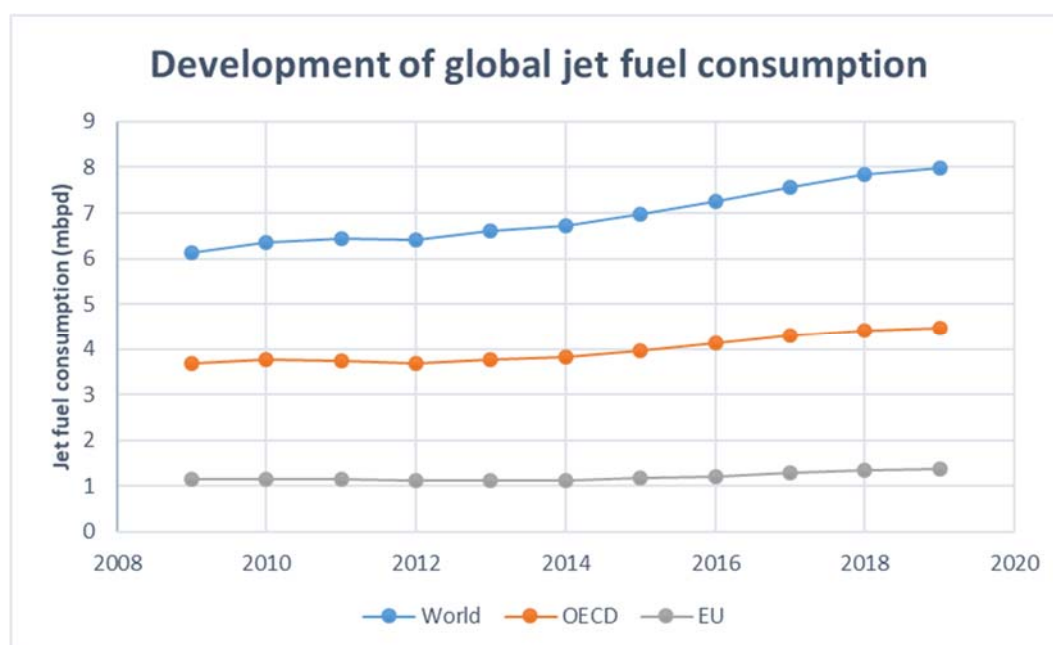


Figure 14: Development of global jet fuel consumption over the past decade. The strong growth of global jet fuel consumption is mainly supported by the Asia Pacific region, growth is also observed in OECD and EU countries. A strong decline is expected for 2020 due to the Covid-19 lockdowns. Data based on BP Statistical Review of World Energy 2020.

Current demand and future demand

Civil aviation is a strongly growing sector. This growth in air traffic demand has led to an almost continuous increase in global annual jet fuel consumption (illustrated in Figure 14 and Figure 15), despite of the aviation industry's efforts to increase fuel efficiency. Annual jet fuel demand meanwhile exceeded 300 Mt in 2019, however, the situation will change dramatically in 2020 due to the restrictions caused by the Covid-19 pandemics²⁰. At the moment, it is uncertain how the situation will evolve. Historically, contractions of air travel due to external shocks were followed by rebound periods of strong growth (see Figure 15, 1990/1991: Gulf war, 2001: September 11 attacks, 2008/2009: financial

²⁰ According to IATA's Air Passenger Market Analysis revenue person kilometers contracted by 86.5% year-on-year in June 2020. International air travel almost came to halt (-96.8%), while domestic air travel is more resilient (-67.6%). Source: www.iata.org/en/publications/economics/

crises). A rebound of air travel demand is certainly expected, but the effect of the Covid-19 crises on civil aviation is historically unmatched, therefore it is hard to predict how jet fuel consumption will evolve during the early 2020ies. In any case, a return to global growth is a likely scenario for the mid-term future due to the ongoing globalization and the strong growth of the middle class in emerging countries. Consequently, a continuous and growing demand of the aviation fuel can be expected. At the same time, there is growing pressure to reduce the sector-specific GHG emissions [56][57][58]. Battery electric aviation is becoming a commercial reality²¹, but the limited energy density of the battery packs limits the range. A potential substitution will likely be limited to the regional market, while middle to long-range aircraft will continue to rely on liquid fuels. Liquefied hydrogen is a potential alternative fuel for the long-term future, here, significant research and development effort is required. For the time being, all new and existing large commercial aircraft rely on liquid hydrocarbon fuel. Renewable jet fuels are still the most plausible option for a significant reduction of the climate impact of aviation.

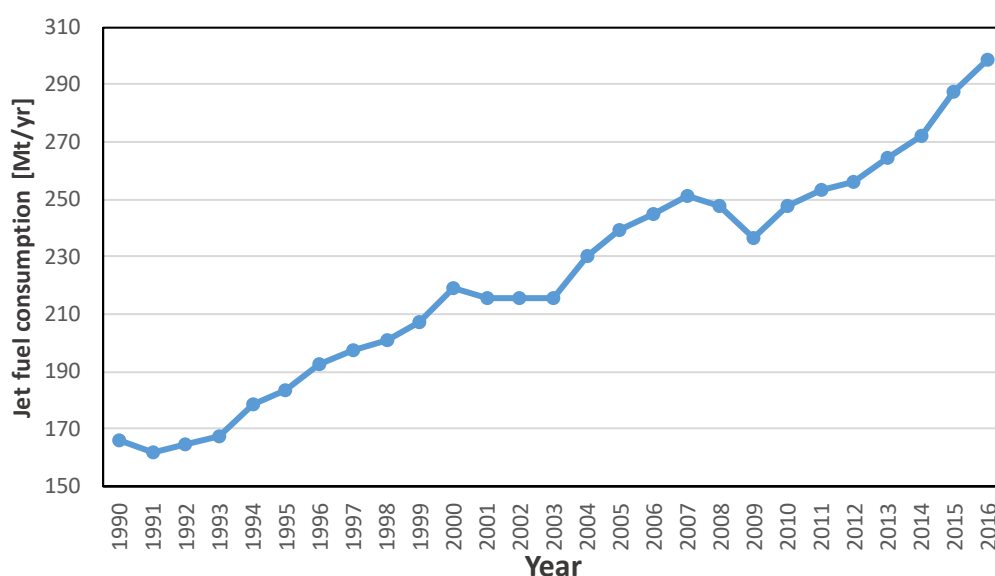


Figure 15: Historic development of global jet fuel consumption. (Source: U.S. Energy Information Administration)

Regulatory issues

The most important specifications for jet fuel for civil aviation are listed in the ASTM D1655 [59] and DEF STAN 91-91 [60] standards. These standards have evolved over the past decades, however always under the assumption that fuels are produced from crude oil. In response to recent interest in synthetic fuels from various alternative sources, the new specification ASTM D7566 [61] has been developed, specifically listing requirements for jet fuel containing synthesized hydrocarbons, often referred to as fuel blends. These requirements relate to physicochemical properties of fuel blends, such as density, viscosity, distillation curves and thermal stability, but also to certain chemical components.

Standard specification ASTM D7566 also defines approved types of synthetic fuels that can be blended with conventional jet fuel. Approved synthetic fuels (i.e. fuel produced

²¹ See e.g. www.pipistrel-aircraft.com/aircraft/electric-flight/ or www.magnix.aero

from other sources than crude oil) are listed with detailed specifications as annexes to ASTM D7566. The annexes also specify the respective production technologies, e.g. Annex A1. *Hydroprocessed synthesized paraffinic kerosene*: “FT-SPK blending components shall be wholly derived from synthesis gas via the Fischer-Tropsch (FT) process using iron or cobalt catalyst.”

After approval of FT-SPK as first synthetic blending component for jet fuel in 2009, a number of other alternative production pathways has been approved and added as annexes to ASTM D7566. The seven hitherto approved synthetic jet fuels are [82]:

- *Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK)*
Fischer-Tropsch synthesis based on synthesis gas derived from, e.g., gasification of biomass
- *Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK)*
Hydroprocessing (hydrotreatment and hydroisomerization) of biogenic oils or fats
- *Hydroprocessed Fermented Sugars to Synthetic Isoparaffins (HFS-SIP)*
Fermentative conversion of sugar feedstock by modified yeast, yielding farnesene. Farnesene is hydrogenated to farnesane that is then used as jet fuel blendstock.
- *Fischer-Tropsch Synthetic Paraffinic Kerosene with Aromatics (FT-SPK/A)*
Similar to FT-SPK, but process includes alkylation of light aromatic compounds
- *Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ-SPK)*
Conversion of alcohols (ethanol or isobutanol) into jet fuel blendstock via dehydration, oligomerization and hydrogenation
- *Catalytic Hydrothermolysis Jet (CHJ)*
Synthesized kerosene containing aromatic compounds produced from hydrothermally processed biogenic oils or fats
- *Synthesized paraffinic kerosene produced from hydroprocessed hydrocarbons, esters and fatty acids (HC-HEFA SPK)*
Paraffins derived from hydrogenation and deoxygenation of bio-derived hydrocarbons, biogenic oils and fats

Additionally, *co-processing* of up to 5% by volume of biogenic fats and oils (specifically, free fatty acids and fatty acid esters found in oils derived from plants and animal fats) in conventional petroleum refineries has recently been approved. Moreover, co-processing of FT-derived crude product (FT-crude) is anticipated to be approved soon.

Hydrothermal liquefaction has not yet been approved as production technology for synthetic jet fuel blending components. ASTM approval of a certain new type of synthetic jet fuel is a lengthy process of several years and is typically driven by the respective producer company. Especially for later stages of the approval process, considerable volumes of fuel are needed to conduct the required testing, e.g. rig testing in jet engines. Consequently, ASTM approval represents a crucial and costly hurdle for new jet fuel

production technologies on their way towards commercial deployment. As HTL-based fuel production has not yet been approved according to ASTM D7566, HyFlexFuel fuel fractions could not be used in jet fuel blends as of today, even if meeting the physicochemical specifications. In this context it has to be noted that ASTM approval of HTL-derived jet fuel could prove particularly challenging: The feedstock-flexibility of the HTL process, in itself a great economic advantage, can be disadvantageous with respect to ASTM approval, as the properties and quality of the products depend on the feedstock. In particular, the primary HTL product biocrude differs substantially from feedstock to feedstock, and first results on catalytic upgrading of biocrude also indicate variations in composition of upgraded product fractions. This could mean that ASTM approval of HTL-derived jet fuel can only be granted for specific types of feedstock. In other words, ASTM approval of HTL-derived jet fuel might be required for each specific type of feedstock. Additionally, it is conceivable that HTL process conditions, particularly process temperature (subcritical, supercritical) and the use of additives and catalysts, will require specific approval.

It should also be noted that jet fuel production through *co-refining of HTL-derived biocrude* in conventional refineries is very likely to require technical approval. This can be concluded from the fact that even co-processing of biogenic oils and fats as well as FT-crude, i.e. homogeneous and valuable feedstock when compared to HTL-derived biocrude, requires approval. This means that renewable jet fuel produced via co-refining of HTL-derived biocrude requires technical approval as well.

Current feedstock supply and alternative fuel use

Essentially all jet fuel supplied and consumed worldwide today is produced from fossil resources. The majority of jet fuel is produced in crude oil refineries, to lesser extent synthetic kerosene (FT-SPK) is produced from coal and natural gas resources. So far, only a very small fraction, well below 1%, is supplied in the form of biogenic jet fuel, mainly in form of HEFA fuels. However, over the past year's the aviation industry is increasingly engaging in sustainable aviation fuels and production capacities are currently build up. Again, the near term growth is mainly based on increased HEFA production capacities using biooils or fats as feedstocks. Nevertheless, several projects aiming at renewable jet fuel production from other approved renewable kerosene production pathways are underway.

Market prices

The market price of conventional jet fuel is volatile and has experienced substantial and sometimes rapid fluctuations during the past years. Similar to other refinery products like gasoline and diesel, the fluctuations are strongly correlated with the fluctuation of the oil price. The spread between the jet fuel price and crude oil spot market prices amounted to 0.05-0.10 €/L (10-20 \$/bbl) over the last years²². Average jet fuel prices exceeded 0.70 €/L in 2007 and 2009-2013, more recently (2016-2019) market prices fluctuated at a level of 0.30-0.50 €/L. In 2020, the unusual situation occurred that jet fuel prices fell below 0.1 €/L and traded below spot market prices of crude oil for weeks²². This indicated that refineries needed to sell jet fuel at a discount compared to other refinery products due to the unusually low jet fuel demand during the Covid-19 pandemic. It is unlikely that the current situation will persist in the long term, especially in the scenario of declining gasoline and diesel demand due to a widespread

²² For a chart referenced to Brent crude oil see e.g. www.iata.org/en/publications/economics/fuel-monitor/

decarbonization of road transportation. The market prices of conventional jet fuel has a strong relevance for the economic potential of alternative jet fuels. As of today, essentially all renewable jet fuel options cannot compete at price levels of 0.30-0.50 €/L for conventional jet fuel.

In the near-term, there is only an economic perspective for HTL-derived jet fuel, if market conditions are adapted through regulatory measures, unless the airline industry is willing to accept a premium for more sustainable fuels. Several measures are currently discussed, such as taxes, subsidies, emission trading, emission offsetting, quota etc. It is beyond the scope of the present report to discuss the benefits and drawbacks of the individual options, but it is obvious that any effective measure must levelize the cost gap between renewable jet fuel and conventional jet fuel. In many Member States of the European Union effective policy measures were developed and provided regulatory or economic incentives to introduce significant amounts of biofuels in road transportation (see Section 4.2.2 and 4.2.4). In the last decade, there was a lack of effective policy measures for the introduction of renewable jet fuels. This situation is about to change, the Renewable Energy Directive defines a multiplier of 1.2 for fuels used in the aviation sector, i.e. at least with respect to the targets defined by the RED renewable jet fuel will have a 1.2 times higher value per unit energy content compared to road transportation fuels. Furthermore, several European States are developing specific regulatory to support renewable aviation fuels. For instance, Norway, Sweden and Finland are targeting a 30% share of renewable jet fuel by 2030²³. In case of blending mandates, or other effective jet fuel specific regulation, renewable aviation fuels do no longer compete with conventional jet fuel. Instead, various renewable jet fuel pathways compete against each other. Currently, the most price-competitive renewable jet fuel are HEFA fuels, derived from biooils or fats. The production cost of HEFA fuels is estimated to be on the order of 1 €/L, the production cost is dominated by the feedstock cost therefore significant cost reductions are unlikely [83]. Other renewable jet fuel pathways tend to be more costly than HEFA fuels [83]. Consequently, there seems to be a market opportunity for advanced bio jet fuel conversion technologies, which can robustly produce jet fuel below 1 €/L.

4.2.4 Diesel

Diesel is currently the most important product of the middle distillate market, it is the dominating fuel for heavy-duty road transportation and an important fuel for passenger vehicles. Similar to gasoline, diesel fueled vehicles can be substituted by vehicles with alternative drivetrains. However, the blending of conventional diesel with renewable fuel usually requires a renewable blend component with more similar physico-chemical properties, e.g. with biodiesel derived from plant oils (FAME, HVO). However, a scaling of plant-oil derived biodiesel production towards diesel fuel substitution would require a massive enlargement of plant oil production. Therefore, renewable diesel production is a major market opportunity for alternative renewable fuel conversion technologies that can provide fuel with diesel-like physico-chemical properties, such as the higher boiling range fraction of upgraded HTL biocrude.

²³ See e.g. <https://biofuels-news.com/news/finnish-government-targets-30-biofuels-share-in-aviation-fuel/>

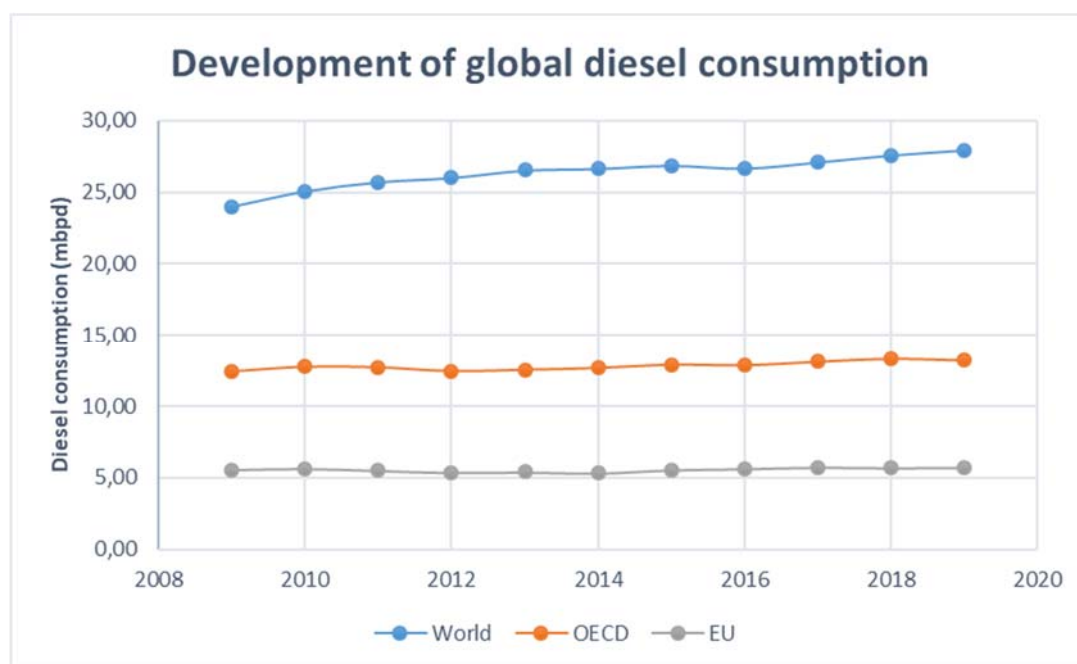


Figure 16: Development of global diesel consumption. Diesel consumption evolved flat in the EU and OECD countries. The global diesel consumption was growing over the past decade at a rate of about 1.1% per year. Data based on BP Statistical Review of World Energy 2020.

Current demand and future demand

In the middle distillate market, the demand for diesel is significantly larger than the current jet fuel demand, but the growth rate of global diesel consumption is slower (see Figure 14 and Figure 16). The diesel consumption within the European Union evolved almost flat over the last decade. For the upcoming years, a declining diesel demand is expected in light of a shift to alternative drive-trains. For diesel powered passenger cars similar substitution dynamics may be expected as for gasoline-powered cars. The situation is different in heavy-duty transportation. A major trend towards electrification is observed in intra-urban transportation. Almost all large European cities are introducing electric busses in their public transportation systems. Similarly, intra-urban logistics is seen as an early market opportunity for electrified trucks. Electrification of intra-urban transportation is especially beneficial due to relative short driving distances, frequent breaking and acceleration, and additional benefits relating to lower noise and air quality emissions. The electrification of long-distance heavy-duty transportation is technologically feasible, especially hydrogen and fuel cells might offer interesting opportunities here. However, diesel engines can operate close to their efficiency maximum on long-distance missions, while batteries and/or hydrogen tanks are penalized by their weight and volume requirements. Therefore, it is expected that a strong diesel demand from heavy-duty transportation over long-distances will persist at least for the next decade.

Regulatory issues

The European specifications for diesel are defined in EN590 (see Table 6). In many aspects, these specifications are less stringent than the jet fuel specifications²⁴. Consequently, it can be expected that an upgraded HTL biocrude that meets jet fuel specifications can also fulfil the requirements as a blendstock to diesel fuel. One important property for the quality of diesel fuel is the cetane rating, in contrast to the octane rating of gasoline for spark ignition engines, ignition under compression is wanted in diesel engines. A cetane number of 100 is assigned to unbranched hexadecane ($n\text{-C}_{16}\text{H}_{34}$), while a cetane number of zero is assigned to 1-Methylnaphthalene ($\text{CH}_3\text{C}_{10}\text{H}_7$) a polycyclic aromatic hydrocarbon. Conventional diesel and the diesel range boiling fraction of upgraded HTL biocrude, are complex mixtures of many compounds. N-alkanes tend to have high cetane number, therefore it is expected that biocrudes from fatty acid rich feedstock will produce a higher quality diesel product, than e.g. lignocellulosic feedstock. EN590 requires a minimum cetane number of 51. In addition to the diesel fuel specification blending quotas are defined by national regulation in many countries, i.e. the blending of HTL derived biodiesel with conventional biodiesel needs to comply with the respective regulations or an extension of existing regulations needs to be established.

Current feedstock supply and alternative fuel use

The feedstock supply for diesel production is similar to the feedstock supply for jet fuel. Conventional diesel is mainly produced from crude oil, to lesser extent, synthetic diesel is produced from natural gas or coal via Fischer-Tropsch synthesis, renewable diesel is mainly produced from plant oil and fats. In contrast to renewable jet fuel, which should be free of oxygen containing species, biodiesel can be produced via transesterification of lipids yielding fatty acid esters (FAME). More recently, biodiesel is increasingly produced via hydroprocessing of lipids (HVO). So far, only marginal amounts of renewable diesel are produced from other renewable feedstocks, e.g. via biomass gasification to form a synthesis gas for the Fischer-Tropsch pathway. Therefore, it is desirable to develop alternative pathways to economic renewable diesel production from sustainable feedstocks, which are available in larger quantities than plant oils or fats. Since diesel fuels are mainly used in road transportation, it is possible to substitute a certain fraction of current diesel consumption by alternative drive-trains. Major non-drop-in fuel and energy options for heavy-duty road transportation include electrification, hydrogen and fuel cells, natural gas in compressed or liquefied form, methanol and DME.

Market prices

The crack spreads for diesel tend to be slightly higher than the crack spreads for gasoline and jet fuel, nevertheless the magnitude is similar (fluctuating around 20 \$/bbl over the last decade). This indicates that diesel is a valuable product in current transportation fuel markets, but the premium is too small to support significant renewable diesel production without regulatory support. Nevertheless, significant amounts of biodiesel are consumed in Europe and worldwide. Currently, biodiesel is mainly produced from plant oils and to lesser extent from other lipids such as greases and fats via the FAME or HVO production pathway. Thus, current biodiesel production relies on the same feedstock basis as current renewable jet fuel production via the HEFA pathway, but the production volumes of biodiesel are much larger due to a more effective regulatory support for biodiesel in many countries. For the market opportunity of HTL diesel, this implies that appropriate regulatory frameworks already exist in many countries. Furthermore, the feedstock availability for FAME and HVO production is limited, especially if the use of

²⁴ Sulphur content is an exception: The maximum sulphur content is limited to 10 ppm (mass) by EN590, while 3000 ppm are allowed for jet fuel (ASTM D1655). Upgraded HTL biocrude is inherently low in sulphur due to the requirements of the catalytic hydrotreatment step.

certain plant oils (e.g. palm oil) is excluded by the respective national regulatory framework. As an example, we discuss the current regulatory framework in Germany. In a Germany an energy based biodiesel quota of 6.25% was replaced legally binding GHG reduction requirement of 6% in 2020. Companies that sell diesel in Germany need to fulfill this GHG reduction requirement, otherwise a penalty of 470 €/t_{CO2} has to be paid. This penalty is sufficiently large (about 1500 €/t_{diesel}) to incentivize the blending of FAME or HVO biodiesel with conventional diesel at the required volumes to fulfill the regulation. Over the past year, biodiesel was blended at a rate of about 7% and biofuel prices in Germany amounted to 70-90 €/L²⁵. It may be expected that HTL derived diesel can be marketed at similar prices or at even higher prices when produced from advanced feedstock. The RED II, which requires a 14% renewable energy consumption in transportation and a 3.5% subquota for advanced renewable fuels (1.75% physically due to multiplication by 2). In addition, the production of biofuels from first generation feedstock is capped at the volume that is used in 2020 and is counted a maximum rate of 7% to the renewable energy quota. Therefore, it may be expected that revised regulatory frameworks may support market prices around 1 €/L for biodiesel that is produced from advanced feedstock.

4.2.5 Marine fuels

The case for marine fuels is more complex than for gasoline, jet fuel and diesel. The marine sector uses a broad variety of fuels such as methane, middle distillates, but mainly different grades of heavy fuel oils, which shows the great fuel flexibility of the marine sector. A major change in the use of marine fuels is caused by the IMO 2020 regulation that reduces the maximum allowed sulfur content from 3.5 wt% to 0.5 wt% for international shipping. Nevertheless, it is expected that the shipping sector will continue to use fuels that have a lower market value than gasoline, jet fuel or diesel. Therefore, the use of upgraded HTL products as marine fuel is only meaningful for product fractions that need to be marketed at a discount, such as the heavy fractions that result from distillation. Another interesting approach is the direct use or blending of raw biocrude fractions, or only mildly upgraded HTL biocrudes in the marine sector.

4.2.6 Struvite as nitrogen and phosphorus fertilizer

Since 2014 phosphorus has been added to the list of critical raw materials by the European Commission, as phosphorus is a limited available resource [84]. The Legislation on the Recovery of phosphorus is currently being enacted at national level. However, there are efforts in Europe to increase the recovery of phosphorus. For example, there has been an amendment to the use of sewage sludge from wastewater treatment plants in Germany since 3rd October 2017. After a transition period of twelve years, sewage sludge from medium and large sewage treatment plants cannot be used as fertilizer anymore. At the same time, a minimum recovery of 50% of phosphorus contained in sewage sludge will be generally mandatory, and even of 80% in cases where sewage sludge is treated thermally, e.g. through hydrothermal processes [85].

Conditions for trade, transport and use of struvite are regulated by rules and regulations at EU and national level. According to EU regulations, struvite can be approved as an

²⁵ www.ufop.de/medien/downloads/agrar-info/marktinformationen/

EC-fertilizer if it complies with the definitions and regulations of the fertilizer regulation EC 2003/2003 [86]. For the classification in this guideline as NP fertilizer, the requirements of at least 3 wt% N and more than 5 wt% P_2O_5 as well as the sum of these two components greater than 18 wt% must be fulfilled. However, the use of struvite from renewable sources as a fertilizer is currently excluded according to EC 2003/2003, as the regulation does not allow the addition of organic nutrients of plant or animal origin in the production of NP fertilizer [87]. However, it should also be added that the EC fertilizer regulation 2003/2003 is currently under revision, whereby struvite is one of the products for which the Joint Research Centre is specifically carrying out studies aimed at proposing possible recovery regulations to the European Commission. The EC 2003/2003 regulation repealed with effect from July 2022 by EU 2019/1009 of European Parliament.

In the light of the current revision of EC fertilizer regulation 2003/2003, it is interesting to evaluate the technical and economic potential of struvite as fertilizer. Besides the recycling of the limited resource phosphorus, the use of renewable struvite provides several benefits compared to conventional fertilizers. For example, eutrophication can be prevented as nutrients are released over a longer period of time. Another advantage of renewable struvite, compared to fossil phosphate mined from phosphate rocks, is the potentially minimal heavy metal contamination (e.g. with cadmium) [88].

In the regulation, struvite is mentioned as certain recovered materials in the same group with biochar and ash-based products. Regulation impose some certain conditions for the waste used as the input of the recovery process. With the scope of avoiding adverse impacts of those fertilizing products to environment and human health, it is required that these products should cease to be regarded as waste within the meaning of Directive 2008/98/EC on Waste Framework [86].

Joint Research Centre of European Commission assessed the existing certain recovered materials as Component Material Categories (CMCs) in EU 2019/1009 Regulation. This assessment considers the candidate materials' requirements that they should comply with and explores the technical and market conditions of these fertilizing products. The title of the project, which is evaluating the possible regulatory framework for safe and effective fertilizer production from recovered, secondary raw materials, is chosen as STRUBIAS (STRUvite, Blochar, AShes).

The benefits expected from EU-wide criteria for fertilizing substances derived from secondary raw materials can be summarized as; reducing the dependence on primary raw materials like phosphate rock, improving the functioning of the internal fertilizing market by allowing safe fertilizers, providing a stable legal framework with certainty to industries and manufacturers to these fertilizers and reducing the administrative burdens related to transportation for environmentally safe materials [89].

A problem associated with the use of struvite as an exclusive fertilizer is related to its intrinsic low N:P ratio. However, it has been shown that struvite can be blended with other fertilizers such as di-ammonium phosphate (DAP) to ensure sufficient N and P supply to the crops [88].

Despite of this limitation, it can be safely assumed that, from an agronomic point of view, a substantial part of the conventional fertilizers consumed in agriculture could be substituted by renewable struvite. The current demand for ammonium phosphate fertilizers in Europe amounts to roughly 1 Mt per year, as can be estimated from data provided by the "International Fertilizer Industry Association" [90] (shown in Figure 17). According to a study by Shu et al. [91], 1 kg struvite per year can be used to cultivate 2.6 ha of arable land.

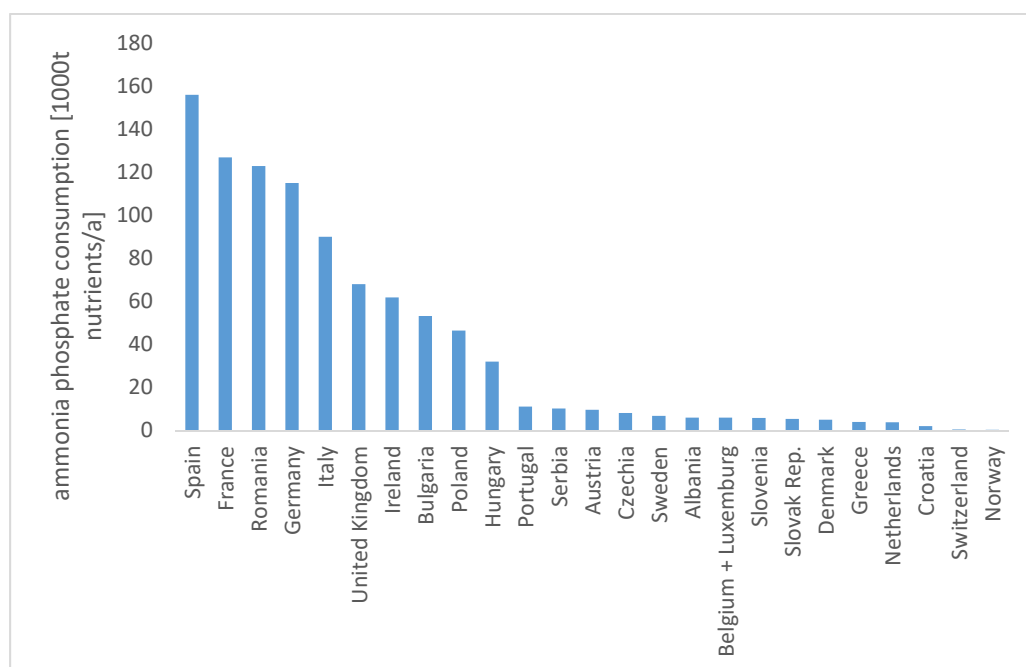


Figure 17: Consumption of ammonia phosphate fertilizer in Europe (2017) [90]

Apart from the utilization of struvite as fertilizer, there are some further benefits related with the usage of struvite in different fields. According to [92] mineralization with struvite improved the fire resistance of wood but also created some minor effects on the other technical properties of the wood. The fire retardant properties of recovered struvite were also studied for cotton fabric [93].

A specific production potential of struvite from HTL process streams, e.g. for Europe, cannot be presented at the moment, as the potential specific yield of struvite depends strongly on the HTL feedstock and its chemical composition (mainly its phosphorus content). For example, analyses in HyFlexFuel revealed a P content ranging from 59.2 mg/kg DM for pinewood to 26100 mg/kg DM for sewage sludge. Blending of feedstock could help to adjust the appropriate nutrient ratios in the HTL process streams.

As there is no existing market for struvite-based fertilizers, potential market prices can only be estimated on the basis of current fertilizer prices and the quantities of phosphorus, magnesium and nitrogen contained in struvite. The estimated market value of struvite ranges from € 188 to € 763 per ton, depending on assumptions [94]. According to Shanmugam et al. the magnesium salts (e.g. $MgCl_2$) that have to be externally supplied for struvite crystallization represent a major part of the production cost [29].

5. Conclusions

Hydrothermal liquefaction (HTL), the core conversion technology of the HyFlexFuel process chain, can be considered a “hot topic” in the field of bioenergy and biofuels that has increasingly gained attention during the past years, as reflected in the exponential growth in pertinent publications in the past years. Many gaps in technology and knowledge remain on the path to understanding the full techno-economic potential, commercial viability and scale-up.

Regarding the HTL process itself, most of the open questions relate to continuous-mode operation, such as effective heat recovery, continuous product phase separation and removal of solid products, e.g. through in-line filtration. The other relevant process steps, i.e. upgrading and refining of biocrude, treatment of the HTL aqueous phase and recovery of inorganic nutrients, have been researched to a considerably lower extent. Consequently, most open questions and technology gaps on the way towards industrial implementation are associated with those process steps, particularly with the treatment of the HTL aqueous phase (inherently representing the largest process stream in terms of volume and mass) and the refining of biocrude into marketable products. HyFlexFuel addresses these open questions and will thereby contribute substantially to the development of HTL-based value chains. The identified technology gaps are intended to serve as guidance for future work in (but also outside of and beyond) HyFlexFuel.

Furthermore, application potentials of and market opportunities for the main HyFlexFuel products have been analyzed, i.e. for the transportation fuel product motor gasoline, jet fuel, diesel and for struvite as a fertilizer product. All major products have a large market potential, concerning existing market volumes and the expected product quality. In road transportation, alternative drive-trains based on electromobility or hydrogen are increasingly introduced into the vehicle fleets, but the consumption of gasoline and diesel is expected to persist at a high level at least for the next decade. Consequently, road transportation can accommodate a large amount of renewable fuel as a blend component in the foreseeable future. While the overall consumption of liquid road transportation fuel is expected to decline, the demand for sustainable biofuel from advanced feedstock is expected to increase in response to the revised renewable energy directive. Struvite produced from biogenic sources is not yet certified as fertilizer according to EU regulations (however, with revision of EU regulations a use of struvite as fertilizer becomes possible), while any kind of alternative jet fuel has to be technically approved according standard jet fuel specifications. HTL-derived jet fuel has not yet been technically approved and can therefore currently not be used in civil aviation. Regulatory boundary conditions need to be adapted to exploit the potentials of the HyFlexFuel products jet fuel and struvite. The requirements to produce blendstocks to gasoline and diesel seem to be easier to achieve compared to the production of an on specification jet fuel blend component. However, national regulations for road transportation fuels need to be considered both from a technical perspective and in terms of national supporting frameworks for biofuels from advanced biomass feedstock. Appropriate supporting schemes for sustainable fuels are key to the commercialization of advanced biofuel technologies, such as HTL conversion, since HTL derived fuels are not expected to be price competitive with conventional fuels unless the crude oil price would significantly increase compared to the level observed over the past five years.

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HyFlexFuel

Public Report: Technology monitoring, application potentials and market opportunities

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No.764734

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