

The logo for CIRCULAIR, featuring the word in a white, sans-serif font with a small white airplane icon integrated into the letter 'I'.

CIRCULAIR



Public report: Process model (for pre-evaluation)

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Abstract

CIRCULAIR investigates the conversion of manure and straw into sustainable fuels for aviation and shipping. The core process, hydrothermal liquefaction (HTL), yields a viscous biocrude, a water phase containing soluble organics, effluent gasses and a solid phase. This report describes the initial version of a process model for HTL conversion, upgrading of HTL biocrudes, wet oxidation of HTL process water and methanol synthesis from evolving CO₂ streams. Preliminary mass and energy balances that are derived from the process modelling provide the basis for an upcoming pre-evaluation of economic and environmental performance parameters. The process model will be further developed and refined over the course of the CIRCULAIR project.

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Glossary

Acronym	Signification
AP	Aqueous phase
BHL	Bauhaus Luftfahrt e. V.
CAPEX	Capital Expenditures
EA	Elemental analysis
GC	Gas Cleaning
GWP	Global Warming Potential
HEX	Heat exchanger
HTL	Hydrothermal Liquefaction
LCA	Life-Cycle Assessment
LHV	Lower Heating Value
MeOH	Methanol
NUTS	Nomenclature of Territorial Units for Statistics
P	Pressure
OPEX	Operational Expenditures
PtX	Power-to-X
RIA	Research and Innovation Action
T	Temperature
TOC	Total organic carbon
UG	Upgrading
VFA	Volatile Fatty Acid
WO	Wet Oxidation

Executive summary

CIRCULAIR is a collaborative Research and Innovation Action funded by the European Union that investigates the conversion of abundant agricultural residues (manure, straw) into sustainable fuels for aviation and shipping, via hydrothermal liquefaction (HTL) and coupling to green H₂ generation. The project has started in January 2023 and has a duration of four years.

All deliverable reports of the CIRCULAIR system analyses work package are public. This implies that intermediate and preliminary results are published before the final project results become available at a later stage of the project. This public report describes a preliminary process model that will serve as a basis for a pre-evaluation of key performance indicators in an early phase of the CIRCULAIR project. The parameters for preliminary modelling are mainly based on previous project results and literature. The process model will be further developed and refined over the course of the CIRCULAIR project, in particular validation and adaption of the process model with respect to experimental results from the CIRCULAIR project will be subject of upcoming work.

The main results of this deliverable are initial energy and mass balances for transportation fuel production via HTL conversion of mixtures of manure and straw, where the HTL process water is treated by wet oxidation to reduce the carbon content and provide process heat to the HTL process. The energy and mass balances corroborate the finding that wet oxidation of HTL process waters can provide significant amounts of process heat for HTL conversion, with potential to achieve autothermal operation (i.e. all external heat requirement for HTL is provided by wet oxidation). Significant amounts of CO₂ evolve mainly from HTL conversion and WO of the HTL process water, and may be utilized for additional fuel synthesis from CO₂ and green hydrogen, here in the form of methanol.

Furthermore, the baseline case for the initial evaluation of economic and environmental parameters is refined with respect to availabilities of agricultural residues and renewable electricity for green hydrogen generation. The mass balance shows that carbon utilisation is significantly boosted (preliminary result: 81% carbon efficiency¹) by coupling with green H₂ for CO₂ utilization, and also point to further optimisation potential.

¹ The carbon efficiency is defined as carbon content in products compared to the carbon content in the feed slurry. The corresponding carbon efficiency without CO₂ utilization is about 66%.

1 Introduction

CIRCULAIR is a collaborative Research and Innovation Action (RIA) that is funded by the European Union EU². The project started in January 2023 and will run for four years. The project website www.project-circulair.eu introduces the project objectives, the roles of the consortium partners, expected innovations, and informs about the results and progress with the project implementation. Key objectives of CIRCULAIR are briefly reviewed in Section 1.1, while Section 1.2 introduces more specifically to the scope of this public report.

1.1 CIRCULAIR: Key Objectives and ambition

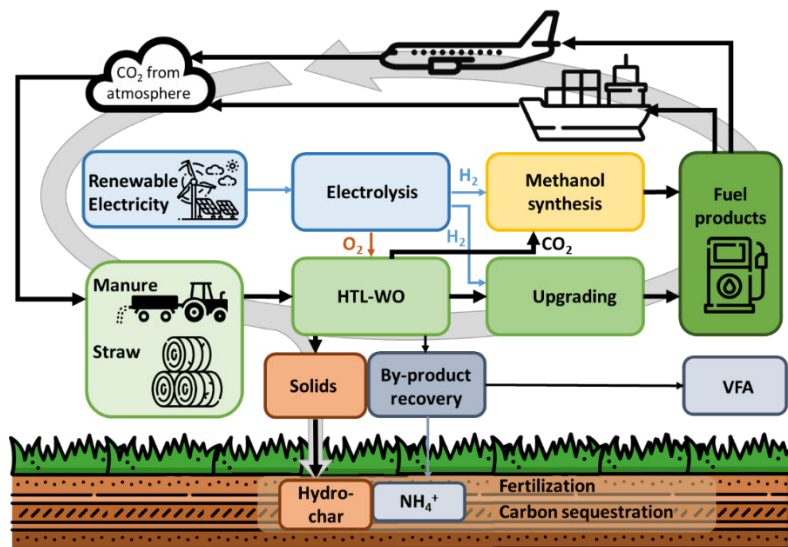


Figure 1: Sketch of the CIRCULAIR concept. The central conversion step is hydrothermal liquefaction (HTL) coupled to a wet oxidation (WO) of the HTL process water. All product phases of HTL conversion are utilized. Coupling with green H₂ enables almost complete carbon to product conversion.

Figure 1 sketches the basic approach of CIRCULAIR. HTL is the central biomass conversion process, abundant agricultural residues (manure, straw) are chosen as feedstock due to availability considerations. Compared to other advanced biofuel technologies, HTL is especially suited for the conversion of wet feedstock such as manures. One of the main innovations of CIRCULAIR is the coupling of HTL with wet oxidation (WO) of the HTL process water. Thereby, the HTL process water is cleaned-up and the external process heat demand for HTL conversion can be greatly reduced, CIRCULAIR aims at the demonstration of thermo-neutral operation. Further important innovations relate to the upgrading of HTL biocrudes to final fuel products with a high share of kerosene that complies jet fuel specifications. The

² <https://cordis.europa.eu/project/id/101083944>

holistic approach of CIRCULAIR foresees the treatment of all HTL product phases by developing suitable valorisation schemes for all relevant side streams. The HTL process water after WO can still contain significant amounts of organic species with a high share of volatile fatty acids (VFA). The recovery of VFA is investigated, furthermore, effluent gases from HTL conversion and from WO of HTL process waters contain a high share of CO₂. Here, coupling with green H₂ is envisaged to utilise the CO₂ streams for methanol synthesis. Finally, a solid phase is evolved, CIRCULAIR will fill a knowledge gap regarding the use of HTL chars for soil application, potentially creating a negative contribution to the carbon footprint.

The CIRCULAIR consortium consists of ten partners from six European countries: Aarhus University (Denmark), Aalborg University (Denmark), Circlia Nordic (Denmark), Topsoe (Denmark), RISE (Sweden), Eni (Italy), Universidad Complutense de Madrid (Spain), Universität Hohenheim (Germany), Bauhaus Luftfahrt (Germany), and L-up (France). The individual roles of the project partners are described on the CIRCULAIR website: <https://project-circulair.eu/partners/>

1.2 Process model for pre-evaluation of key performance indicators

This public report “Process model (for pre-evaluation)” is the second out of a series of eight public reports from the CIRCULAIR system analysis work package that are planned to be published over the course of the project:

1. Assessment framework for CIRCULAIR process
2. Process model (for pre-evaluation)
3. Pre-evaluation of key economic and environmental parameters
4. Optimized process model
5. Techno-economic evaluation and market analysis
6. Socio-economic impact assessment
7. Life cycle analysis
8. Trade-off studies, synthesis of results and roadmap

The main objective of this public deliverable is to report on an initial version of a process model that is capable to provide preliminary mass and energy balances. This evaluation will serve as a basis for a first estimate of key performance parameters, such as fuel production cost or Global Warming Potential (GWP), in the consecutive public report “Pre-evaluation of key economic and environmental parameters”. This pre-evaluation can assist the internal decision making within the CIRCULAIR project implementation from techno-economic and

environmental perspectives. Furthermore, the results serve for communication and dissemination during the project duration, until final results from the system analysis work package become available towards the end of the project.

Many results of CIRCULAIR's experimental campaigns cannot be reflected by the preliminary model as they become available at a later stage of the project. Consequently, the quantitative values in this report need to be handled with care, they should be considered as preliminary indications until the final results become available.

2 Model development

This chapter describes the framework and methodology for which the pre-validation model is built.

2.1 Methodology

The model presented in this document is capable to provide quantitative parameters for a pre-evaluation of key economic and environmental indicators. This requires a representation of the process in the form of mass and energy balances. The mass and energy balances were modeled based on available literature and taking into account early experimental results from CIRCULAIR, especially with respect to wet oxidation.

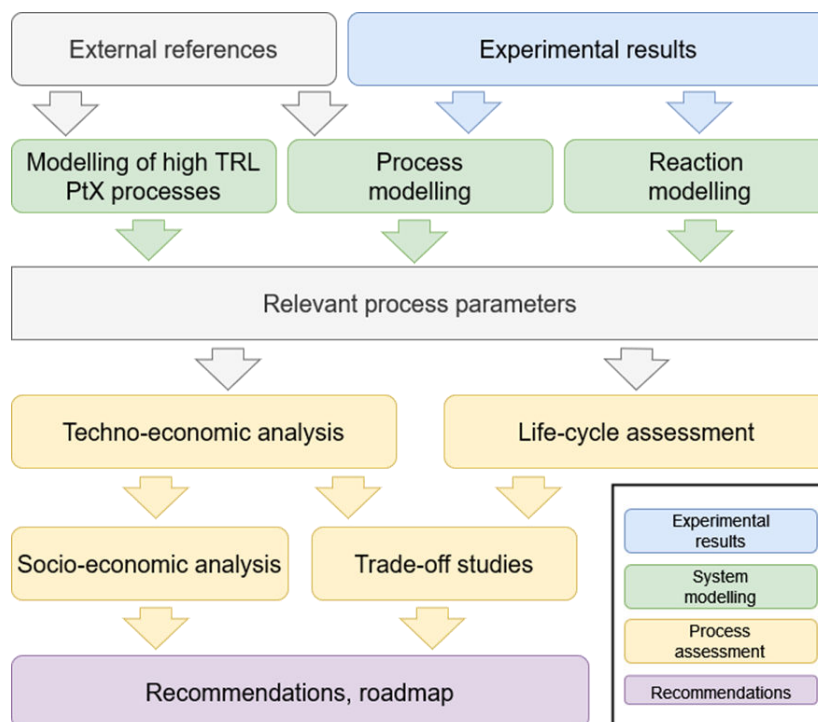


Figure 2: Modelling framework for system analyses within CIRCULAIR. Taken from [1].

The structure of CIRCULAIR's overall modelling framework is outlined in Figure 2. The present report is focussed on system modelling and the pre-evaluation of relevant process parameters. The modelling includes processes that are technologically mature and for which sufficient external literature is available, such as electrolysis or methanol synthesis, as well as processes that are developed and optimized within CIRCULAIR, such as HTL and the utilization of the evolving process streams.

The focus of the process modeling is primarily on the latter category, including technological process specifications and reaction modeling, to evaluate relevant process parameters such as mass and energy balances, but also product compositions. The pre-evaluation of process parameters are the basis for a preliminary techno-economic analysis and a life-cycle assessment in a consecutive step. The process model will be further refined over the course of the project.

2.2 Feedstock supply and regional context

Process modelling, as well as the evaluation of techno-economic and environmental parameters, requires the definition of a baseline case that has been described in detail in the preceding public report “Assessment framework for CIRCULAIR process” [1]. Manure and mixtures of manure with straw have been chosen as feedstock because they are abundant in the agricultural context (compare to Section 2.2.1). Furthermore, previous work has shown a potential benefit in biocrude yield resulting from a co-liquefaction of manure and straw [2]. A hub and spoke approach was selected, where a central upgrading plant is supplied with biocrude produced in several HTL plants. The regional HTL plants themselves aggregate feedstock from a number of farms at local level. The example in Figure 3 shows an arrangement of several HTL facilities and a centralized upgrading plant in central Denmark.

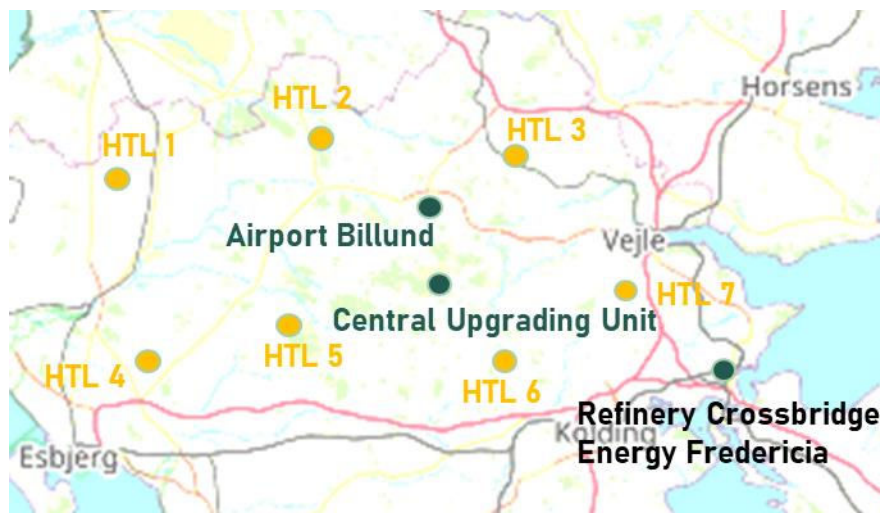


Figure 3: Conceptual distribution of HTL plants, a central upgrading unit and a fuel consumer in the form of the airport at an example in central Denmark.

The initial process modelling assumes a feed slurry with DM content of 15 wt% corresponding to a manure/straw ratio of 80:20 on a dry base. The assumed DM content of manure is 11 wt%, while straw is almost a dry feedstock (96 wt% DM), this means that significant quantities of water must be removed from the feed slurry. The chosen DM content of 15 wt% is low enough

to ensure pumpability of the HTL slurry, on the other hand it is high enough to expect a high biocrude yield and thermal efficiency.

2.2.1 Feedstock supply

The Central Denmark Region is chosen as regional context for the initial evaluation, as good availability of both manure and straw for HTL conversion coincide with favourable conditions for green H₂ generation from wind energy.

Table 1: Feedstock and energy supply at NUTS3 regions in Denmark.

NUTS 3 regions	Cereal straw [t DM/km ²] [3]	Cattle excretions [t DM/km ²] [4]	Mean wind speed* [km/h] [5]
Byen København	5.9	1.4	6.8
Københavns omegn	16.7	2.5	7.8
Nordsjælland	42.4	18.9	8.5
Bornholm	61.3	21.7	8.3
Østsjælland	75.0	10.7	8.5
Vest- og Sydsjælland	87.0	20.3	8.3
Fyn	61.7	45.2	8.0
Syddjylland	58.5	111.9	8.4
Vestjylland	61.3	97.5	8.7
Østjylland	59.2	46.9	8.6
Nordjylland	56.1	91.2	8.3

(*Data for 10% windiest area in 9 km², height 100 m)

Table 1 lists average feedstock densities and mean wind speeds across Denmark at NUTS3³ level. The mean wind speeds are high almost everywhere in Denmark. Manure is the primary feedstock in CIRCULAIR, in turn, regions with high cattle excretion density are preferred locations. Different regions in Central Denmark (Syddjylland, Vestjylland and Nordjylland) show high feedstock density both for manure and straw. An investigation of the average farm

³ NUTS (Nomenclature of Territorial Units for Statistics) is a geocode standard for referencing the administrative divisions of countries for statistical purposes.

size in South Denmark resulted in 220 cattle per farm, which corresponds to an annual feedstock availability of about 2.4 kt of wet cattle manure per year [4].

For the initial modelling of HTL conversion, we assume a mixing ratio of dry manure and straw of 80:20 and a feed slurry supply of about 6700 kg/h (corresponds to 1000 kg/h biomass on a dry basis), which roughly matches the manure generation of 15 farms and an additional supply of straw (105 farms for the upgrading plant). The conversion of this feed stream results in a biocrude production of about 400 kg/h at a single HTL plant.

2.2.2. Logistic concept

The HTL scenario in Denmark described in Section 2 is associated with transportation of the manure, biocrude and fuel product. It is assumed that the transport radius of the manure to the HTL plant is 20 km. In the modeling, this transportation is carried out by trucks that carry the wet manure (dry matter content 11 wt%). The maximum transportation distance for transporting the biocrude to a central upgrading plant is 100 km. A maximum transport distance of 50 km is assumed for the transportation of the final fuel products to their respective customers.

It was assumed that biocrude and liquid fuels are also transported by truck. The road network was taken into account by determining a factor that reflects the relationship between the linear distance and the use of the existing roads. A dry biomass input of 1000 kg_{DM}/h results in a biocrude production of about 400 kg/h at a single HTL conversion plant.

The assumption was made that all HTL plants and the upgrading unit have an annual capacity utilization of 90 %. For comparison, the upgraded biocrude production of one upgrading unit would correspond to 0.7 % of the upgrading capacity of the crude oil refinery in Frederica.

2.2.3 Renewable energy supply

CIRCULAIR investigates the coupling of advanced biofuel and green H₂ production. Green H₂ is mainly used for two purposes, for methanol synthesis in combination with CO₂ streams evolving from biomass conversion and as a source of refinery H₂ at the centralised upgrading facility. It is a well-established finding that the cost and Greenhouse Gas (GHG) emissions associated with H₂ generation play a key role in Power-to-X (PtX) schemes. This contributed to the choice of Central Denmark as regional context for the initial evaluation as it is well suited for competitive H₂ generation from wind energy.

For the design of the electrolyser a mean capacity factor for wind turbines in Denmark of 40 % was taken into account. Based on an electricity consumption of 50.0 kWh_{el}/kg_{H2} (66.7 % energy conversion efficiency on LHV⁴ basis), electrolyser capacities of 36.3 MW for the overall demand of seven HTL plant sites (5.2 MW per plant) and 20.8 MW for the central upgrading plant site are derived.

⁴ Lower Heating Value

2.3 Process modelling

The process model was developed in Aspen Plus®. The core of the model is based on an adaption of an existing process model that was developed in the EU-funded project HyFlexFuel⁵. The core model includes the process steps of hydrothermal liquefaction (HTL) and biocrude upgrading, while further process step models, in particular, wet oxidation (WO) of the HTL aqueous phase (AP) and methanol synthesis from CO₂ from the HTL and WO gas phase have been newly developed. Additional process steps, namely gas cleaning, volatile fatty acid extraction and ammonia extraction are subject to detailed analysis within the project. However, as reliable experimental results will only become available at a later stage in the project, these processes have been modelled as black boxes in this report. In the following, each process step model will be described in more detail.

2.3.1 HTL-WO

HTL conversion and the utilization of the resulting product phases is at the core of the CIRCULAIR approach (see Figure 1). HTL can convert various organic feedstock into a biocrude, the reaction chemistry is complex and depends critically on process conditions (typically T = 300-350°C, p = 180-230 bar) and feedstock composition. Rigorous modelling of the complex reaction network is beyond current capabilities, nevertheless, process modelling based on representative modelling compounds provides important insights into the reaction chemistry and shows reasonable agreement with experimental results [6]. After biocrude separation, soluble compounds remain in the aqueous phase and are fed into a wet oxidation reactor. Biocrude is further upgraded into liquid fuel products, while the gas phases are cleaned and remaining CO₂ is utilized in a methanol synthesis process. The solid phase is treated in order to improve its properties as soil amendment.

In the following, the three main building blocks of the model, coupling of HTL-WO, upgrading and methanol synthesis will be discussed in more detail. Figure 4 displays a block flow diagram with the blocks indicating the different unit operations in the process model and the arrows indicating the streams between the unit operations. The overall process chain starts with the feedstock, the composition of the feedstock is represented by a set of 51 model compounds, whose input mass can be adapted according to the specific case. Potential pre-treatment steps of the feedstock are not shown here, but can be considered if necessary. The feed pump pressurizes the slurry up to pressures of 200 bar. The cold feed slurry enters a

⁵ H2020 HyFlexFuel: <https://www.hyflexfuel.eu/>

into the Aspen model via a calculator block. Heat release was calculated based on standard values for the heat of formation. The stream leaving the WO reactor is cooled down and depressurized. The gas phase from WO is separated from the remaining AP and sent to the gas cleaning section. The WO AP is sent to VFA and ammonia recovery. As indicated above, the latter two process steps are not yet modelled in detail, which is why no methodological approach is described here. The cleaned gas phase (purified CO₂) is then sent to the methanol synthesis section.

2.3.2 Biocrude upgrading

HTL biocrudes are energy dense substances, but other properties of raw HTL biocrudes require further upgrading to produce suitable fuels for transportation⁶. In this model for pre-evaluation, the biocrude upgrading process is modelled in a simplistic way: A single stage hydrotreatment to saturate double bonds and remove heteroatoms such as O, N, and S, furthermore bottom residues are hydrocracked to increase the kerosene yield. In a later stage of the project, several aspects of the model will be refined according to experimental results. This involves multistage upgrading strategies, which are usually needed to prevent clogging and enable almost complete heteroatom removal. The upgrading of HTL biocrude in fixed bed hydrotreatment reactors also requires appropriate solid separation and biocrude de-mineralization, however, the initial process model does not focus on these process steps yet.

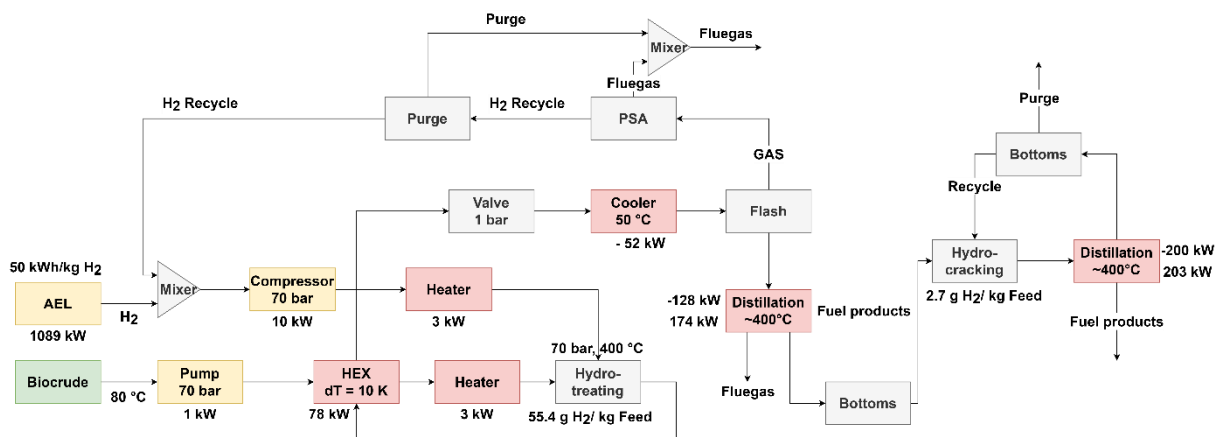


Figure 5: Flow chart of the upgrading process with details of the process conditions.

Figure 5 shows a block diagram of the simplified biocrude upgrading model. At the upgrading plant the biocrude is pressurized to 70 bar and pre-heated with the product stream through a heat exchanger. The remaining temperature difference is covered by an additional heater.

⁶ Raw or mildly upgraded HTL biocrudes may be suitable as marine or heating fuels.

Hydrogen for upgrading is assumed to be produced through electrolysis at a pressure of 30 bar. Fresh hydrogen is mixed with the recycled hydrogen and subsequently compressed to 70 bar. The remaining difference in heat is covered by another heater. The hydrotreating step is represented by a single stage process at severe conditions (70 bar, 400 °C) for deep denitrogenation. In a real world application, applying such harsh conditions would almost certainly result in unwanted polymerization reactions. The full process model will involve additional pre-stabilization steps⁷, nevertheless, a single step at harsh conditions should be a good approximation for a first evaluation of performance parameters. After passing the heat exchanger, the product stream is depressurized and cooled down for phase separation. The liquid phase is sent into a distillation column, while the gas phase is run through a cleaning process involving separation of hydrogen for the recycle and a purge stream. Distillation results in liquid fuel products, a bottom fraction and another stream of gaseous hydrocarbons. The cut of the bottom fraction can be varied depending on the desired fuel products. In this model, the distillation cut is set to include the diesel fraction as a fuel product while compounds with a higher boiling point are in the bottom fraction. The bottom fraction is then sent to a hydrocracking unit in order to produce a second set of fuel products. The remaining bottom fraction is recycled and a small fraction is purged to prevent accumulation of stable compounds. The purged stream can again be used for heat generation.

2.3.3 Methanol synthesis

CIRCULAIR aims at near-complete carbon utilization. CO₂ streams that evolve during HTL conversion and WO are a main lever to achieve this target (compare to Figure 11). Various CO₂ utilization schemes are conceivable, methanol synthesis from CO₂ and green H₂ is favoured in CIRCULAIR as it seems suitable to utilize the relatively small scale CO₂ streams that evolve at the distributed HTL-WO plant sites.

A flow chart of the methanol synthesis unit is shown in Figure 6, after gas cleaning CO₂ is sent from the HTL plant to the methanol plant. At the methanol plant it is pressurized and heated to the reaction conditions (60 bar, 250 °C) and mixed with hydrogen and the subsequent recycle stream. Hydrogen is produced via electrolysis and also compressed and heated to the reaction conditions. Due to the reduced pressure of the recycle stream, a further compression step of the mixture is needed. The compressed stream is pre-heated with the product stream through a heat exchanger and remaining heat demand is provided by an

⁷ To be described in future CIRCULAIR public report "Optimized process model"

additional heater. Methanol synthesis is represented by a kinetic model based on the kinetic parameters provided by Moser et al. [6]. After passing the heat exchanger, the product stream is further cooled down to $-40\text{ }^{\circ}\text{C}$ to guarantee good separation efficiency of the gas phase from the liquid phase. A small fraction of the recycled gas phase is purged as an off-gas, which can be used for heat generation. The liquid phase containing methanol and water is heated again in order to enter a distillation column separating methanol as the final product.

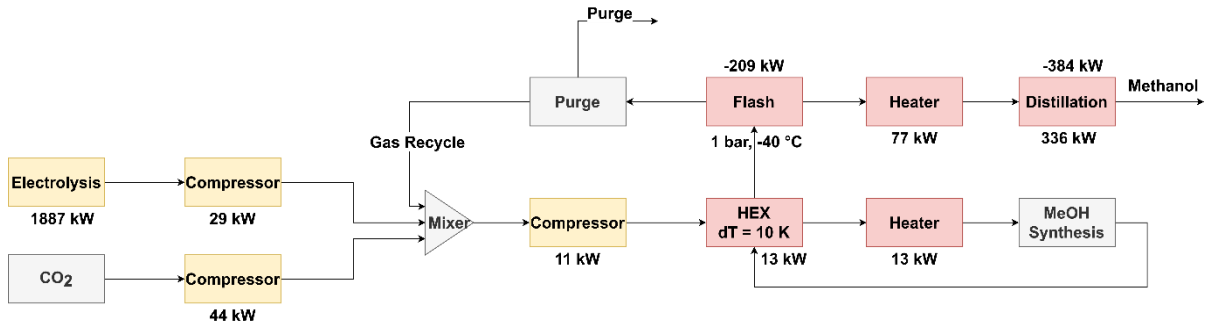


Figure 6: Flow chart of the methanol synthesis with details of the process conditions.

2.3.4 Heat requirements

In process design, heat integration plays an important role for optimizing the utility needs and supply of a process. Using internally produced heat can significantly reduce the external heat demand and thereby also energy cost and the environmental footprint.

Since the CIRCULAIR process is a highly integrated process concept, there are different possibilities for heat integration. In the current version of the model for pre-evaluation, heat integration is implemented in two ways.

The first implementation is focused on heat exchange within the individual process steps, where hot streams flowing out of a reactor are connected with the incoming cold stream in a heat exchanger (see e.g. Figure 4). Thereby, heat is transferred from the hot product stream to the cold stream, effectively pre-heating the cold feed stream. In the Aspen model, a temperature difference of 10 K was chosen between the hot and the cold stream, which effectively means that the hot stream is able to transfer the amount of heat that is needed for the cold stream to be heated to the temperature of the hot stream minus 10 K. The hot stream is thereby cooled down. This also means that after the heat exchanger, there is still a temperature difference of 10 K between the incoming stream and the reactor conditions. Currently this heat difference is covered by external heating, except for the HTL reactor.

The second implementation of heat integration in the current model is specific for the integration of HTL with WO. WO is an exothermic process and the heat released during the

oxidation is used to replace the external HTL heater. This simplification for initial process modelling is also illustrated in Figure 4.

For the final model, further implementations of heat integration have to be investigated. Several possible heat sources have been identified and are discussed in more in detail in Section 3.4. It is also anticipated that heat integration represents an important lever for overall plant optimization. The initial modelling within this report suggests that the integration of WO into HTL can result in excess heat generation (see Figure 12), which raises the question of a meaningful valorisation of this heat.

3 Parameters and results for pre-evaluation

3.1 Model composition of educts and products

The assumed biochemical composition and experimental elemental analysis of the individual feedstock as well as the 80/20 mixture of cow manure with wheat straw is shown in Table 2. These values are based on Dos Passos et al. [2] and it is important to mention that feedstock composition can vary significantly, especially in the case of manures, where compositional changes can result from differences in feeding, manure collection and storage [6].

Table 2: Biochemical composition of pure cow manure and wheat straw, as well as a feedstock mix in a mixing ratio of 80:20 (on a dry basis).

Biomass	Cow manure	Wheat straw	80/20 mixture	Element	Cow manure	Wheat straw	80/20 mixture
Protein	14.1	3.6	12.0	C	52.9	46.9	51.7
Extractives	4.3	6.9	4.8	H	7.3	6.5	7.1
Cellulose	21.0	39.7	24.7	N	2.7	0.6	2.3
Hemicellulose	21.0	30.5	22.9	O	36.5	45.9	38.4
Lignin	23.7	16.5	22.3	S	0.6	0.1	0.5
Ash	15.9	2.7	13.2	-	-	-	-
Sum	100.0	100.0	100.0	Sum	100.0	100.0	100.0

The comparison of experimental and model elemental analysis (EA) is shown in Figure 7. The results show a good agreement with the literature values. All relative differences are below 10 % and result from the approximation of feedstock composition by modelling compounds, the higher deviations of nitrogen and hydrogen are most likely observed because not all amino acids present in the protein fraction are modelled, consequently it is likely to obtain a certain deviation.

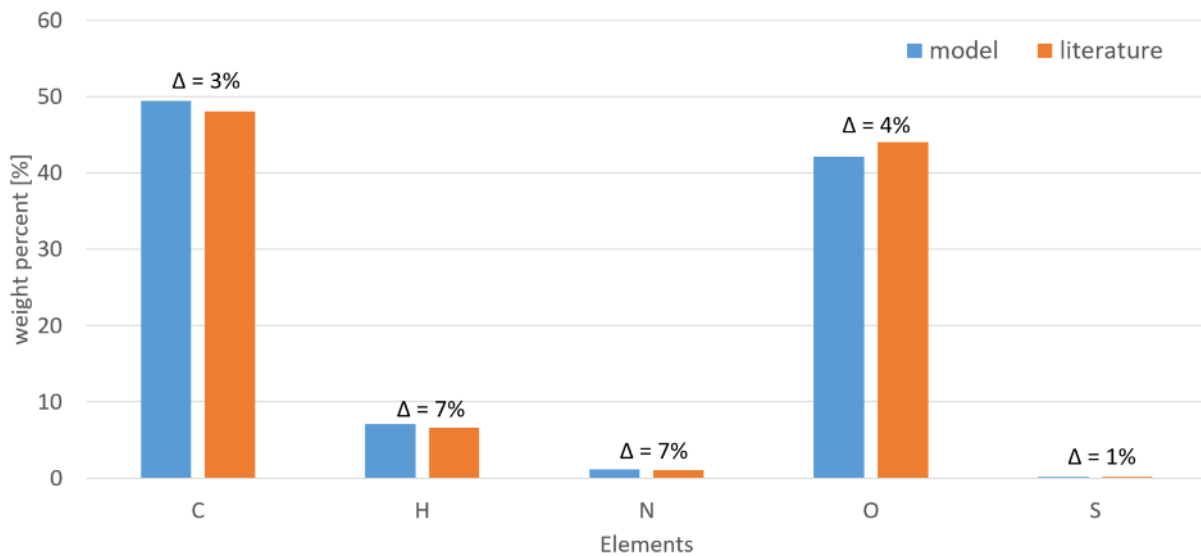


Figure 7: Elemental analysis of the feed slurry (80/20 mixture of cow manure and wheat straw). Orange bars correspond to literature values, blue bars correspond to the mixture of modelling compounds. The values on top of the bars represent the relative difference between the respective model and literature value.

Figure 8 shows the EA results of the modelled biocrude and modelled upgraded biocrude streams. It can be clearly seen that compared to the feedstock, the amount of carbon is increased significantly in the biocrude, while the hydrogen content is only slightly increased. Nitrogen, oxygen and sulphur content is reduced. A similar behaviour can be observed for the transformation of biocrude to upgraded biocrude, however, the relative increase in carbon is smaller, while the relative increase in hydrogen is substantial. Oxygen (564 ppm) and sulphur (6 ppm) are almost completely removed, while there is still a significant amount of nitrogen (3938 ppm) present in the upgraded biocrude. The representation of feedstock, biocrude and upgraded biocrude composition via modelling compounds will be refined as more experimental data becomes available over the course of the CIRCULAIR project.

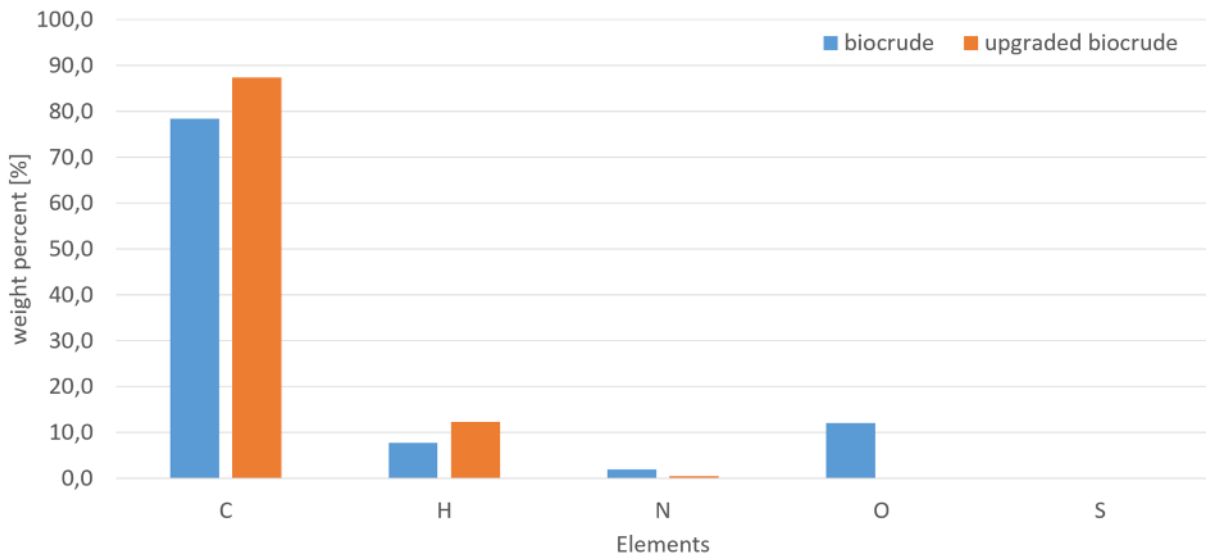


Figure 8: Elemental analysis of modelled biocrude and modelled upgraded biocrude stream.

Further analysis of the modelled biocrude and upgraded biocrude was done by calculating boiling point curves. These are shown in Figure 9. Most compounds in the biocrude are found in the range of 250 °C to 400 °C and above 500 °C (not shown). The steepest increase can be observed in the range between 350 °C and 400 °C, which indicates larger amounts of single model compounds, e.g. fatty acids, long chain alcohols/amines/amides or alkanes/alkenes. The boiling points of the upgraded biocrude are shifted towards lower values due to the reduction in heteroatoms (O, N, S), which in turn reduces the strength of intermolecular bonds and the boiling temperature of compounds.

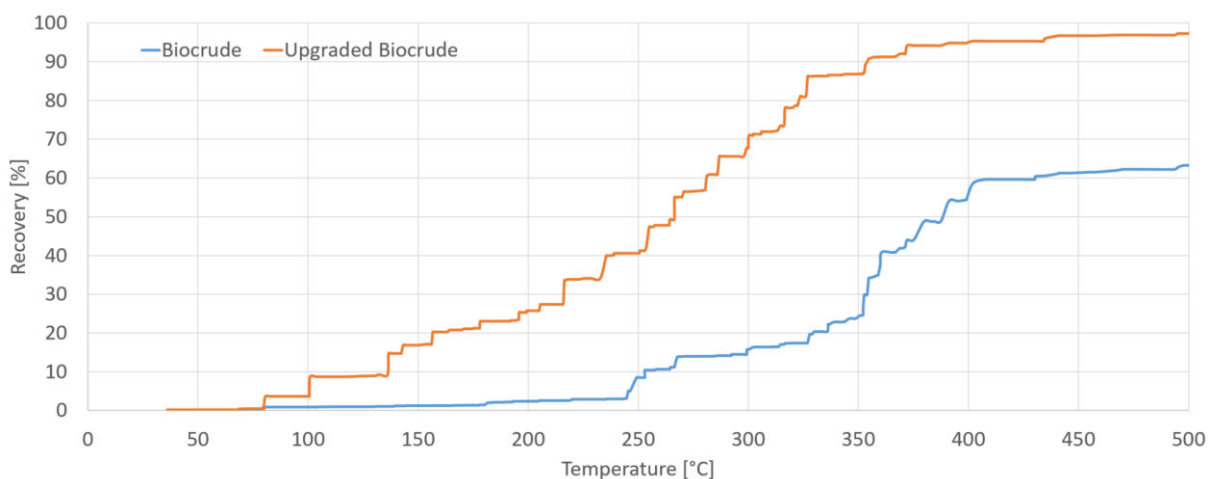


Figure 9: Calculated boiling point curve based of the modelled biocrude and upgraded biocrude composition.

The upgrading process yields two streams of fuel products, one after hydrotreating and one after hydrocracking. After distillation, the corresponding fuel fractions are combined, results for the combined product are displayed in Table 3.

Table 3: Definition of the distillation cuts based on their boiling point range. Fuel fractions refer to the cumulated amounts of upgraded product from the biocrude input of seven HTL plants (see Figure 3).

Fraction	Boiling point range [°C]	Mass flow of fuel fraction [kg/h]	Fuel fraction [wt%]
Gas	< 30	339	13
Naphtha	30 - 205	722	27
Kerosene	190 - 300	1061	39
Diesel	300 - 400	368	14
Bottom	> 400	206	8

3.2 Mass balances

This section describes overall mass balances that were created using the process model. Figure 10 shows the mass balance that results from the modelling CIRCULAIR process. The illustration in Figure 10 is simplified, a spatial separation of the HTL plants and centralized upgrading, as envisaged in Figure 3, is neglected here as the mass balance is not changed by biocrude transport. Furthermore, several HTL plants feed a centralized upgrading plant in the baseline case, while Figure 10 shows a single HTL plant and the throughput of the upgrading process is adapted accordingly. It should also be noted that this mass balance is a preliminary modeling result, in particular not all process steps are modelled with the same level of detail at this stage. For example, solid treatment and the treatment of gases and wastewater are not yet part of the process modeling, but will be added in the course of the project.

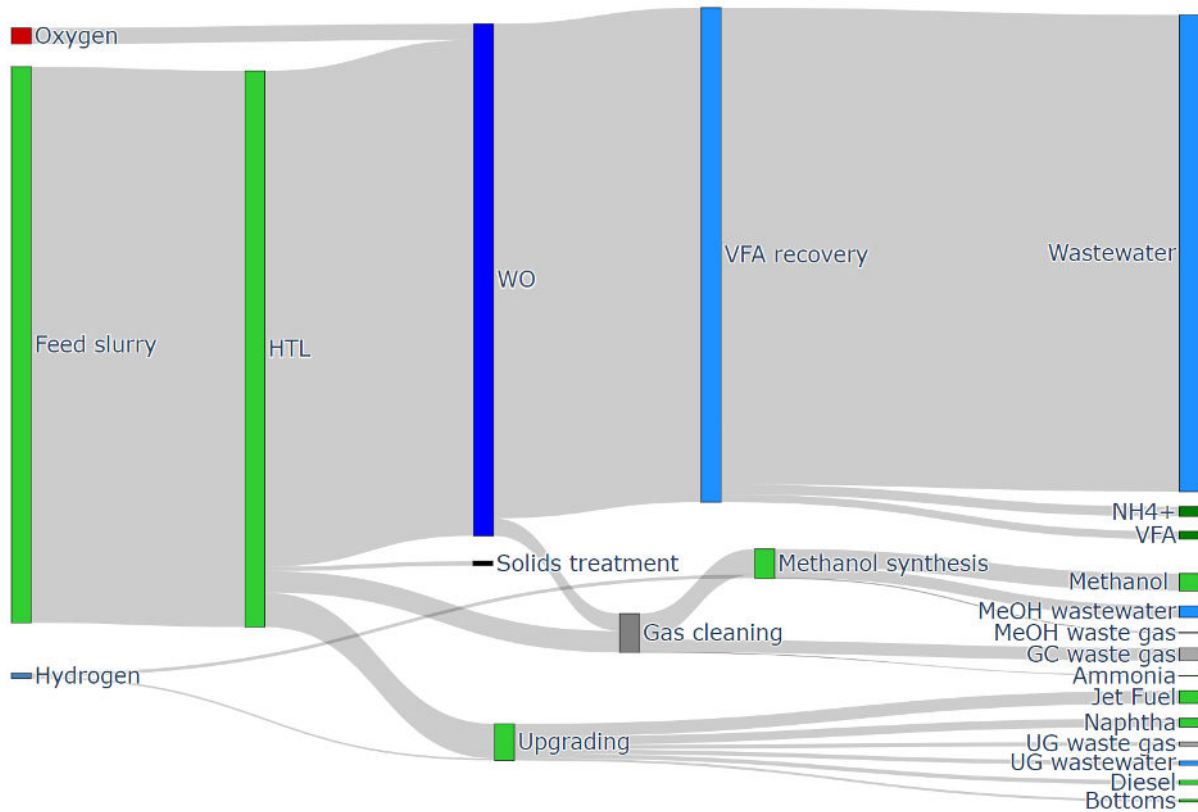


Figure 10: Preliminary mass balance of the overall CIRCULAIR process based on the biomass input. In the baseline scenario several HTL plants feed one upgrading.

At first glance, it is apparent that streams with high water content (feed slurry, HTL-WO aqueous phase, wastewater) are the dominating contribution to the total mass flow, while mass flows of the energy products are comparatively small. This illustrates that large quantities of water have to be transported, heated, cooled, and treated, which has a significant impact on operating and investment costs and highlights the importance of heat exchange and thermal management. The required quantities of hydrogen are barely visible in Figure 10, normalized to 1 kg of biocrude, 0.10 kg of hydrogen is required for methanol synthesis and 0.06 kg for upgrading. However, hydrogen is an important factor in the energy balance (see Section 3.4).

3.3 Carbon balances

Figure 11 illustrates the carbon balance of the CIRCULAIR process. The majority of the educts is made up of the fuel fractions from biocrude upgrading with carbon shares of 26% for jet fuel, 18% for naphtha and 9% for diesel. 16% of the carbon ends up in methanol, also representing an energy product. 8% of the carbon is found in the VFA. According to current modelling, 81% of the carbon input can be converted to products.

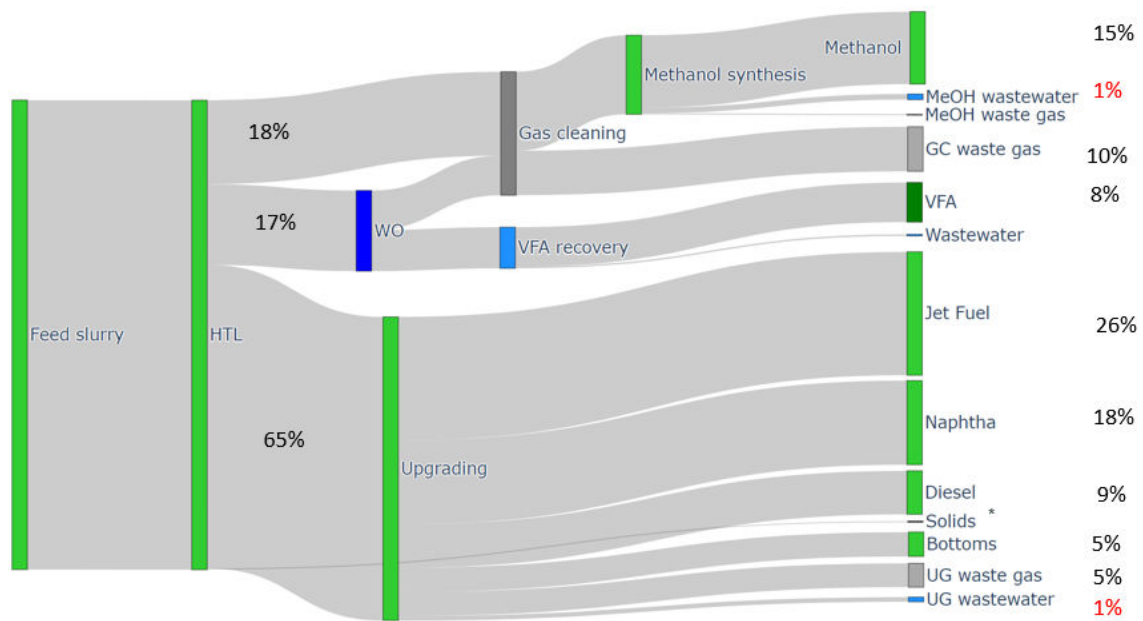


Figure 11: Preliminary carbon balance of the overall CIRCULAIR process (*Value is underestimated in the modelling).

The pre-modeling quantifies persistent leaks in the carbon balance and identifies mainly gaseous product streams that may be utilized to further increase carbon efficiency towards the CIRCULAIR target of 95 % carbon utilization. In particular, exhaust gases from upgrading (5%) and gas cleaning upstream of methanol synthesis (10%) need to be utilized to achieve the target. Prospectively, combustible species in the exhaust gases can be used for energy generation, furthermore CO₂ may be separated and utilized for additional methanol synthesis. The treatment and use of these gas streams is the subject of economic and ecological optimization and will be addressed in the further course of the CIRCULAIR project.

3.4 Energy balances

The energy balances are of particular importance, as they quantify energy inputs to the process and the energy content of the final fuel products. The CIRCULAIR baseline scenario considers several decentralized HTL plants that feed a centralized upgrading plant, consequently separate energy balances are evaluated for the HTL plant sites and for the upgrading plant site. The energy balance of the HTL process including the wet oxidation and methanol synthesis is shown in Figure 12.

The biomass, methanol and the upgraded biocrude (shown in green color in Figure 12) contain chemically bound energy, i.e. energy that can be released during thermal conversion. Chemically bound energy is also present in the gas streams from the HTL and methanol synthesis (gray color in Figure 12). The energy for the biomass, the biocrude, the organic

content in the aqueous phases and the fuel products was calculated using the higher heating values (HHV) according to Milne based on elemental composition and ash content (elemental and ash fraction in wt%; HHV in MJ/kg).

$$HHV_{Milne} = 0.341 C + 1.322 H - 0.12 O - 0.12 N + 0.0686 S + 0.0153 ash$$

The calorific value of the gases is calculated using the literature-based calorific value of the respective gas components.

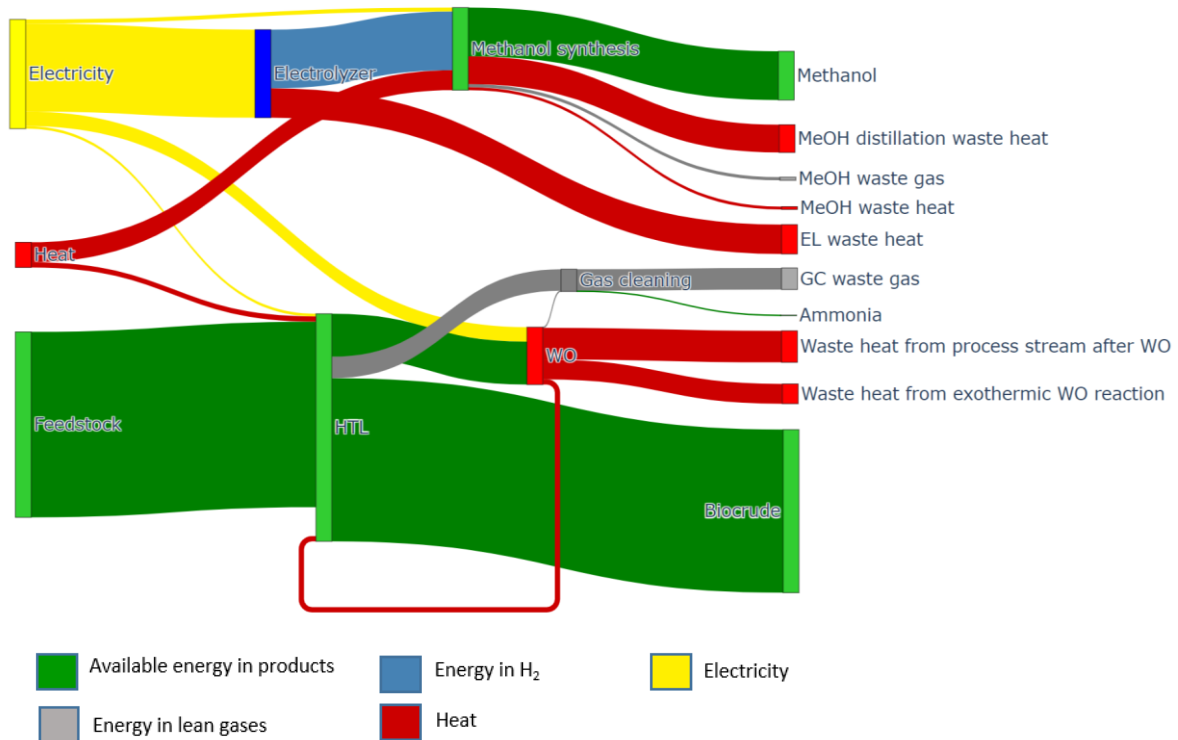


Figure 12: Preliminary energy balance of the CIRCULAIR process. The color code in the figure indicates the type of energy and process streams.

As described in Section 2.3.4 an internal heat recovery with a temperature difference of 10K for both the HTL-WO process and methanol synthesis is assumed. Heat recovery will be mapped in more detail in the future, taking into account the experimental results obtained within the CIRCULAIR project. Also the overall heat management of the CIRCULAIR process will be a subject that will be investigated in more detail.

The energy balance shows that significant amounts of waste heat stemming from WO at temperature levels of up to 270°C and 350°C are released. For this, an application of district heating is conceivable and will be subject for further studies. In terms of electricity consumption, the electrolyzer for H₂ provision is the main factor; the energy consumption for the individual sub-processes is less significant. The energy balance of the upgrading process is shown in Figure 13.

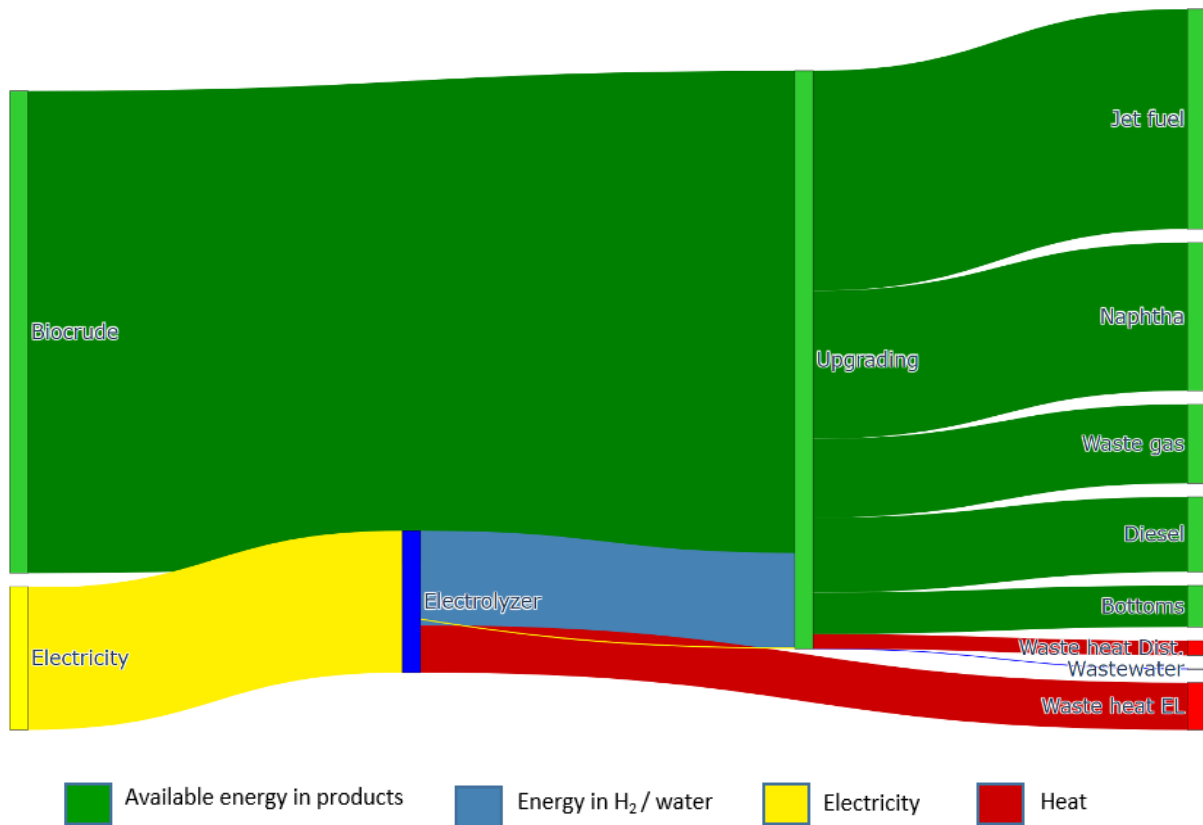


Figure 13: Preliminary energy balance of the biocrude upgrading process. The color code in the figure indicates the type of energy and process streams.

The energy balance of the upgrading process clearly shows that, in addition to the energy that ends up in the fuel products, a significant proportion is also found in the off-gases. Figure 13 also shows the energy supplied to the system in the form of hydrogen. The energy content of the hydrogen accounts for around 20 % of the total energy input.

Besides the chemical energy bound in the educts and products, both heating and cooling must be supplied in order to operate several subsystems at the HTL-WO plant sites and the central upgrading plant. As already indicated in Section 2.3.4, several heat sources have been identified that could be used in a highly integrated system. Furthermore, different options for waste heat use have been identified. All relevant heat streams are listed in Table 4.

Table 4: Heat streams from the CIRCULAIR process with their corresponding temperature levels.

Stream	Source/sink	Temperature
Waste heat from exothermic WO reaction	Source	350 °C
Waste heat from process stream after WO	Source	270 °C
Waste heat from MeOH production	Source	260 °C
Waste heat from Electrolyzer	Source	80 °C
Methanol-water distillation	Sink	110 °C
Electrolysis heat	Sink	80 °C
District heating	Sink	45-70°C
Electricity storage	Sink	-

In addition to the significant electricity demand for electrolysis, there is also electricity demand for gas compression which is necessary in the WO process. The current WO model is run with pure oxygen, supplied by the water electrolysis unit with a pressure of 30 bar. The electricity demand for compression of the oxygen demand referenced to 1000 kg/h dry HTL feedstock input is 15 kW. For the same amount of oxygen present in air and starting from the standard pressure of 1 bar, the electricity demand for compression would be 243 kW, which is almost 16-fold compared to pure oxygen from the electrolysis. Additionally, the use of air implies that huge amounts of nitrogen and small amounts of trace gases will be present in the resulting WO gas phase, which might complicate the gas cleaning process for methanol synthesis.

At first sight, these results clearly suggest the use of pure oxygen, especially when pressurized oxygen is available from an electrolysis unit. However, there are also challenges related to the use of pure oxygen, such as safety concerns and corrosion issues that need to be considered. This may lead to higher CAPEX cost and additional cost for safety measures.

4 Conclusions and Outlook

CIRCULAIR investigates an HTL based advanced biofuel pathway that can convert manure and straw into transportation fuels and further valuable products. WO of the HTL aqueous phase can clean-up the process water and provide process heat to the HTL conversion step. The energy balances confirm the potential to eliminate external process heat demand and thereby enable autothermal operation. Coupling CO₂ streams evolving from HTL and WO with green hydrogen generation enables a boost in biomass resource utilization, yielding substantial amounts of methanol as a by-product.

The mass and energy balances derived from the initial version of the process model illustrate a number of key motivations behind the CIRCULAIR approach:

- Water dominates the mass balance of HTL conversion: Hydrothermal processing enables the utilization of wet feedstock, but also implies that large amounts of water need to be heated to reaction temperatures of 300–350°C. Heat exchange is crucial, furthermore, CIRCULAIR aims at providing the remaining process heat demand by WO of the HTL aqueous phase.
- The HTL aqueous phase contains a significant amount of organic compounds. WO plays a crucial role for process water clean-up as most organic compounds get oxidized, in addition WO generates process heat at useful temperature levels for HTL conversion.
- The process water that results from WO can contain a significant amount of volatile fatty acids (VFA), mainly in form of acetic acid. VFA recovery increases biomass utilization and may generate additional revenue.
- HTL and WO also produce a gaseous phase that is rich in CO₂. Utilizing these CO₂ streams as a carbon source for Power-to-X processes can significantly boost the overall carbon efficiency compared to a case without CO₂ utilization.
- The upgrading of HTL biocrudes via hydrotreatment yields a significant fraction of heavy compounds with high boiling temperatures. Further processing steps, such as hydrocracking, can significantly increase the kerosene yield.

The findings that are itemized above are not new, they rather represent the basic considerations behind the concept. Nevertheless, the preliminary quantification of mass and energy balances may be seen as an affirmation of the initial approach of CIRCULAIR.

The next step within the work plan foresees a pre-evaluation of key economic and environmental parameters that will be published in a consecutive public report. The mass and energy balances (see Section 3.2, 3.3 and 3.4) will serve as a quantitative basis. Furthermore, a refinement of the baseline-case (see Section 2.2) provided the regional

context for this pre-evaluation. Central Denmark was chosen due to high regional feedstock densities for agricultural residues and favourable conditions for green hydrogen generation from wind energy. The envisaged supply concept foresees distributed HTL plants that aggregate feedstock from several farms at regional level, the biocrude is then transported to a centralized upgrading facility. The definition of this baseline-case was guided by rough economic considerations, such as economies of scale, feedstock transportation or green hydrogen costs. Nevertheless, this still represents a starting point that will likely be further refined once first results from techno-economic modelling become available.

Likewise, GHG emissions will be quantified. Here, it is anticipated that the provision of hydrogen from green electricity and process energy demand from WO will significantly reduce GHG emissions compared to fossil hydrogen and process energy generation. In the long run, CIRCULAIR aims at a net-negative life-cycle greenhouse gas balance, key levers to achieve negative contributions include carbon sequestration via HTL solids and the avoidance of emissions that result from current manure handling. These negative contributions are not directly linked to the process modelling that was discussed in this report⁸, however, minimizing positive contributions to the GHG budget is a prerequisite to achieve net-negative emissions. The carbon balances in Figure 11 indicate that sequestration of CO₂ streams that evolve from HTL and WO establish a third option to generate negative contributions to the GHG balance. The trade-off between high fuel yield via CO₂ utilization and negative emissions via CO₂ sequestration is obvious⁹.

Further preliminary result from this report provide early indications for further investigations within the CIRCULAIR project

- Significant amounts of H₂ are needed for methanol synthesis, but also for biocrude upgrading. It is anticipated that low-cost availability of green hydrogen at the locations and scale of the distributed HTL-WO plants will play a key role in techno-economic analyses.
- The concept foresees the utilization of O₂ from water electrolysis as an oxidizing agent for WO. The energy requirement for gas compression is much lower compared to WO

⁸ The potential of carbon sequestration via HTL solids is investigated within CIRCULAIR by project partner UHOH. These results will be available at a later stage of the project. Avoided emissions compared to current manure handling are an external factor that is not influenced by process modelling of HTL conversion.

⁹ The CIRCULAIR approach aims at high fuel yield, however, carbon capture and sequestration will be discussed as an alternative option in the final public report "*Trade-off studies, synthesis of results and roadmap*".

using air, due to the additional requirements resulting from N₂ compression, but also due to the option to operate pressurized electrolyzers.

- Preliminary energy balances indicate that WO of the HTL aqueous phase can generate heat in excess of the process heat demand HTL. Utilization of excess heat generation, e.g. for district heating may be an important consideration.

The initial process model will be further refined over the course of the CIRCULAIR project. An important aspect of this refinement is the modelling of subsystems that are currently treated by a black box approach, such as volatile fatty acid recovery. Furthermore, a multi-step upgrading strategy should be implemented and models for HTL conversion and WO should be refined based on experimental results of the CIRCULAIR implementation. Further important improvements relate to product separation and to the provision of green hydrogen from intermittent renewable electricity such as wind power.

5 References

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