

# Report

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## Impacts of low carbon technologies on environmental parameters: air/water/waste

Consultation and literature review



# Impacts of low carbon technologies on environmental parameters: air/water/waste

## *Consultation and literature review*

G. Valastro (Concawe Science Executive), T. Greaves (Concawe Science Executive)  
E. Vaiopoulou (Concawe Science Executive)

This report was prepared by: Ben Warren, Matt Osund-Ireland, Nicholas Marzorati, Luciano Rossi (Wood)

Under the supervision of: T. Megaritis (Concawe Science Associate), M. Hjort (Concawe Science Associate), M. Yugo (Concawe Science Executive)

At the request of:

Concawe Air Quality Management Group (AQMG)

Concawe Water Soil Waste Management Group (WSWMG)

Thanks for their contribution to:

Members of AQMG: P. Grabowski, L. Sibue

Members of WSWMG: J. Smith, K. Vincze

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## ABSTRACT

Concawe's Low Carbon Pathways (LCP) programme aims to identify opportunities and challenges for different low-carbon technologies and feedstocks to achieve a significant reduction of the carbon dioxide (CO<sub>2</sub>) emissions associated with both the manufacturing and use of refined products in Europe in the medium (2030) and longer-term (2050). The low carbon technologies/feedstocks explored under the LCP work identified significant positive effects on reducing CO<sub>2</sub> emissions associated with the refining system by 2050. However, the associated effects on other environmental parameters, such as air quality, water quality, water usage and waste, are not yet well defined.

This report provides a summary of the findings of an industry consultation and literature review carried out on four LCPs explored previously by Concawe [Concawe 2019a, 2019b]. It presents information on the likely environmental emissions and demands relating to air, water, and waste (other than CO<sub>2</sub>) associated with the four LCP, and identifies where gaps exist.

## KEYWORDS

Lipids hydrotreatment, Gasification, Fischer-Tropsch, Pyrolysis, E-fuels, Low Carbon Pathways, Air, Water, Waste, Emissions, CO<sub>2</sub>

## INTERNET

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## SUMMARY

Concawe is exploring a cross-sectorial Low Carbon Pathways (LCP) programme, identifying opportunities and challenges for different low-carbon technologies and feedstocks to achieve a significant reduction of the carbon dioxide (CO<sub>2</sub>) emissions associated with both the manufacturing and use of refined products<sup>1</sup> in Europe in the medium (2030) and longer-term (2050).

The main objective of this project is to make an appraisal of the level of change in air, water and waste parameters for potential 2030/2050 refineries when considering low carbon technologies and feedstocks. An analysis to explore the deployment of different low carbon technologies and feedstocks in a refinery and the associated impact in terms of unabated air pollutant emissions, water consumption, unabated aqueous process effluent quality and waste generation is performed.

The report aims to determine what information already exists for each of four specified LCPs regarding air, water, and waste parameters. CO<sub>2</sub> emissions are not considered in detail in the scope of this project, however information has been presented for reference when interrelated with other parameters. The LCPs evaluated are as identified in the Concawe Report 9/19 [Concawe 2019b] and include the following main categories:

- Lipids hydrotreatment.
- Gasification of lignocellulosic biomass (such as wood) followed by Fischer-Tropsch synthesis and hydrocracking.
- Hydrotreatment-hydrocracking of pyrolysis- or hydrothermal liquefaction (HTL) oils (made from lignocellulosic/woody biomass).
- E-Fuels production from captured CO<sub>2</sub> and electrolytic hydrogen (H<sub>2</sub>) made into syngas by Reverse Water Gas Shift (RWGS) and hence into hydrocarbons by Fischer-Tropsch (FT) synthesis with subsequent hydrocracking to produce suitable boiling range fuels.

This report provides a summary of the industry consultation and literature review carried out for the four LCPs.

The findings of this study are summarised in the following tables. Summary **Table 1** summarises the ease of implementation and maturity of each of the LCPs, alongside the advantages and disadvantages with respect to the receiving environment that have been identified. Summary **Table 2** summarises the information collected on each of the LCPs, considers the robustness of the information and the gaps identified in the information. The table is coloured green where a relatively complete evaluation can be made based on the literature review and industry survey, amber where some gaps exist and red where significant gaps exist, which largely relates to technology maturity.

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<sup>1</sup> Including fuels, distillates, petrochemicals, gasoline etc.

**Summary Table 1** Summary of LCP and environmental advantages/disadvantages

LCP	Ease of implementation	Maturity	Environmental Advantages	Environmental Disadvantages
Lipids hydrotreatment (Section 4.1)	Relatively easy to implement with conventional petroleum refining. Co-processing is also a promising route for production of advanced fuels.	Hydroprocessing-derived renewable diesel from fats and oils is already produced at a commercial scale and is considered a mature pathway. Co-processing of lipidic feedstock in Fluidized Catalytic Cracker (FCC) Unit and in Hydrocracking Unit is still in the relatively early stages of development.	The technology has potential to reduce emissions to air during production relative to conventional refineries particularly when using dedicated hydrotreaters. Potentially significant lifecycle GHG emissions reduction with respect to the conventional liquid fuel production case, depending on the source of lipids.	High hydrogen (and therefore energy) requirements, so careful consideration of the source is required. As hydrotreatment is an exothermic process, cooling water is required. Sour Water is a major by-product of hydrotreatment and must be treated. Exhausted catalysts and wastewater pre-treatment sludge are additional waste streams that must be dealt with.
Gasification of lignocellulosic biomass (such as wood) followed by Fischer-Tropsch (FT) synthesis and hydrocracking (Section 4.2)	New gasification/FT systems are required, but there is potential for using existing hydrocrackers.	Gasification of biomass and waste feedstocks is considered a mature pathway that is used at a commercial scale. Syngas purification for downstream FT synthesis is still in its relatively early stages of development (Technology Readiness Level (TRL) 5-6). FT synthesis is an established technology, for large scale plants. There are several examples of gasification-FT synthesis facilities using biomass and waste feedstocks in operation around the world, although most of them are at pilot scale.	Plants using the FT process can potentially export electricity to grid and therefore offset indirect emissions. Significant lifecycle GHG emissions reduction with respect to the conventional liquid fuel production case.	Feedstock supply may involve significant emissions due to transport Energy required for biomass preparation (e.g. particle size, moisture content). Potential emission of PM during biomass pre-treatment stage. Energy required for gasification. Processing of waste from gasification (e.g. tar and char). Wastewater from FT process. Possibility of air emissions from Syngas cleaning and conditioning (depending on the process configuration).
Hydrotreatment-hydrocracking of pyrolysis- or hydrothermal liquefaction oils (made from lignocellulosic/woody biomass) (Section 4.3)	New systems are required for the treatment of pyrolysis/HTL oils. However, there is potential for existing infrastructure to be reused with minimal adjustment.	First commercial scale Pyrolysis plants have been commissioned in recent years. HTL is not a mature technology; there are no commercial-scale projects currently in operation. There are no commercial examples of bio-oil from pyrolysis or upgraded bio-oil being used as a transport fuel.	An advantage of HTL is its potential flexibility, as the process can use feedstocks with qualities that can be difficult for other technologies like hydrotreatment and gasification to handle.	Feedstock supply may involve significant emissions due to transport Energy required for biomass preparation (to obtain e.g. appropriate particle size, moisture content). The HTL process generates aqueous phase pollutants (i.e. carbon oxygenates and



			<p>Biochar produced by pyrolysis has multiple potential benefits when applied to the soil.</p> <p>Significant lifecycle GHG emissions reduction with respect to the conventional liquid fuel production case.</p>	<p>other organic materials suspended in water).</p>
<p>E-Fuels production from captured CO<sub>2</sub> and electrolytic Hydrogen made into Syngas by RWGS (Reverse Water Gas Shift) and hence into hydrocarbons by Fischer-Tropsch (FT) synthesis with subsequent hydrocracking. (Section 4.4)</p>	<p>New electrolyzers, CO<sub>2</sub> capture units, RWGS and FT reactors required but there is potential for using existing hydrocrackers.</p> <p>Needs to be associated with a source of renewable electricity. High energy production cost is a major barrier without a low-cost source of renewable energy.</p> <p>Needs to be associated with a source of fresh water for H<sub>2</sub> production by electrolysis</p>	<p>Alkaline electrolyzers are already proven at commercial scale.</p> <p>First commercial scale PEM (Polymeric Electrolytics Membrane) plants have been commissioned in recent years.</p> <p>SOEC (Solid Oxide Electrolyser Cells) electrolyzers are at an earlier stage of development.</p> <p>CO<sub>2</sub> capture from industrial processes can already be implemented at commercial scale.</p> <p>Direct Air Capture is still in its relatively early stages of development (TRL 5-6).</p> <p>The RWGS process has not been developed at industrial scale yet.</p> <p>FT synthesis is an established technology.</p>	<p>Plants using the FT process can potentially export electricity to grid.</p> <p>Significant lifecycle GHG emissions reduction with respect to the conventional liquid fuel production case.</p>	<p>If amine-based Carbon Capture technology is employed to provide the required CO<sub>2</sub> there is potential for amine slip in emissions to air and amines in wastewater which would require treatment.</p> <p>Wastewater from FT process.</p>

**Summary Table 2** Data Collection Overview

LCP		Robustness	Completeness	Gaps & Limitations
Lipids hydrotreatment	Dedicated Hydrotreatment (HT)	Two relevant Licensors contributed to the project. Information relevant to preliminary evaluation of typical plant.	Technical details: Overall complete evaluation. Environmental Parameters: Overall complete evaluation.	Complete evaluation. Low level of detail in contaminants specification in liquid effluent from Pre-treatment Unit.
	Co-Processing in Gasoil Hydrotreater (GHT)	No Licensor contributed to the study.	Pre-treatment process is the same used for dedicated Hydrotreatment.	Difficulty in evaluating the emissions owed only to lipidic feedstock in co-processing cases. Limited co-processing rate (max ~15% Wt.) in conventional hydrotreaters.
	Co-Processing in Fluid Catalytic Cracker (FCC)	No Licensor contributed to the study.	-	Early stage of development. Difficulty in evaluating the emissions owed only to lipidic feedstock in co-processing cases.
	Co-Processing in Hydrocracker (HC)	No Licensor contributed to the study.	-	Early stage of development. Difficulty in evaluating the emissions and waste generation owed only to lipidic feedstock in co-processing cases.
Gasification of lignocellulosic biomass (such as wood) followed by Fischer-Tropsch synthesis and hydrocracking		Only a small number of Licensors contributed to the study, for the complete chain.  Data obtained is referred to early stage of project (as regards complete chain).  Three Licensors contributed to the study for the gasification process and Syngas cleaning.	Technical details: Low level of detail for the process parameters of the complete chain. Environmental Parameters: Low level of detail regarding emissions to water (as regards complete chain).	Reliability and usefulness of the data relevant to complete chain limited by the following factors: - Only a small number of Licensors provided information relevant to the complete chain. - Low level of detail in the process description. - Moisture content of input wet biomass is not specified, making it difficult to compare specific environmental data with other cases. - Comprehensive information on water contaminants in process effluent stream(s) were not provided.
Hydrotreatment-hydrocracking of pyrolysis- or hydrothermal liquefaction oils (made from lignocellulosic/woody biomass)		Information relevant to preliminary evaluation of typical plant.	Technical details: Overall complete evaluation with regards to Pretreatment + Pyrolysis sections.	Missing detailed information relevant to emissions generated by downstream processing, due to early stage of development.

	Only a small number of Licensors contributed to the study (Pyrolysis oil product is intended to be further processed in FCC Unit).	Environmental Parameters: Overall complete evaluation with regards to Pretreatment + Pyrolysis sections	
E-Fuels	No Licensor contributed to the study.	-	Early stage of development of RWGS and of Fischer-Tropsch process at small scale (FT process optimized for large scale).

## 1. INTRODUCTION

Wood Group UK (hereafter ‘Wood’) has been contracted by Concawe to provide an analysis of the changes in air pollutant emissions, water consumption, aqueous process effluents and waste that may result from the deployment of different low carbon technologies and feedstocks in refineries. Whilst all of the low carbon technologies discussed have the potential to reduce carbon dioxide (CO<sub>2</sub>) emissions, these benefits are not considered in detail in the scope of this project. Information has been presented for reference when interrelated with other parameters.

The report is structured as follows:

- Section 2 sets out the project context and objectives;
- Section 3 presents the methodology for the collection of data and information;
- Section 4 presents the results for the pathways considered; and
- Section 5 presents preliminary conclusions and recommendations.

## **2. PROJECT CONTEXT AND OBJECTIVES**

### **2.1. CONCAWE LOW CARBON PATHWAYS PROGRAMME**

Concawe is exploring a cross-sectorial Low Carbon Pathways (LCP) programme, identifying opportunities and challenges for different low-carbon technologies and feedstocks to achieve a significant reduction of the CO<sub>2</sub> emissions associated with both the manufacturing and use of refined products in Europe in the medium (2030) and longer-term (2050).

One of the developments of the LCP programme is to explore the potential of different technologies to effectively contribute to the EU decarbonisation goals. It focuses on the transition of the refining industry towards a low-CO<sub>2</sub> intensive economy and explores the technical implications of such a transition for the refining industry across Europe.

Under this area, Concawe has recently published two reports that focus on the potential of different technologies and operational measures to achieve CO<sub>2</sub> emissions intensity reduction in the 2030 and 2050 horizon [Concawe, 2019a] and explore the potential introduction and processing of low fossil carbon feedstocks in European refineries within the context of demand scenarios for 2050 [Concawe 2019b].

The low carbon technologies/feedstocks explored under the LCP work identified significant positive effects on reducing CO<sub>2</sub> emissions associated with the refining system by 2050. However, the associated effects on other environmental parameters, such as air quality, water consumption, aqueous process effluent quality and waste generation, are not yet well defined. As such, Concawe is seeking to expand the focus of its previous research beyond CO<sub>2</sub> and other Greenhouse Gases (GHGs).

### **2.2. PROJECT OBJECTIVES**

The main objective of this project is to make an appraisal of the level of change in air, water and waste parameters for potential 2030/2050 refineries when considering low carbon technologies and feedstocks. The project aims to perform an analysis that will explore the deployment of different low carbon technologies and feedstocks in a refinery and the associated impact in terms of unabated air pollutant emissions, water consumption, unabated aqueous process effluent quality and waste generation. The technologies evaluated are as identified in the Concawe Report 9/19 and include the following main categories:

- Lipids hydrotreatment.
- Gasification of lignocellulosic biomass (such as wood) followed by Fischer-Tropsch synthesis and hydrocracking.
- Hydrotreatment-hydrocracking of pyrolysis- or hydrothermal liquefaction oils (made from lignocellulosic/woody biomass).
- E-Fuels production from captured CO<sub>2</sub> and electrolytic hydrogen (H<sub>2</sub>) made into syngas by Reverse Water Gas Shift (RWGS) and hence into hydrocarbons by Fischer-Tropsch synthesis with subsequent hydrocracking to produce suitable boiling range fuels.

The aim of this report is to determine what information already exists for each of the specified LCPs regarding various environmental parameters and to identify where gaps exist. This report provides a summary of the industry consultation and literature review carried out for the four identified technologies.

### **3. APPROACH TO DATA COLLECTION**

#### **3.1. OVERVIEW OF APPROACH**

The project required the collation and synthesis of data and information for each of the identified technologies (i.e. lipids hydrotreatment; gasification of lignocellulosic biomass; hydrotreatment-hydrocracking of pyrolysis- or hydrothermal liquefaction oils; E-Fuels production).

This was accomplished through consultation with industry and a complementary literature review. The literature review aimed to identify any information available within the public domain concerning the wider environmental impacts of the technologies which are the focus of the study.

#### **3.2. INDUSTRY CONSULTATION**

##### **3.2.1. Request for Information (RFI)**

Wood used an internal database of licensors/equipment suppliers related to the technologies, which are the focus of the study to identify suitable contacts within the industry. These were contacted to ascertain their willingness and availability, to support the project.

Wood then issued a Request for Information (RFI) document to the key identified licensors or equipment suppliers for the LCP technologies. The RFI provided the background to the project, the key assumptions around the technology and requested the information detailed in **Table 1**.

In addition, each licensor was invited to share any relevant documents or technical articles specific for the technology that have been published.

**Table 1** Request for Information Details

	Category	Information Requested
Technical Details	Process Details	<ul style="list-style-type: none"> <li>Process description</li> <li>Typical process flow diagram (PFDs)</li> <li>Overall material and energy balance, including typical yields in main product cuts (e.g. diesel, kero, naphtha, LPG, etc.)</li> <li>Utility consumption list (Main Utilities)</li> <li>Please, distinguish between High Pressure (HP), Medium Pressure (MP), and Low Pressure (LP) Steam. Please, consider Delta T (DT)=10°C for cooling water</li> <li>Chemical and additives consumption list (if relevant from an environmental standpoint)</li> <li>By-products amount and characteristics</li> </ul>
	Implementation Considerations	<ul style="list-style-type: none"> <li>Technology Readiness Level</li> <li>Reference plants, indicating the type of facility (e.g. pilot plant, demonstration plant, industrial plant, etc.) and the quality/source of feedstock</li> <li>Technological barriers or risks associated with the proposed design</li> </ul>
	Energy Usage	<ul style="list-style-type: none"> <li>Energy usage (electricity and fuels) and hydrogen consumption</li> </ul>
Environmental Parameters	Air pollutants	<ul style="list-style-type: none"> <li>Sulphur oxides (SO<sub>x</sub>/SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>/NO<sub>2</sub>), particulate matter (PM<sub>2.5</sub>/PM<sub>10</sub>), carbon monoxide (CO), Non-methane volatile organic compounds (NMVOCs), Any other relevant pollutants</li> </ul>
	Greenhouse gases	<ul style="list-style-type: none"> <li>Carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), etc.</li> </ul>
	Aqueous process effluent	<ul style="list-style-type: none"> <li>Total suspended solids (TSS), Chemical Oxygen Demand (COD), Biological oxygen demand after 5 days (BOD<sub>5</sub>), hydrogen sulphide, ammonium, total nitrogen (TN), total phosphorus (TP), lead (Pb), cadmium (Cd), nickel (Ni), mercury (Hg), vanadium (V), benzene, ethylbenzene, toluene, and xylenes (BTEX), Hydrocarbon Oil Index (HOI) and any other relevant substances</li> </ul>
	Water Quantity	<ul style="list-style-type: none"> <li>Freshwater requirements</li> <li>Wastewater volumes</li> <li>Degree of water efficiency inside process (water re-use/ recycling)</li> </ul>
	Waste	<ul style="list-style-type: none"> <li>Types and quantities of hazardous and non-hazardous waste produced</li> </ul>



### 3.2.2. Input from Industry

Companies which provided information as part of the industry consultation process are reported below:

- BTG-Bioliquids;
- Eqtec;
- NextChem;
- Nexterra;
- Shell;
- Velocys; and
- VTT

Technical and environmental data received from Licensors are reported in the Industry Survey Appendix. In the interest of confidentiality, the name of the Licensor is not reported in the Appendix.

## 3.3. LITERATURE REVIEW

### 3.3.1. Research Protocol

The starting point for the literature review was the list of references in the annexes to the published Concawe reports [8/19 and 9/19]. The literature list was then developed by searching for relevant documents related to each of the technologies. To enable the systematic searching of information, search terms were recorded. In view of the anticipated rapid development of the technologies, priority was given to documents produced from 2018 onwards, and any documents older than fifteen years (pre-2006) were excluded from the literature review.

Where available, quantitative information has been collected. Where this approach was not possible, qualitative descriptions are included. For each parameter, where there is a range of values presented in the literature, this has been reported, ideally along with the reason for the range. The types of information collated through the literature review are detailed in **Table 2**.

**Table 2** Literature Review Template

Column Heading	Details
ID	Unique ID for the project
Author	Author, to show whether the document was produced by academics or an industry organisation
Year	Date of publication. To enable prioritisation of more recent sources
Title	Document title
Description	Brief description highlighting the information contained
Link / Source	Hyperlink if available
Researcher	Wood researcher who reviewed the document
Search Criteria	The search term(s) used to find the document
Document Type	Public bodies, technical publications by industry bodies, techno-scientific literature, other grey literature, or academic paper
Note on document quality	Comment on accuracy of data / robustness, etc
Low carbon feedstock	Feedstock
Low carbon pathway / process	Process technology
Air quality pollutants	Any details contained on emissions. Quantified where possible
Water process effluent parameters	Any details contained on emissions. Quantified where possible
Water quantity	Input and output quantity
Waste	Quantity and type (hazardous/non-hazardous) produced
Energy usage	Electricity and liquid/gaseous fuels and hydrogen consumption (+ CO <sub>2</sub> emissions)
Gaps and limitations	Note on data gaps and limitations

### 3.3.2. Overview of Sources

During the literature review, 137 articles and documents were reviewed. Of the documents reviewed, 92 were peer-reviewed academic articles and book chapters, 37 were technical reports produced by industry and government and 8 were assorted presentations and policy reports.

After extracting and appraising the literature, the robustness of the data was considered in terms of the source data, type of research and relevance to the LCPs considered in this article. Information gaps, which are anticipated for more recent technological developments, have also been highlighted.

## 4. RESULTS

A technology summary is provided for each technology to provide context before the environmental impacts are described. This information is taken from Concawe report 9/19 [Concawe 2019b], with additional references where stated.

Information presented is not specific to any of the Licensors mentioned in the report, and it is obtained from a synthesis of both industry and literature data.

### 4.1. LIPIDS HYDROTREATMENT

#### 4.1.1. Technology Summary

##### 4.1.1.1. Feedstock

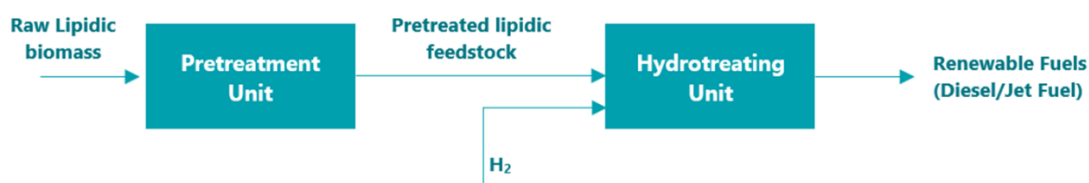
Typical feeds currently include vegetable oils, animal fats and cooking oil. A study [Van Dyk et al, 2019] suggests that lipids, such as used cooking oil, are in short supply and other feedstocks, such as palm and canola, are likely to be costly and come with sustainability concerns. Bio-feedstock availability is further evaluated in a 2021 study commissioned by Concawe [Concawe 2021].

An alternative for the future expansion of this pathway is the development of viable algal oil technology and the establishment of algal farming as a significant new agricultural sector. Several papers [e.g. Chu 2017, Zhou & Hu 2020] have highlighted the potential of hydrotreating algal derived oil, to reduce the oxygen content and remove nitrogen and sulphur, in order to produce high-grade biofuel hydrocarbons. Reports reviewed indicate that this has a Technology Readiness Level (TRL) of around 5-6 [Kleinegris 2017].

##### 4.1.1.2. Process

Hydrotreatment involves the saturation of the triglycerides in the feedstock with hydrogen to remove all the oxygen from the aliphatic chain and results in a blend of saturated hydrocarbons regardless of the initial feedstock [Douvartzides et al 2019]. The process is favoured by mild temperatures, mild pressures and catalysts of mild acidity. The most common types of catalysts used are the sulphided Ni-W/ $\text{Al}_2\text{O}_3$ , Co-Mo/ $\text{Al}_2\text{O}_3$  and Ni-Mo/ $\text{Al}_2\text{O}_3$  which are also used for the hydrodesulfurization of petroleum distillates [Douvartzides et al 2019]. The process is illustrated in **Figure 1**.

**Figure 1** Lipids Hydrotreatment Schematic



Lipid hydrotreatment can be carried out in dedicated hydrotreaters (through conversion of existing hydrotreaters, or addition of 100% lipid units). Lipids can also be co-processed with fossil gas oil. Typical co-processing mixtures are 5-10% lipid. Co-processing in conventional hydrotreaters can only be carried out to limited rates

(max ~15% lipidic feedstock) mainly due to the increased hydrogen requirements, and acidity of the feed. Up to 30% lipid co-processing with fossil gas oil in technically suitable hydrotreaters may be achievable with suitable upgrades and technology development. This is driven by sustained economic incentives for bio-content.

Some issues with co-processing have been highlighted, including the potential need to pre-treat feedstocks that contain water and high fatty acid content, reduced yields and sulphur removal at higher lipid ratios, and the need for higher hydrogen pressure [Bezergianni et al 2018], the need to add quench to the existing reactors to control temperature rise due to exothermic hydrotreatment, the need to account for CO, CO<sub>2</sub> and water production, and upgrades to the metallurgy to handle fatty acids [Baldiraghi et al 2009]. As such, some companies prefer to use dedicated hydrotreaters that avoid these issues [Baldiraghi et al 2009].

#### 4.1.1.3. Products

Hydrotreatment of lipids produces a synthetic fuel that has a similar chemical composition and similar physio-chemical properties to petroleum diesel. Therefore, products can be blended with conventional refinery products and are sometimes known as green diesel [Baldiraghi et al 2009]. They can also be known as Hydrotreated Vegetable Oil (HVO) and Renewable Diesel [Cheah et al 2017]. It is also possible to produce jet fuel, known as SAF (Sustainable Aviation Fuel), by increasing the degree of hydrocracking and isomerization in the process. Some LPG and Naphtha are also produced as by-products.

#### 4.1.1.4. Changes to refineries required

There is a high synergy with existing refining assets as lipid hydrotreatment uses technology that is very similar to conventional refinery technology, and the hydrocarbon product is almost interchangeable with fossil distillates. Conventional hydroprocessing technology is already widely deployed in refineries and hence, hydrotreatment can utilise the existing refinery infrastructure and fuels distribution system [Baldiraghi et al 2009]. It has been reported that hydroprocessing of lipids does require modification to enable a two-stage process, consisting of mild-hydrotreating followed by an isomerization stage [Bezergianni et al 2018].

Hydrotreatment is considered to be an energy-intensive process as it consumes large quantities of high-pressure molecular hydrogen. At the level of chemical reactions, at least 3 moles of hydrogen molecules are required for complete deoxygenation of 1 mole of fatty acid [Cheah et al 2017]. Several studies note that the process results in an increase in hydrogen consumption compared to hydrodesulfurization of crude oils in a standard refinery [Bezergianni et al 2018, Van Dyk et al 2019, Karatzos et al 2014]. Further examples include:

- Stengel & Vium [2015] report that energy use during production of 1 MJ fuel from HVO rapeseed is 0.14 MJ/MJ<sub>fuel</sub> compared to 0.1 MJ/MJ<sub>fuel</sub> for standard diesel (GHG emissions during production of: 6.8 g CO<sub>2</sub>/MJ<sub>fuel</sub> compared to 8.6 g CO<sub>2</sub>/MJ<sub>fuel</sub> for standard diesel).
- Karatzos et al [2014] report studies showing that for 100% renewable feed, a hydrogen consumption of 300-400 Nm<sup>3</sup> /m<sup>3</sup> is not unusual compared with about 34 Nm<sup>3</sup> /m<sup>3</sup> for the hydrotreating of 1% sulphur petroleum.
- Chu et al [2017] report values of hydrogen input for hydrotreatment of 22-40 kg/tonne of oil for a variety of feedstocks.

The source of the hydrogen, which may be from the steam reforming of natural gas in the near-term, will also have an impact on the life cycle analysis, with subsequent carbon intensity of the biofuel probably influencing the economics of upgrading.

Oxygen removal generates significant heat and temperature through the exothermic reaction in the reactor and has to be controlled to prevent unwanted reactions from taking place. As a result, modified cooling systems are required to prevent uncontrolled increases in temperature [Van Dyk et al 2019, Baldiraghi et al 2009] which may result in increased requirement for water usage.

#### **4.1.1.5. Technology and Supply-Chain Readiness**

Commercial lipid hydrotreatment has recently become well established with a few stand-alone operations of up to one million tonnes per annum. A study [Chu et al 2017] suggests that, due to its technological maturity, this pathway will play a major role in producing low carbon intensity jet fuels.

The conversion technology for the pathway exists and the feedstock can be supplied through the conventional supply chain. There are, however, high external requirements as a sustainable feedstock is needed. As mentioned above, some lipids may be in short supply and others have sustainability concerns. Therefore, future expansion is likely to require the development of new algae technology and the establishment of a significant new agricultural industry.

#### **4.1.2. Environmental Impacts**

##### **4.1.2.1. Air Emissions**

Van Dyk et al [2019] report that although hydrotreating is routinely used in refineries for removal of sulphur and nitrogen, the concentration of these contaminants is typically very low (average 1.8% S, 0.1% N in typical crude oil) when compared to the oxygen levels in biobased feedstocks (~10% in vegetable oil and up to 40% in bio-oil). The industry survey confirmed that the off-gases produced are typically processed to avoid direct release to the atmosphere such that the only direct emissions relate to the flue gases from the fired heater for the hydrotreatment unit.

Karatzos et al [2014] report that the presence of oxygen in the feed results in the formation of gaseous by-products such as water, CO<sub>2</sub>, carbon monoxide and methane. Propane is created because of the three-carbon backbone present in the triglyceride structure [Baldiraghi et al 2009]. Chu et al [2017] report CO<sub>2</sub>, CO, water and propane outputs per tonne of oil from a variety of feedstocks.

The gases produced must be removed by increasing the gas purge rate in the system. If not removed, these gases can: reduce catalyst activity; compete with S- and N-species for hydrotreating catalyst sites (CO and CO<sub>2</sub>); form corrosive carbonic acid (water and CO<sub>2</sub> reaction). The formation of these carbonaceous by-product gases diverts carbon from the final fuel and thus reduces process yields compared to fossil diesel hydrotreating. Propane can be used to support the energy needs of the facility.

Emissions need to be considered within the whole refinery, rather than the hydrotreater. Concawe [2019a] previously reported that, for biofuels from both vegetable oils and algae, lower utilisation of the Fluidized Catalytic Cracker (FCC) and Coker would be expected, which may result in lower emissions to air. It has been reported [ENI 2018] that a green refinery (with dedicated hydrotreaters) produced 88%, 15%, 68% and 26% lower SO<sub>2</sub>, NO<sub>x</sub>, particulate and CO emissions,

respectively, compared with a ‘traditional’ refinery. It is not clear to what degree this reduction can be attributed to the use of hydrotreatment relative to other differences in configuration.

An assessment of a proposed green diesel facility was obtained in the literature review [US Department of Energy 2011]. Numerous emission sources were identified, including storage vessels, process heaters, transfer and storage of particulate materials, cooling tower drift, wastewater pre-treatment and conveyance, and emissions from the flare during start-up, shutdown, and any emergency or upset events. However, emissions to air from the facility were not considered to be a concern as it was reported that air emissions would be less than the major source thresholds and the significance thresholds established by USEPA. Emissions were subsequently updated for a later permit renewal to incorporate new diesel engines, which increased total plant emissions [Diamond Green Diesel 2014]. Potential emissions from all sources are reported in **Table 3**.

In the following tables, the results of the literature and industry survey concerning the main emissions to air produced by lipidic biomass processing are reported. In the industry survey, only information relevant to hydrotreatment of lipidic feedstock in a dedicated unit was obtained.

The scope of the evaluation includes both the biomass pre-treatment and hydrotreatment units, while auxiliary units, such as hydrogen generation, are not included. Tallow and used cooking oil have been considered as feedstock and emission values are reported relative to the input of raw lipidic biomass.

**Table 3** Air emissions from Dedicated HT of lipidic biomass

Air emission	UoM	Value	Reference
<i>air pollutants</i>			
Sulphur oxides (SO <sub>x</sub> /SO <sub>2</sub> )	g/tonne LIPIDIC BIOMASS	0.035-0.036 0.27 15.76	Industry survey US Department of Energy 2011 Diamond Green Diesel 2014
Nitrogen oxides (NO <sub>x</sub> /NO <sub>2</sub> )	g/tonne LIPIDIC BIOMASS	2.6-2.8 5.2 33.2	Industry survey US Department of Energy 2011 Diamond Green Diesel 2014
Particulate matter (PM <sub>2.5</sub> /PM <sub>10</sub> )	g/tonne LIPIDIC BIOMASS	N/A 1.8 4.4	Industry survey US Department of Energy 2011 Diamond Green Diesel 2014
Carbon monoxide (CO)	g/tonne LIPIDIC BIOMASS	2.6-2.8 2.5-2.7 12.4 31.5	Industry survey Chu et al 2017 US Department of Energy 2011 Diamond Green Diesel 2014
Non-methane volatile organic compounds (NMVOCs)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
<i>Greenhouse gases</i>			
Carbon dioxide (CO <sub>2</sub> )	kg/tonne LIPIDIC BIOMASS	5.2-5.5 54-104	Industry survey Chu et al 2017
Methane (CH <sub>4</sub> )	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Nitrous Oxide (N <sub>2</sub> O)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Remarks	(1), (2)		

(1) - Only direct gaseous emission to atmosphere is owed to Thermal Duty to Hydrotreatment Unit (typical natural gas composition has been assumed for fuel).

(2) - Off-gas stream containing mostly H<sub>2</sub>, different hydrocarbons (mostly methane, ethane, LPG), CO, CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub>O is produced.

#### 4.1.2.2. Water emissions (including process effluent volumes)

The pre-treatment required for the use of feedstocks of lower quality containing water and a high fatty acid content [Van Dyk et al 2019] is likely to produce effluent that requires processing. In addition, as discussed in 4.1.2.1, water is a major by-product of the hydrotreatment process [Pattaniak & Misra 2017]. Water must be removed to avoid reducing the catalyst activity and producing corrosive carbonic acid. It is therefore anticipated that water process effluent volumes are likely to increase at refineries using lipid hydrotreatment.

Tao et al [2017] report that the wastewater generated in the conversion process is typically sent to a wastewater treatment (WWT) system, which can be costly, and existing WWT systems may need to be upgraded. Following treatment, reusable water can reduce both the fresh makeup water demand and discharge to the environment. For the US Green Diesel plant [US Department of Energy 2011], it is reported that approximately 39 gpm (gallons per minute) of wastewater would be

generated. Prior to sending wastewater to external WWT Plant, it would be treated using an oil/water separator, a Dissolved Air Flotation (DAF) unit and biological treatment to remove traces of fats and most solids (such systems are currently used in refineries [OJEU, 2014]). This resulted in an 80% reduction in BOD and COD of this effluent.

In the following tables, the results of the literature and industry survey concerning wastewater produced by lipidic biomass processing are reported, for each of the different routes listed above.



**Table 4** Wastewater produced from Dedicated HT of lipidic biomass

Wastewater flow rate & contaminants	UoM	Effluent 1 (Sour water)	Effluent 2 (Blowdown from steam boiler)	Effluent 3 (Lipidic Biomass Pre-treatment Unit Wastewater)	Reference
Wastewater specific flow rate	L/tonne LIPIDIC BIOMASS	112.1-112.3 34-87 95	3.5-5.9	50-53	Industry survey Chu et al 2017 US Department of Energy 2011
Total suspended solids (TSS)	g/tonne LIPIDIC BIOMASS	N/A	0.03-0.05	N/A	Industry survey
Chemical Oxygen Demand (COD)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Biological oxygen demand after 5 days (BOD5)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Hydrogen Sulphide	g/tonne LIPIDIC BIOMASS	42.3-42.4	N/A	N/A	Industry survey
Ammonium	g/tonne LIPIDIC BIOMASS	158.8-159.1	N/A	N/A	Industry survey
Total nitrogen (TN)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Total phosphorus (TP)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Lead (Pb)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Cadmium (Cd)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Nickel (Ni)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Mercury (Hg)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Vanadium (V)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Benzene, ethylbenzene, toluene, and xylenes (BTEX)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Hydrocarbon Oil Index (HOI)	g/tonne LIPIDIC BIOMASS	N/A	N/A	N/A	Industry survey
Dissolved CO <sub>2</sub>	g/tonne LIPIDIC BIOMASS	273.9-274.6	N/A	N/A	Industry survey
Total Dissolved Solids (TDS)	g/tonne LIPIDIC BIOMASS	N/A	8.8-14.7	N/A	Industry survey
Alkalinity (ALK)	g/tonne LIPIDIC BIOMASS	N/A	0.9-1.4	N/A	Industry survey
Silica	g/tonne LIPIDIC BIOMASS	N/A	0.1-0.2	N/A	Industry survey
Oily content	kg/tonne LIPIDIC BIOMASS	N/A	N/A	0.5-1.1	Industry survey
Remarks		(1)		(2)	

(1) - To be sent to Sour Water Stripper (SWS).

- Overhead vapor from SWS to be sent to Sulphur Recovery Unit (SRU).

It is expected to release to environment following gaseous pollutants from SRU, derived from SWS overhead:

$\text{SO}_2 = 0.08 \text{ g/tonne Feedstock}$

$\text{CO}_2 = 0.3 \text{ kg/ tonne Feedstock}$

- Stripped water from SWS shall be sent to Wastewater Treatment Unit (WWT).

After treatment in WWT, it is expected to release into environment following contaminants into discharged water:

$\text{H}_2\text{S} = 0.6 \text{ g/ tonne Feedstock}$

$\text{NH}_4^+ = 0.1 \text{ g/ tonne Feedstock}$

(2) - To be sent to Wastewater Treatment unit (WWT).

- After treatment, it is expected to release into environment following contaminants into discharged water:

Oily content =  $0.005\text{-}0.01 \text{ g/ tonne Feedstock}$

#### 4.1.2.3. Water (re)use

As hydrotreatment is an exothermic process, cooling water is required to control temperatures. This is a particularly important consideration when the hydrotreatment involves co-processing using existing facilities [Baldiraghi et al 2009]. Pearlson [2011] reports a total water demand for the process of 0.9 gallons per gallon of vegetable oil (~4 litres of water per 4.5 litres of vegetable oil).

This may be expected to increase water consumption, however, as with air emissions, the configuration of the refinery needs to be considered. It has been reported [ENI 2018] that a green refinery (with dedicated hydrotreaters) reduced water consumption for both process and cooling by 50%.

From literature and industry survey, it is concluded that:

- Approximately  $0.115\text{-}0.119 \text{ m}^3_{\text{FRESH WATER}}/\text{tonne}_{\text{RAW LIPIDIC FEEDSTOCK}}$  are consumed (chemically reacted or contaminated) in the process.
- Approximately  $5.6\text{-}6.5 \text{ m}^3_{\text{FRESH WATER}}/\text{tonne}_{\text{RAW LIPIDIC FEEDSTOCK}}$  are circulated for cooling (closed loop).

#### 4.1.2.4. Waste

Van Dyk et al [2019] report that hydrotreating reactors are mostly fixed catalyst beds, with cobalt and molybdenum sulphide on alumina catalysts most often used and that catalysts are typically regenerated at an off-site facility after months or years of operation. Some studies [e.g. Stengel & Vium 2015, Baldiraghi et al 2009] suggest that the catalyst can be reused for a long time (e.g. very good stability and product selectivity during the first 2000 hours of stream) while others [e.g. Douvartzides et al 2019] report that the activity of the sulphided catalysts decreases over time. This is due to a loss in active sites and to the presence of water. This means that a continuous supply of a sulphiding agent, such as  $\text{H}_2\text{S}$ , is necessary in order to avoid either the oxidation of the sulphide catalyst or the reduction by hydrogen of the sulphide phase. It may therefore be expected that used sulphide catalysts may be an increased waste stream relative to fossil fuel desulphurisation.

Tao et al [2017] report that all residual oil and unconverted carbon, plus waste water treatment biogas, sludge, and other gas streams, are combusted in an on-site boiler/steam turbine system to produce steam and electricity, which are used to help meet the energy demands of the facility.

For the US Green Diesel plant [US Department of Energy 2011], it is reported that operation of the green diesel plant would generate non-hazardous industrial solid waste, primarily consisting of sludge from wastewater pre-treatment and spent filter cake from the raw material pre-treatment process. No hazardous wastes would be generated by the green diesel plant.

In the following tables, the results of the literature and industry survey concerning the main wastes produced by lipidic biomass processing are reported, for each of the different routes listed above.

**Table 5** Waste produced from Dedicated HT of lipidic biomass

Solid Waste	UoM	Value	Waste management method	Reference
Spent catalyst	kg/kg LIPIDIC BIOMASS	N/A	Different possibilities: - Dumping at a controlled landfill after a rough carbon burn (incineration); - Processing for reclamation of metals; - Splitting into components and recycling; - Recycling via other processes.	Industry survey
Gums	kg/kg LIPIDIC BIOMASS	10-11	N/A	Industry survey
Spent Earth	kg/kg LIPIDIC BIOMASS	26-27	N/A	Industry survey
Spent Filter Cake	kg/kg LIPIDIC BIOMASS	0.015	Landfill	US Department of Energy 20211
Wastewater Sludge	kg/kg LIPIDIC BIOMASS	0.006	Landfill	US Department of Energy 20211
Remarks	- Gums mainly contain moisture and volatile matters, oil (5%w) and main contaminants present in the feed (Nitrogen, Chloride, Phosphatides, insoluble matters). - Spent Earth (earth used in bleaching process) contains 20-25%w of fatty matter.			

#### 4.1.3. Upstream (pre-treatment) and downstream environmental impacts

##### 4.1.3.1. Upstream

Numerous studies viewed in the literature review [e.g. Cheah et al 2017, Pattanaik & Misra 2017, Živković & Veljković 2018, Vignesh et al 2021] focus on the importance on the source of feedstock on environmental impacts across the lifecycle, considering factors like transportation, irrigation and food security.

When they have been obtained, lipidic feedstocks need to be pre-treated prior to being fed to process units. The pre-treatment step is required to remove

contaminants, such as water, solids, gums, or trace metals, that could damage downstream equipment.

Therefore, in addition to the data reported above, emissions and waste production associated with lipidic feedstock pre-treatment need to be accounted for. The pre-treatment step is considered the same for all the lipids processing routes presented above.

Generally, the pre-treatment of lipidic biomass does not involve emissions to air. Although, in some cases, pre-treatment steps requiring process heating in fired furnace releasing flue gas to atmosphere may be considered.

In the following table, the results of the industry survey concerning wastewater produced by lipidic biomass pre-treatment are reported.

**Table 6** Wastewater produced from lipidic biomass pre-treatment

Wastewater flow rate & contaminants	UoM	Pre-treatment Unit Wastewater	Reference
Wastewater specific flow rate	L/tonne LIPIDIC BIOMASS	50-53	Industry survey
Total suspended solids (TSS)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Chemical Oxygen Demand (COD)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Biological oxygen demand after 5 days (BOD5)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Hydrogen Sulphide	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Ammonium	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Total nitrogen (TN)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Total phosphorus (TP)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Lead (Pb)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Cadmium (Cd)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Nickel (Ni)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Mercury (Hg)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Vanadium (V)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Benzene, ethylbenzene, toluene, and xylenes (BTEX)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Hydrocarbon Oil Index (HOI)	g/tonne LIPIDIC BIOMASS	N/A	Industry survey
Oily content	kg/tonne LIPIDIC BIOMASS	0.5-1.1	Industry survey
Remarks	(1)		

(1) - To be sent to Wastewater Treatment unit (WWT).

- After treatment, it is expected to release into environment following contaminants into discharged water:

Oily content = 0.005-0.01 g/tonne Feedstock

From literature and industry survey, it is concluded that:

- Approximately 0.088-0.093 m<sup>3</sup><sub>FRESH WATER</sub>/tonne<sub>RAW LIPIDIC FEEDSTOCK</sub> are consumed (chemically reacted or contaminated) in the process.
- Approximately 5.3-5.6 m<sup>3</sup><sub>FRESH WATER</sub>/tonne<sub>RAW LIPIDIC FEEDSTOCK</sub> are circulated for cooling (closed loop).

In the following table, the results of the literature and industry survey concerning main waste produced by lipidic biomass pre-treatment are reported.

**Table 7** Waste produced from lipidic biomass pre-treatment

Solid Waste	UoM	Value	Waste management method	Reference
Gums	kg/kg LIPIDIC BIOMASS	10-11	N/A	Industry survey
Spent Earth	kg/kg LIPIDIC BIOMASS	26-27	N/A	Industry survey
Remarks	- Gums mainly contain moisture and volatile matters, oil (5%w) and main contaminants present in the feed (Nitrogen, Chloride, Phosphatides, insoluble matters). - Spent Earth (earth used in bleaching process) contains 20-25%wt. of fatty matter.			

#### 4.1.3.2. Downstream

Downstream impacts within the refinery boundary, such as treatment of waste, are discussed above.

#### 4.1.4. Data gaps and limitations

Generally speaking, the information obtained on lipids hydrotreatment enables a relatively complete evaluation of technical and environmental parameters. There are operational plants for which data was obtained from the literature and industry survey. Some of this information was available for an entire plant, rather than particular process units. Relatively little detail of liquid effluent contaminants from pre-treatment Units was obtained.

In the industry survey, only information relevant to hydrotreatment of lipidic feedstock in a dedicated unit was obtained. This may be due to the difficulty in evaluating the emissions from the lipidic feedstock in co-processing cases, and to the early stage of development of co-processing of lipids and fossil fuels in FCC and Hydrocracking Units.

The scarcity of the data gathered from industry may be owed to:

- The high level of detail for the data requested;
- The high workload of Technology Licensors, which prioritize profitable activities;
- The low number of operating plants; and
- The fact that some Licensors might not be willing to share data relevant to their technology due to confidentiality and Intellectual Property issues.

## **4.2. GASIFICATION OF LIGNOCELLULOSIC BIOMASS SUCH AS WOOD FOLLOWED BY FISCHER-TROPSCH SYNTHESIS AND HYDROCRACKING**

### **4.2.1. Technology Summary**

#### **4.2.1.1. Feedstock**

Lignocellulosic biomass is the structural material recovered from woody plants and it is one of the most plentiful sources of biomass [Gudde, N. 2019]. Given the costs and the ease of logistics, lignocellulosic biomass is typically supplied from forests [Gudde, N. 2019]. It is composed of cellulose and hemicellulose polysaccharides, lignin aromatic polymers, as well as proteins, resins, and inorganic matter, the proportion of which varies among different plants. [Jensen, C.U. 2017]. Lignocellulosic biomass is mainly composed of carbon, hydrogen, and oxygen. The high content of oxygen makes the biomass less desirable for the production of transport fuel compared to petroleum [Jensen, C.U. 2017]. For this reason, during the production pathway, the biomass goes through a deoxygenation process.

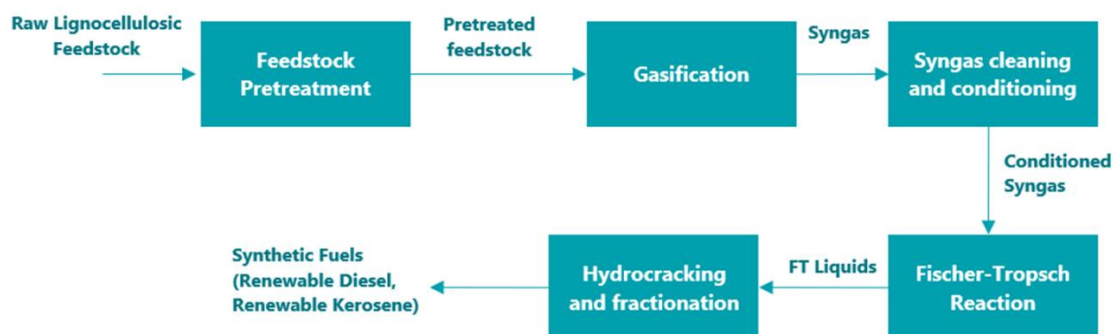
As part of a UOP project [UOP 2016] aimed at designing a pathway for an integrated biorefinery to process solid biomass into transportation fuel blendstocks, different types of lignocellulosic biomass were evaluated. Clean woodchips, switchgrass and bagasse were found to produce the highest liquid yield [UOP 2016]. The methanol produced from the gasification of wood has a 1.5 to 2 higher yield when compared to the gasification of sugar and starch crops [Bazzanella, A. 2017].

The use of lignocellulosic biomass for product manufacturing scores well for some sustainability criteria, including GHG balance, competition with food, biodiversity, and local environmental issues [van der Meijden 2011]. Specifically, lignocellulosic biomass is a renewable source loaded with solar energy [Chen, H. 2021]. It represents the residual of materials such as wood processing residues and waste-wood from industry, corn cobs, sugarcane bagasse, agricultural residues and energy crops. Feedstocks can grow on land not suitable for food crops [Chan, Y. 2019], and may not therefore have a negative impact on food security [de Rezende Pinho, A. 2017]. In addition, the efficient use of this material that otherwise could be disposed of is in line with EU Circular Economy Action [European Commission 2020] and the Waste Framework Directive [The European Parliament and the Council 2018]. Feedstock issues are discussed further in [Concawe 2021].

#### **4.2.1.2. Process**

Lignocellulosic biomass can be converted to biofuel through gasification followed by chemical conversion to liquid, or through thermochemical conversion by pyrolysis or hydrothermal liquefaction (HTL), followed by chemical processing. This first process, also known as Biomass to Liquid (BTL) and discussed in this section, is illustrated in **Figure 2**.

**Figure 2** Schematic of gasification of lignocellulosic biomass such as wood followed by Fischer-Tropsch synthesis and hydrocracking



Gasification is a thermochemical process that converts the lignocellulosic biomass into a combustible gas at high temperature (with less oxygen than needed for combustion). Gasification operated at high temperature results in high CO and hydrogen content and low tar content [Molino, A. 2018]. The syngas produced mainly contains CO, CO<sub>2</sub>, hydrogen, water, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>, in addition to various pollutants, that are then removed once the gas cools down [van der Meijden 2011]. The gas can be used to produce energy or transport fuels [E4Tech 2009].

Gasification occurs mainly at supercritical temperatures or above, between 450 °C and 600 °C and at pressures in the range of 50 to 250 bar [Jensen, C.U. 2017]. VTT Technical Research Centre of Finland [VTT, 2021] reports that lower pressures are also considered for biomass gasification applications (e.g. Fluidized Bed Gasifiers work at 1-20 bar).

The bed material has different roles in the gasification process. It can be an energy transfer at the conversion stage. The type of material affects the synthetic gas quality and the quantity of captured CO<sub>2</sub>. The most used materials are silica, dolomite, olivine, limestone, alkaline metal oxides and Ni and K-based catalysts [Molino, A. 2018].

The gasification agent affects the quality of the syngas with regards to composition and heating value [Molino, A. 2018]:

- Both air and oxygen gasification lead to a gas with a lower concentration of CO and hydrogen, which results in an increase in CO<sub>2</sub> concentration during combustion.
- Steam leads to higher hydrogen concentration.
- A combination of steam and oxygen leads to a syngas with higher CO<sub>2</sub> concentration and a decrease in CO and hydrogen.
- CO<sub>2</sub> gasification requires an external heating source and produces a CO rich syngas.

Prior to gasification, it is necessary to dry the biomass as it can contain up to 70% water [Bazzanella, A. 2017]. One study found that the thermal efficiency of FT syncrude production increased from 47.7% to 54.6% as the moisture mass fraction of the biomass feed was reduced from 30% to 8% [Tuomi et al 2019]. The pre-treatment stage depends on the lignocellulosic feedstock used [Casaneve, D. 2007].



Once the biomass is ready, the process of gasification is used to produce a synthetic gas [Casaneve, D. 2007]. Pyrolysis, one of the main processes used for gasification, is used to vaporise the volatile part of the feedstock. This stage plays a more important role in the gasification of biomass compared to the gasification of coal because of the higher share of volatile components in biomass [E4Tech 2009]. In this phase, solid char and ash are produced. Pyrolysis products are further broken down, provided that additional heating is present. The necessary heating is generated from the partial combustion of the feedstock in the reactor, or it can come from external sources [E4Tech 2009]. Following the gasification, a gas cleaning step removes tars, dust, and inorganic contaminants [Bazzanella, A. 2017].

A viable way to increase the product yield from biomass gasification is represented by “Hydrogen Enhanced Gasification”, which consists of increasing the hydrogen fraction in Syngas produced from biomass gasification by injecting a pure hydrogen stream before downstream conversion to liquid fuels. This reduces biomass demand by 30%-50% [Koponen, K. 2017].

Fischer-Tropsch (FT) synthesis is used to convert the hydrogen and the carbon monoxide (CO) in the gas to hydrocarbon chains through a catalyst [E4Tech 2009]. Syngas purification for downstream FT synthesis is still in its relatively early stages of development. It is considered to have a TRL of 5-6 [Boymans and Liakakou 2018]. The three reactions in FT synthesis are shown below [Atashi & Veiskarami 2018].



The products of FT synthesis depend on catalyst and operational conditions applied. Cobalt and iron catalysts are typically used. It has been suggested that when the synthesis gas ( $H_2$ , CO,  $CO_2$ ) is extracted from forest waste, the  $H_2$ /CO ratio is lower and iron-based catalysts are used [Hannula and Kurkela 2013]. The choice of catalyst is also made in relation to the desired product. The catalyst converts the water, that is always a by-product, to additional hydrogen for the FT synthesis by the water-gas shift reaction (WGS - reaction 3). FT synthesis can generate surplus electricity (depending on plant design) as a result of the high power efficiency of a condensing steam system and by the additional heat recovery from syngas associated with cooling the gas to filtration temperature (550 °C) [Hannula and Kurkela 2013].

Finally, FT waxes are hydrocracked and fractionated into high quality liquid fuels.

#### 4.2.1.3. Products

The main products resulting from the gasification of lignocellulosic biomass, downstream FT synthesis are high-quality distillates such as paraffinic diesel and jet fuel, possibly with co-products such as chemical naphtha or wax. Value added products are methane, biohydrogen, and biogas [Olatunji, O. 2020]. FT-based diesel has very similar properties compared to conventional diesel, except that it contains no sulphur and no aromatics, which reduces downstream emissions of those compounds drastically [Dieterich et al 2020].

Hydrocracking of the paraffins produced during the FT synthesis yields final products, such as gasoline, kerosene, and diesel [Casaneve, D. 2007]. Unlike the

hydrotreatment of vegetable oil, the process is able to convert the whole lignocellulosic material [Casaneve, D. 2007].

#### **4.2.1.4. Changes to refineries required**

There is considered to be a moderate synergy with existing refining assets. Biomass gasification is associated with high energy costs because of the need to reduce the biomass size at the beginning of the process [Molino, A. 2018]. Different technologies, and thus energy sources can be used for the biomass size reduction. For example, for agricultural and forestry residues hammer-mills, knife mills and tub grinders are typically used. The energy costs vary because of different factors, such as the moisture content of the biomass, its initial size and properties, and the properties of the mill [Koppejan, J. 2019]. Existing systems would need to be adapted in terms of feed system, burner, and reactor wall [Gudde, N. 2019]. The production of liquid biofuel makes use of the same infrastructure, storage system, and transportation of Liquefied Petroleum Gas, making it a cost-effective process [Molino, A. 2018].

Necessary adjustments would relate to the tar conversion and the syngas processing. Some refineries in the EU already use gasifiers to convert residual oils to syngas. These could be modified for the use of ground biomass or a “liquefied” bio-feed, although this has yet to be demonstrated on a large scale [Gudde, N. 2019]. In addition, new FT systems would be required. The FT reaction is very exothermic, and the reactor must be built so that it can handle large heat flux.

The heating necessary for gasification can be auto-thermally provided by exothermic combustion reactions [Molino, A. 2018] and biomass gasification requires less energy (with respect to the energy it produces) compared with petroleum-derived diesel or gasoline [Consiglio D. 2017].

#### **4.2.2. Technology and Supply-Chain Readiness**

Conversion technologies have been commercialised separately in other sectors (power, natural gas) but have not been demonstrated at scale as an integrated process at a refinery.

Gasification of raw biomass such as wood chips or pre-processed biomass such as torrefied wood or pyrolysis oil resembles a technology used in the power sector.

Syngas processing followed by FT synthesis resembles a technology used from coal and natural gas conversion. Upgrading of raw FT product (“wax”) to meet the demand for different lighter products resembles refinery hydrocracking, providing options from low-level co-processing to complete Hydrocracker transformation.

There are some forestry supply chains with large scale (>1 Mt/a), but significant scaling-up of capacity would be needed. Large amounts of lignocellulosic biomass would be required to replace the current fuel with biocrude, which raises other issues such as transport of biomass and land-take from other uses. This could have an impact on indirect emissions associated with land use change, as well as on deforestation. However, existing refinery infrastructure can be reused with few adjustments [Chan, Y. 2019]. External requirements for this pathway are considered to be very high because of these supply chain requirements and the need for low-carbon electricity.

### 4.2.3. Environmental Impacts

#### 4.2.3.1. Air Emissions

In general, the gasification of biomass produces less sulphur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ) emissions with respect to conventional technologies if suitably managed. Several respondents to the industry survey reported that the plant is not expected to generate air pollutants as the syngas produced in gasification system will be processed and converted to liquid fuels.

The amount of emissions depends on different factors, such as the temperature at which the gasification takes place, the steam to biomass ratio, the adsorbent to biomass ratio, or the biomass particle size. During gasification, the nitrogen in the biomass can be converted to ammonia ( $\text{NH}_3$ ) and molecular nitrogen, which can result in  $\text{NO}_x$  formation if not removed [Kumar, A. 2009]. The  $\text{NH}_3$  can be removed by catalytic decomposition to form  $\text{N}_2$  and  $\text{H}_2$  [Chunbao, X. 2010]. The syngas resulting from the gasification may contain increased amount - compared to conventional technologies - of  $\text{NH}_3$ , hydrogen cyanide (HCN), hydrogen sulphide ( $\text{H}_2\text{S}$ ) and hydrogen chloride (HCl). Polycyclic Aromatic Hydrocarbons (PAH) can also be created, especially when straw is used as feedstock [Banner, C. 2019].

The product gas stream can contain particulates, such as ash, tar (the unconverted organic material produced after biomass has been devolatilized during gasification) and char (a high carbon solid by-product of pyrolysis, gasification, and incomplete combustion of biomass) [Baldino et al 2019]. These are removed through cyclone separators (for particulates of diameter above  $5\text{ }\mu\text{m}$ ), wet scrubbers (above  $1\text{ }\mu\text{m}$ ), and barrier filters ( $0.5$  to  $100\text{ }\mu\text{m}$ ) [Kumar, A. 2009]. These systems increase the energy requirements and waste produced must be dealt with.

Sulphur can be converted to  $\text{H}_2\text{S}$  and  $\text{SO}_x$  during gasification. However, given the low content of sulphur in biomass with respect to coal, the gas sulphur content is small [Kumar, A. 2009].

Another study [Monir, M. 2018] on the gasification of the lignocellulosic biomass of coconut shell found that the biomass has relatively low moisture, ash content, and volatile matter, but higher fixed carbon, with respect to charcoal. Similarly, the ultimate analysis shows a lower carbon and sulphur content in terms of percentage of the total weight compared to charcoal [Monir, M. 2018]. Higher percentages of hydrogen, nitrogen and oxygen were recorded [Monir, M. 2018]. During the gasification, the carbon reacts with oxygen in the reactor leading to the formation of CO and  $\text{CO}_2$ . Given the higher content of hydrogen, coconut shell is the main source of hydrogen and water formed during the process [Monir, M. 2018]. Hydrogen and CO are the main components of the syngas produced through gasification. The sulphur content observed (even if low) is emitted as  $\text{SO}_x$ .

Reducing the moisture content of the feedstock increases the energy efficiency, the synthetic gas quality, and decrease the emissions related to the conversion process [Molino, A. 2018]. However, this could increase the requirements for space and processing at the refinery.

The environmental impacts of gasification have also been considered in the power sector. A recent study [Safarian, S. 2021] evaluated the global warming, acidification, and eutrophication potentials from the production of electricity through the gasification of 28 woody biomass and forestry residues. The GHG emissions released were found to be between 39 and 56  $\text{kgCO}_2\text{eq}$  per tonne of feedstock. What contributes the most to the global warming potential is the

feedstock transport, followed by drying, cutting, and handling during the pre-process stage. The carbon released during the conversion stage represents the smallest contribution of emissions because it is a biogenic  $\text{CO}_2$  [Safarian, S. 2021]. Acidic gases are created mainly during the conversion stage in the range of 21 to 67  $\text{kgSO}_{2\text{eq}}$  per tonne of raw feedstock [Safarian, S. 2021]. Finally, eutrophic gases are released at levels between 88 and 224  $\text{kgNO}_{3\text{eq}}$ . PM,  $\text{N}_2$ , NO,  $\text{NO}_3$ , and  $\text{NH}_3$  are mainly released during the combustion stage [Safarian, S. 2021].

With regards to the FT process, the off-gas produced is a mixture of the light hydrocarbons that are either too small to be sold as fuel, unreacted syngas, or include any inert gases that were contained in the process stream. This is typically recycled through the FT reactor used on-site as a combustion source for other processes including on-site energy recovery or drying of the biomass feedstock [Baldino et al 2019, Tuomi et al 2019].

In the following table, the results of the literature and industry survey concerning the main emissions to air produced by the gasification of lignocellulosic biomass (including pre-treatment steps) followed by FT Synthesis and Hydrocracking are reported.

The scope of the evaluation includes biomass drying and pre-treatment, gasification, Syngas cleaning, FT synthesis, upgrading (Hydrocracking of FT products), fractionation and associated utilities.

By-products of lumbering operations on tree plantations, consisting of wet woody biomass have been considered as feedstock and emission values are reported relative to the input of wet woody biomass.

**Table 8** Air emissions from the gasification of lignocellulosic biomass followed by Fischer-Tropsch Synthesis and Hydrocracking

Air emission	UoM	Value	Reference
Air pollutants			
Sulphur oxides (SO <sub>x</sub> /SO <sub>2</sub> )	g/tonne LIGNOCELLULOSIC BIOMASS	35	Industry survey
Nitrogen oxides (NO <sub>x</sub> /NO <sub>2</sub> )	g/tonne LIGNOCELLULOSIC BIOMASS	199	Industry survey
Particulate matter (PM <sub>2.5</sub> /PM <sub>10</sub> )	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Carbon monoxide (CO)	g/tonne LIGNOCELLULOSIC BIOMASS	583	Industry survey
Non-methane volatile organic compounds (NMVOCs)	g/tonne LIGNOCELLULOSIC BIOMASS	211	Industry survey
Total Particulate Matter	g/tonne LIGNOCELLULOSIC BIOMASS	271	Industry survey
Hazardous Air Pollutants (HAP)	g/tonne LIGNOCELLULOSIC BIOMASS	5.3	Industry survey
H <sub>2</sub> S	g/tonne LIGNOCELLULOSIC BIOMASS	1.1	Industry survey
NH <sub>3</sub>	g/tonne LIGNOCELLULOSIC BIOMASS	0.16	Industry survey
Lead	g/tonne LIGNOCELLULOSIC BIOMASS	0.002	Industry survey
Greenhouse gases			
Carbon dioxide (CO <sub>2</sub> )	kg/kg LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Methane (CH <sub>4</sub> )	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Nitrous Oxide (N <sub>2</sub> O)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
CO <sub>2</sub> equivalent	kg/tonne LIGNOCELLULOSIC BIOMASS	1060	Industry survey

Sulphur oxides and nitrogen oxides values align with those found in Safarian, S. [2021].

#### 4.2.3.2. Water emissions (incl. process effluent volumes)

The factors affecting the water footprint of biofuel are the type of feedstock, where it was grown, the conversion technology, and the feedstock mix of the biofuel [Wu, M. 2019].

The FT reaction produces water as a by-product. The produced syncrude is recovered by condensation, together with the aqueous product fraction that contains water and a small amount of oxygenated hydrocarbon residues and is treated as wastewater [Hannula et al 2020].

The literature review did not provide quantitative information on the water emissions associated with the gasification of lignocellulosic biomass.

In the following table, the results of the industry survey concerning wastewater produced by lignocellulosic biomass processing are reported.

**Table 9** Wastewater produced from the Gasification of lignocellulosic biomass followed by Fischer-Tropsch Synthesis and Hydrocracking

Wastewater flow rate & contaminants	UoM	Value	Reference
Wastewater specific flow rate	L/kg LIGNOCELLULOSIC BIOMASS	0.793	Industry survey
Total suspended solids (TSS)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Chemical Oxygen Demand (COD)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Biological oxygen demand after 5 days (BOD5)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Hydrogen Sulphide	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Ammonium	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Total nitrogen (TN)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Total phosphorus (TP)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Lead (Pb)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Cadmium (Cd)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Nickel (Ni)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Mercury (Hg)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Vanadium (V)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Benzene, ethylbenzene, toluene, and xylenes (BTEX)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Hydrocarbon Oil Index (HOI)	g/tonne LIGNOCELLULOSIC BIOMASS	N/A	Industry survey
Remarks			

#### 4.2.3.3. Water (re)use

Most of the literature sources considered evaluated water use in relation to the production of the feedstock. Thus, the literature review did not provide information on the water use during the gasification process.

One study suggested that the production of biofuel through the gasification of cellulosic biomass requires 9 litres (2 gallons) of water per 4.5 litres (1 gallon) of biofuel [Wu, M. 2019]. Chiu, Y. [2013] analysed the impact of the forest-based fuel obtained through a mixed alcohol gasification process on the water resources. The results show a minimal impact on surface and ground water used for irrigation and conversion [Chiu, Y. 2013]. The rainfall level associated with feedstock growth and conversion is part of the water consumption associated with a production system. The study showed that the type of biomass determines the water footprint.

From literature and industry survey, it is concluded that:

- Approximately 0.18-0.2 m<sup>3</sup><sub>FRESH WATER</sub>/tonne LIGNOCELLULOSIC BIOMASS are consumed (chemically reacted or contaminated) in the process.
- Approximately 6.53 m<sup>3</sup><sub>FRESH WATER</sub>/tonne LIGNOCELLULOSIC BIOMASS are circulated for cooling (closed loop).

#### 4.2.3.4. Waste

The gasification process leads to a series of by-products including char, ash, and condensable compounds like tars and oils [Arnava, M. 2019]. Syngas produced from biomass has a totally different composition compared to syngas from natural gas, with a lower H<sub>2</sub>/CO ratio and more contaminants, requiring more gas cleaning stages. Conventional gas cleaning is effective but produces waste water that can be difficult to dispose of [Rauch et al 2013]. Tars and particulates can be removed using methods such as scrubbers, cyclone separation, and bag filters [Rauch et al 2013].

There is potential for sustainable recycling solutions and technical applications thanks to their chemical and structural properties of these by-products [Arnava, M. 2019]. For example, they contain compounds like phosphorus that can be reused. In addition, the residual char can be used as biochar for soil amendment, remediation, and carbon sequestration [Arnava, M. 2019]. Char and ashes can also be sold as substitutes for fertilisers or active carbon [Arnava, M. 2019].

In the following table, the results of the literature and industry survey concerning the main wastes produced by lignocellulosic biomass processing are reported.

**Table 10** Waste produced from lignocellulosic biomass followed by Fischer-Tropsch Synthesis and Hydrocracking

Solid Waste	UoM	Value	Waste management method	Reference
Tramp metals	kg/tonne LIGNOCELLULOSIC BIOMASS	N/A	Recycle	Industry survey
Ash	kg/tonne LIGNOCELLULOSIC BIOMASS	5.1	Landfill	Industry survey
Salt cake	kg/tonne LIGNOCELLULOSIC BIOMASS	2.4	Cake disposed to landfill	Industry survey
Sulphur cake	kg/tonne LIGNOCELLULOSIC BIOMASS	0.25	Landfill	Industry survey
Slag	kg/tonne LIGNOCELLULOSIC BIOMASS	0.7	Third party disposal	Industry survey
Spent catalyst	kg/tonne LIGNOCELLULOSIC BIOMASS	N/A	Returned to supplier for metals recovery	Industry survey
Spent absorbents	kg/tonne LIGNOCELLULOSIC BIOMASS	N/A	Landfill	Industry survey
Bio sludge	kg/tonne LIGNOCELLULOSIC BIOMASS	1.6	Onsite recycling/Third party treatment	Industry survey
Oily sludge	kg/tonne LIGNOCELLULOSIC BIOMASS	N/A	Reprocessed/incinerated	Industry survey
Sooty sludge	kg/tonne LIGNOCELLULOSIC BIOMASS	N/A	Recycled to biomass dryer/Third party disposal	Industry survey

#### 4.2.4. Upstream (pre-treatment) and downstream environmental impacts

##### 4.2.4.1. Upstream

As mentioned in 4.2.3.1, pre-treatment to reduce particle size and moisture content can be used to improve efficiency. Smaller feedstock particle sizes increase the surface area and reduces diffusion resistance [Molino, A. 2018]. The gasification efficiency is thus enhanced, resulting in higher synthetic gas yield. The pre-treatment costs would increase as an additional step is required to reduce the particle size [Molino, A. 2018].

##### 4.2.4.2. Downstream

Gasification leads to the formation of toxic gases, such as CO, SO<sub>x</sub>, NO<sub>x</sub>. Therefore, the gasification process within the refinery should prevent leakages and ensure a gas clean-up system to avoid the release of PM [Luo, X. 2018].

The fuel produced from biomass is considered carbon negative when a portion of the biomass is returned to the soil by, for example, reducing it to biochar through pyrolysis [Mathews 2008]. As a matter of facts, biochar has multiple benefits when



applied to the soil. For example, biochar can act as a store of nutrients for the soil; it has some potential to store atmospheric carbon; it increases the soil pH thus increasing the microbial activity and supporting the decomposition of organic matter; it can modify the soil physical characteristics such as the pore-size distribution and the water holding capacity.

As a result, biofuels are an attractive option in terms of GHG emissions [van der Meijden 2011]. Using lignocellulosic biomass to produce energy is a carbon-efficient solution for emission mitigation, as it would offset the carbon that would otherwise be released through the burning of fossil fuels [O’Laughlin, J. 2008]. In addition, the use of fuels derived from lignocellulosic biomass can reduce the emission of other pollutants, for example bioethanol does not produce SO<sub>2</sub> which can lead to the formation of acid rain and of PM when it reacts with other compounds in the atmosphere [Olatunji, O. 2020]. Finally, because of their biodegradability, the environmental impact of bioethanol and biodiesel on water and soil is drastically lower than that of petroleum-based fuel [Olatunji, O. 2020].

#### 4.2.5. Waste gasification environmental impacts

Another way to generate a syngas suitable for the production of liquid fuels is represented by the gasification of waste (including non-recyclable waste, in accordance with hierarchy defined by EU waste directive).

The process can be arranged as follows: the gasification is carried out in a high temperature gasifier to avoid the production of tar, other heavy hydrocarbons, and polluting compounds. Then the syngas is compressed and purified of any entrained dusts, metals, chlorinated compounds, and sulphur. Finally, Syngas is conditioned through Water Gas Shift Reaction to increase hydrogen content and CO<sub>2</sub> removal to reach proper composition for downstream processing.

It should be noted that some Licensors deem that methanol/ethanol/hydrogen/ammonia production represents a more valuable downstream processing pathway than using FT synthesis.

In the following tables, the results of the literature and industry survey concerning main emissions to air produced by waste gasification are reported. Reference is made to a waste feedstock composed by 25% Plasmix (a heterogeneous mix of non-recyclable plastics derived from packaging) and 75% RDF (Refuse-derived fuel).

The scope of the evaluation includes waste gasification and syngas purification sections.

**Table 11** Air emissions from waste gasification

Air emission	UoM	Value	Reference
Health-Related air pollutants			
Sulphur oxides (SO <sub>x</sub> /SO <sub>2</sub> )	g/tonne WASTE FEEDSTOCK	0.99	Industry survey
Nitrogen oxides (NO <sub>x</sub> /NO <sub>2</sub> )	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Particulate matter (PM <sub>2.5</sub> /PM <sub>10</sub> )	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Carbon monoxide (CO)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Non-methane volatile organic compounds (NMVOCs)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Greenhouse gases			
Carbon dioxide (CO <sub>2</sub> )	kg/tonne WASTE FEEDSTOCK	44.3	Industry survey
Methane (CH <sub>4</sub> )	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Nitrous Oxide (N <sub>2</sub> O)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Remarks	(1)		

(1) Gaseous emissions estimated from combustion of vent gas streams reported in material shared by Licensor.

In the following table, the results of the literature and industry survey concerning wastewater produced by waste gasification are reported.

**Table 12** Wastewater produced from waste gasification

Wastewater flow rate & contaminants	UoM	Purified Water (after physical-chemical treatment) from gasification Wastewater Unit	Reference
Wastewater specific flow rate	L/kg WASTE FEEDSTOCK	0.25	Industry survey
Total suspended solids (TSS)	g/tonne WASTE FEEDSTOCK	20	Industry survey
Chemical Oxygen Demand (COD)	g/tonne WASTE FEEDSTOCK	40	Industry survey
Biological oxygen demand after 5 days (BOD5)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Hydrogen Sulphide	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Ammonium	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Total nitrogen (TN)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Total phosphorus (TP)	g/tonne WASTE FEEDSTOCK	2.5	Industry survey
Lead (Pb)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Cadmium (Cd)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Nickel (Ni)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Mercury (Hg)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Vanadium (V)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Benzene, ethylbenzene, toluene, and xylenes (BTEX)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Hydrocarbon Oil Index (HOI)	g/tonne WASTE FEEDSTOCK	N/A	Industry survey
Total Hydrocarbons (oils and waxes)	g/tonne WASTE FEEDSTOCK	2.5	Industry survey
N.NH <sub>4</sub>	g/tonne WASTE FEEDSTOCK	3.8	Industry survey

From literature and industry survey, it is concluded that:

- Approximately  $0.54 \text{ m}^3_{\text{FRESH WATER}}/\text{tonne}_{\text{WASTE FEEDSTOCK}}$  are consumed (chemically reacted or contaminated) in the process.
- Approximately  $107 \text{ m}^3_{\text{FRESH WATER}}/\text{tonne}_{\text{WASTE FEEDSTOCK}}$  are circulated for cooling (closed loop).

In the following table, the results of the literature and industry survey concerning main waste produced by waste gasification are reported.

**Table 13** Waste produced from waste gasification

Solid Waste	UoM	Value	Waste management method	Reference
Inert Granulate	$\text{kg}/\text{tonne}_{\text{WASTE FEEDSTOCK}}$	167	Recycled in civil/metal industry	Industry survey
Sludge	$\text{kg}/\text{tonne}_{\text{WASTE FEEDSTOCK}}$	39.2	N/A	Industry survey
Sulphur Cake	$\text{kg}/\text{tonne}_{\text{WASTE FEEDSTOCK}}$	3.5	N/A	Industry survey

#### 4.2.6. Data gaps and limitations

The literature review yielded minimal quantified information, largely because the gasification-FT synthesis facilities using biomass and waste feedstocks in operation around the world are mostly at pilot scale. It is anticipated that further data will be available in coming years. The robustness and usefulness of the data collected are limited by the following factors:

- Only a small number of Licensors shared information relevant for the whole chain from biomass to liquid fuels;
- Licensors provided a low level of detail in the process description;
- The moisture content of input wet biomass is not specified, making it difficult to compare specific environmental data with other cases; and
- Comprehensive information on water contaminants in the water process effluent stream were not provided or obtained from the literature.

The scarcity of the data gathered from industry may be owed to:

- The high level of detail for the data requested;
- The high workload of Technology Licensors, which prioritize profitable activities;
- The early development stage of the technology and the low number of operating plants; and
- The fact that some Licensors might not be willing to share data relevant to their technology due to confidentiality and Intellectual Property issues.

### 4.3. HYDROTREATMENT-HYDROCRACKING OF PYROLYSIS- OR HYDROTHERMAL LIQUEFACTION OILS MADE FROM LIGNOCELLULOSIC/WOODY BIOMASS

#### 4.3.1. Technology Summary

##### 4.3.1.1. Feedstock

As mentioned in 4.2.1, lignocellulosic biomass is the structural material recovered from woody plants and it is one of the most plentiful sources of biomass [Gudde, N. 2019]. Lignocellulosic biomass includes wood and residues from forestry, waste-wood from industry, agricultural residues, and energy crops.

The bio-oil resulting from the HTL process varies in composition and yield based on the lignocellulosic biomass chosen, as each feedstock has a different share of its main components (cellulose, hemicellulose, and lignin) [Jindal, M. 2016].

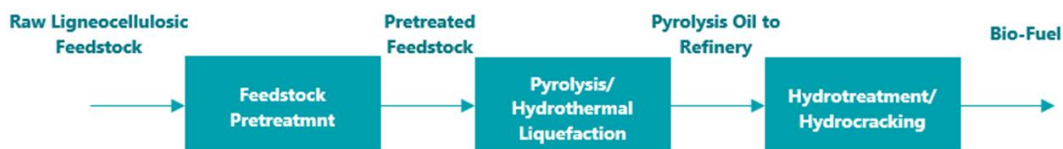
The feedstock that enters that refinery is the raw bio-oil, which can be imported or made on site.

Among the different types of lignocellulosic biomass, microalgae has also been considered as a potentially suitable feedstock for bio-oil production by thermochemical conversion from wet biomass, such as HTL [López Barreiro, D. 2013]. However, algae have a high mass fraction of water (between 80% and 90%) such that traditional thermochemical processes like pyrolysis or gasification are less economically viable than HTL, as the latter does not require dry biomass [López Barreiro, D. 2013].

##### 4.3.1.2. Process

HTL or fast pyrolysis of lignocellulosic biomass is followed by hydrotreatment or hydrocracking to produce hydrocarbon fuels. It can be operated as distributed pyrolysis followed by centralised hydrotreatment, or as integrated pyrolysis (or hydrotreatment) when biomass and hydrogen are available [Elliott, D.C. 2015]. The process is illustrated in **Figure 3**.

**Figure 3** Schematic of hydrotreatment-hydrocracking of pyrolysis- or hydrothermal liquefaction oils made from lignocellulosic/woody biomass



Pyrolysis requires a dry feedstock with total solids concentration of 80-90%, therefore a thermal drying step is performed when dealing with wet biomass. For example, microalgae contain only 20-30% total solids after the harvesting-dewatering stage [Bennion, E. 2015, Handler, R. M. 2014]. Biomass is then heated to a temperature ranging between 400°C and 600°C in the absence of oxygen and under atmospheric pressure. The biomass is then rapidly cooled down [Handler, R. M. 2014].

The process generates char, vapours, and aerosols, and upon condensation it results in a liquid bio-oil. The latter can be either combusted to generate electricity or stabilised through hydrotreating or hydro processing to produce biofuel [Handler, R. M. 2014].

HTL, also known as hydrothermal upgrading, is a process that converts high-water content biomass, or biomass slurries, into liquid fuel. The biomass slurry is heated and pressurized to convert it to bio-crude which can be hydroprocessed in a manner similar to conventional crude oil [Baldino et al 2019].

In contrast to pyrolysis, HTL is suitable for both dry and wet biomass, as drying of the feedstock is not necessary [Rocca, S. 2015]. This is because the whole biomass is decomposed to fine particles and converted in hot compressed water [López Barreiro, D. 2013].

The HTL processing parameters and the composition of the biomass affect the final product distribution, composition, and properties [Jindal, M. 2016]. For example, the temperature range for bio-oil formation from wood is between 200°C and 420°C, the bio-oil yield increases with increasing temperature up to an optimum and then decreases with a further increase in temperature [Jindal, M. 2016]. Pressure is also important as it increases solvent density, facilitating biomass decomposition and extraction. However, excessively high pressure reduces the decomposition reaction rate. Maintaining optimal temperature and pressure is therefore fundamental for the energy consumption during the whole HTL process [Jindal, M. 2016]. It has also been reported that usually, HTL takes place near or below the critical point of water with a temperature ranging between 280°C and 374°C, and with a pressure ranging between 50 and 350 bar [Jensen, C.U. 2017].

The industry survey shows that it is possible to achieve conversion of pyrolysis oil into liquid fuels by co-processing it with fossil feedstock in FCC units. Pyrolysis oil is catalytically cracked together with regular FCC feed, and the biomass-derived carbon is distributed across the various FCC products and coke. Data relating to a FCC demo plant (200 kg/h unit) indicate that co-processing up to 5% wt. of Pyrolysis oil with VGO (Vacuum Gas Oil) has little effect on the yield of the main products [Talmadge et al 2016].

Alternatively, in order to reach higher co-feeding rates or to enable stand-alone upgrading, an intermediate stabilization step is generally required, in which reactive ketones and aldehydes are de-functionalised and converted (preferentially) into alcohols. Hence, the stabilized oil can be upgraded to renewable fuel in an FCC or in an hydrotreating Unit.

#### **4.3.1.3. Products**

The final product is a mix of renewable gasoline and diesel (bio-gasoline and bio-diesel). In terms of characteristics and properties, the products derived from HTL of woody biomass have more oxygenated compounds and are relatively aromatic compared to petroleum [Elliott, D. C. 2015].

The products derived from HTL contain, in decreasing proportions: carbon, oxygen, hydrogen, and sulphur. Major product compounds include monoaromatics, fatty acids, alkanes, polyaromatic compounds, and nitrogen compounds [Gollakota, A. 2018].

#### **4.3.1.4. Changes to refineries required**

Large amount of lignocellulosic biomass would be required to replace the current feedstock with biocrude. However, it is suggested that existing infrastructure can be reused with few adjustments [Chan, Y. 2019].

In general, there is considered to be significant synergy with existing refining assets as the products derived from HTL are compatible with existing petroleum infrastructure such as pipelines, stations, and engines [Jensen, C.U. 2018].

Pyrolysis oil could be upgraded in refinery hydrotreaters or hydrocrackers [Gudde, N. 2019]. However, in such conventional refineries there is severe fouling risk because of the poor thermal stability of raw oils, and the high quantity of oxygen create a risk for excessive temperatures and/or insufficient hydrogen supply. In addition, the process conditions can differ among the refinery units. As a result, much of the oxygen should be removed through hydrotreatment so that pyrolysis oil can be used in common refineries [Gudde, N. 2019].

As stabilised pyrolysis oils have similar to lower oxygen content with respect to lipids, it can be assumed that they can go through the same processes. The biomass logistics can be simplified by making the pyrolysis oil in the refinery. This would mean either co-processing in existing hydrotreating units or converting the hydrotreater for renewable feed [Gudde, N. 2019]. Low-grade oils may need a dedicated stabilizer hydrotreater to prevent operational problems farther downstream in refinery hydrotreating or hydrocracker units.

An intermediate option studied by the UOP project [UOP 2016] is the co-processing of the pyrolysis oil where refineries partially produce renewable fuels. Low capital costs are required as only pyrolysis oil storage tanks and feed line piping to the fluid catalytic cracking unit need to be added [UOP 2016].

Several studies report reductions in total GHG emissions from the production of HTL biofuels compared to the petroleum baseline [e.g. Tews, I. J. 2014, Jensen, C.U. 2018]. Emissions related to HTL are lower because of a lower energy consumption [Tews, I. J. 2014]. Use of renewable energy would therefore reduce the carbon intensity further.

However, the pre-treatment stage of HTL, to prepare the biomass, can be defined as a net-zero user of energy [Chan, Y. 2019]. The primary energy necessary for the pre-treatment can be supplied by the downstream processing occurring at higher temperatures. The pre-treatment in turn can supply secondary heat to the rest of the system [Galbe, M. 2019]. The overall energy use is affected by the pre-treatment process, by the potential use of a by-product from the biorefinery, or by the potential external energy supply [Galbe, M. 2019].

#### 4.3.1.5. Technology and Supply-Chain Readiness

Pyrolysis technologies have been demonstrated in a few small commercial operations, mainly in the heat and power sectors. Upgrading to transport fuel is still under development at a small scale and therefore has a TRL of 5-6 [Gudde, N. 2019]. HTL is not a mature technology; there are no commercial-scale projects currently in operation [Baldino et al 2019]. However, a few facilities at demonstration scale exist:

- Licella (Australia, New South Wales) <https://www.licella.com.au/>
- Muradel (Australia) <https://arena.gov.au/projects/advancing-marine-microalgae-biofuel-to-commercialisation/>
- Silva Norway <https://www.statkraft.com/about-statkraft/where-we-operate/norway/silva-green-fuel/>

- Altaca Energy in Turkey <http://www.altacaenerji.com/projeler/catliq-demo-tesisi/>

For refineries that integrate biomass conversion to be economically competitive, it is fundamental for the lignocellulosic biomass to be available throughout the whole year at a competitive cost. In addition, a full working supply chain must be available, which includes transport and storage [Galbe, M. 2019]. This highlights the importance of the relative locations of the refinery and supply chain.

Especially in the power sector, a few forestry/waste supply chains have been established, but significant replication of these would be required to expand the use of the pathway [Gudde, N. 2019].

#### **4.3.2. Environmental Impacts**

##### **4.3.2.1. Air Emissions**

The main gaseous products of the HTL of lignocellulosic biomass are CO<sub>2</sub>, CO, H<sub>2</sub>, and CH<sub>4</sub> [Chen, H. 2021]. These off-gases are typically burned to supply heat or power for the process [Baldino et al 2019]. Higher volumes of the mentioned gases are produced when using branches rather than leaves as feedstock, but CO<sub>2</sub> is the largest gas component for both types of biomasses [Cao, L. 2016]. Steele et al [2012] provides emissions details for bio-oil production through pyrolysis.

**Table 14** reports the results of the industry and literature survey concerning the main emissions to air produced by the pyrolysis of lignocellulosic biomass. In the industry survey, only information relevant to fast pyrolysis (pyrolysis process involving moderate pyrolysis temperature and rapid heating rates) was obtained. Therefore, in the following table, the results of the industry survey concerning the main emissions to air produced by the fast pyrolysis of lignocellulosic biomass are reported. Reference is made to a biomass feedstock having 55% wt. moisture content. The scope of the evaluation includes biomass drying and pyrolysis sections, and associated utilities.



**Table 14** Air emissions from the pyrolysis of lignocellulosic biomass

Air emission	UoM	Effluent 1 (Flue Gas to Stack)	Effluent 2 (Dryer Outlet)	Reference
Air pollutants				
Sulphur oxides (SO <sub>x</sub> /SO <sub>2</sub> )	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	900 2.15	N/A	Industry survey Steele et al 2012
Nitrogen oxides (NO <sub>x</sub> /NO <sub>2</sub> )	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	900 1,221.6	N/A	Industry survey Steele et al 2012
Particulate matter (PM <sub>2.5</sub> /PM <sub>10</sub> )	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	938.3	N/A	Steele et al 2012
Carbon monoxide (CO)	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	2,751.3	N/A	Steele et al 2012
Non-methane volatile organic compounds (NMVOCs)	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	N/A	N/A	Industry survey
Dust	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	30	350	Industry survey
Greenhouse gases				
Carbon dioxide (CO <sub>2</sub> )	kg/kg <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	N/A	N/A	Steele et al 2012
Methane (CH <sub>4</sub> )	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	N/A	N/A	Industry/literature survey
Nitrous Oxide (N <sub>2</sub> O)	g/tonne <sub>DRY</sub> LIGNOCELLULOSIC BIOMASS	N/A	N/A	Industry/literature survey
Remarks		(1)(2)		

(1) Adoption of SNCR (Selective Non Catalytic Reduction) system reduces NO<sub>x</sub> emissions to 300 g/TONNE DRY LIGNOCELLULOSIC BIOMASS, with an Ammonia slip of 15 g/TONNE DRY LIGNOCELLULOSIC BIOMASS

(2) Overall, 0.058-0.090 kgCO<sub>2</sub>/kg TONNE DRY LIGNOCELLULOSIC BIOMASS are emitted in pyrolysis oil production

#### 4.3.2.2. Water emissions (including process effluent volumes)

The water phase as a by-product of HTL is affected by different processing factors, such as temperature, pressure, and type of biomass [Chen, H. 2021]. During the process, 10% to 50% of carbon and 50% to 70% of nitrogen are released to the aqueous phase [Chen, H. 2021]. Other substances detected are organic acids, alcohols, inorganic metallic substances, and ketones [Chen, H. 2021].

During the HTL process, 20 to 50% of organics are transferred to the HTL water phase [Chen, H. 2021]. This, together with additional factors such as the complexity of the biomass, the diversity of raw materials and of reaction products, make the composition of the HTL water phase complex [Chen, H. 2021]. As a result, direct unabated emissions from the water phase may be harmful to the environment, as products like furans, pyridines and phenols have toxic effects on the marine species, as well as a negative impact on their fertility [Chen, H. 2021].

Given the negative impact that the organic carbon and nutrients derived from the aqueous phase could have on the environment, it is important to reduce or recover them [Chen, H. 2021]. The aqueous phase can be recycled, reducing requirements for fresh water and potentially enhancing the total yield [Baldino et al 2019].

The industry survey suggests that no substantial water process effluent is foreseen from the fast pyrolysis process.

#### 4.3.2.3. Water (re)use

Energy production from biomass requires water usage for both biomass growing and conversion to fuel. Specifically, the HTL of a whole tree and forest residues implies the availability of water indirectly for the energy used in the system, and directly for the final production [Wong, A. 2016].

A study [Wong, A. 2016] on the production of hydrogenation-derived renewable diesel from lignocellulosic biomass estimated that the waste water from the HTL process sent to treatment for off-gas production corresponds to a water loss of 1.17 L H<sub>2</sub>O/kg dry wood. Similarly, the indirect water consumption for energy production is estimated to be 0.35 L H<sub>2</sub>O/kg dry straw [Wong, A. 2016]. Considering that 80% of water is from recycled sources, the direct water consumption required from purging to waste water treatment is 1.17 L H<sub>2</sub>O/kg dry straw [Wong, A. 2016].

From literature and industry survey, it is concluded that:

- Approximately 0.1 m<sup>3</sup><sub>FRESH WATER</sub>/tonne<sub>DRY LIGNOCELLULOSIC BIOMASS</sub> are consumed (chemically reacted or contaminated) in the pyrolysis process (1.2 m<sup>3</sup><sub>FRESH WATER</sub>/tonne<sub>DRY LIGNOCELLULOSIC BIOMASS</sub> for HTL process).
- Approximately 29.2 m<sup>3</sup><sub>FRESH WATER</sub>/tonne<sub>DRY LIGNOCELLULOSIC BIOMASS</sub> are circulated for cooling (closed loop).

#### 4.3.2.4. Waste

Unlike combustion, HTL can convert lignocellulosic biomass into harmless by-products that do not cause air pollution, including bio-oil, biochar, biogas, and water-soluble matter [Chen, H. 2021].

The solid residue of the HTL process is composed by ash and char with high content of carbon, hydrogen, and nitrogen that can be used as soil amendments [Chen, H. 2021].

In the following table, the results of the industry survey concerning the main wastes produced by pyrolysis of lignocellulosic biomass processing are reported.

**Table 15** Waste produced from the Pyrolysis of lignocellulosic biomass

Solid Waste	UoM	Value	Waste management method	Reference
Pyrolysis Oil Slurry	m <sup>3</sup> /tonne DRY LIGNOCELLULOSIC BIOMASS	0.00014	Stored in closed container	Industry survey
Ash from Boiler	kg/tonne DRY LIGNOCELLULOSIC BIOMASS	5	Stored in closed container (can be employed as fertilizer)	Industry survey
Ash from filter	kg/tonne DRY LIGNOCELLULOSIC BIOMASS	5	Stored in closed container	Industry survey
Dust from belt cleaning to sewer	kg/tonne DRY LIGNOCELLULOSIC BIOMASS	N/A	Sewer	Industry survey
Dust from dryer cleaning to waste	kg/tonne DRY LIGNOCELLULOSIC BIOMASS	N/A	Waste	Industry survey

### 4.3.3. Upstream (pre-treatment) and downstream environmental impacts

#### 4.3.3.1. Upstream

The pre-treatment of the biomass is important to recover polymers and other compounds in the biomass and to limit the formation of toxic and inhibitory compounds [Galbe, M. 2019]. Different pre-treatment methods are available. However, given the variation of lignocellulosic feedstocks makes it difficult to define the best pre-treatment method or to outline a general one. The choice of the methods depends on the bio-oil application, and it is based on a techno-economic evaluation [Galbe, M. 2019]. For example, acid and alkaline methods are based on the hydrolytic action at low or high pH. Steam explosion methods are based on the release of steam in the cell structure, followed by its expansion. Hydrothermolysis uses liquid water under pressure at high temperatures. Finally, Pre-treatments aided by an organic solvent, such as ethanol, acetone, or organic acids, cause the biomass dissolution [Galbe, M. 2019].

The impact on the carbon footprint of the use of biomass can be reduced by reducing the distance between the production site and storage from the storage location [Bazzanella, A. 2017].

#### 4.3.3.2. Downstream

The combustion of fuel derived from lignocellulosic biomass generates less SO<sub>x</sub> and NO<sub>x</sub> emissions than petroleum-based fuel, as the biomass contains less sulphur and nitrogen [López Barreiro, D. 2013]. The biocrude oil derived from the HTL of microalgae has low SO<sub>2</sub> emissions and it releases little PM because of its low ash content. However, due to high amount of nitrogen in microalgae cells, NO<sub>x</sub> emissions are high with respect to petroleum crude oil [López Barreiro, D. 2013].

A recent study [Sippula, O. 2019] compared the particulate emissions between fast pyrolysis bio-oil made of lignocellulosic biomass, heavy fuel-oil, and wood fired boilers. The total suspended particulate matter and fine particulate matter concentrations in the first were higher before filtration compared to the second, and lower or similar compared to the third [Sippula, O. 2019].

#### 4.3.4. Data gaps and limitations

The literature review yielded general commentary on emissions but little quantified information on environmental parameters.

Only a small number of Licensors shared data relevant to environmental impact of biomass pyrolysis process. However, the information received is considered suitable to enable a comprehensive evaluation of technical details and environmental parameters with regards to pre-treatment and pyrolysis, although downstream processing is a gap. This is considered to be the result of the relatively early stage of technological development.

The scarcity of the data gathered from industry may be owed to:

- The high level of detail for the data requested;
- The high workload of Technology Licensors, which prioritize profitable activities;
- The early development stage of the technology and the low number of operating plants; and
- The fact that some Licensors might not be willing to share data relevant to their technology due to confidentiality and Intellectual Property issues.

#### **4.4. E-FUELS PRODUCTION (FROM CAPTURED CO<sub>2</sub> AND ELECTROLYTIC HYDROGEN)**

##### **4.4.1. Technology Summary**

###### **4.4.1.1. Feedstock**

E-Fuels are gaseous and liquid fuels produced from captured CO<sub>2</sub> and electrolytic hydrogen made into syngas by RWGS and hence into hydrocarbons by FT synthesis with subsequent hydrocracking to produce suitable boiling range fuels.

Captured CO<sub>2</sub> can be obtained from various sources such as biomass combustion, industrial processes (flue gases from fossil oil combustion), biogenic CO<sub>2</sub> and CO<sub>2</sub> captured directly from the air. Pure CO<sub>2</sub> with a very low oxygen content is needed to avoid damaging the catalysts used for methanisation and Fischer-Tropsch synthesis [Concawe 2020].

In biomass combustion, the concentration of CO<sub>2</sub> in flue gas from solid biomass fired heaters ranges from 10 to 13% [Dena 2018]. CO<sub>2</sub> is extracted from flue gas via scrubbing with amines such as monoethanolamine (MEA) or advanced proprietary amine-based solvent formulations. The scrubbing agent washes the CO<sub>2</sub> from the gas stream and is regenerated through heating.

CO<sub>2</sub> can also be obtained from industrial processes (such as refineries) or power generation plants. The CO<sub>2</sub> content of concentrated sources range from 2% (coke-oven gas) to 18% (blast furnace gas) [Dena 2018]. CO<sub>2</sub> is extracted similarly to the previous case.

Biogenic CO<sub>2</sub> sources include biogas-upgrading plants, CO<sub>2</sub> from ethanol plants, and CO<sub>2</sub> from the combustion of biogas. The CO<sub>2</sub> content of biogas ranges from 25 to 55% [LBST and Dena 2017]. The CO<sub>2</sub> can be separated from the biogas stream via scrubbing with amines or via pressure swing adsorption (PSA). Both technologies provide high CO<sub>2</sub> purity (99%).

Various technologies are also being investigated to extract CO<sub>2</sub> from the air where the CO<sub>2</sub> concentration is 0.04% through Direct Air Capture (DAC). This is by far the most expensive carbon capture technology to supply CO<sub>2</sub> [Concawe 2020] and has a TRL of 5-6 [Viebahn et al 2019].

E-Hydrogen, produced by electrolysis from water, is the other feedstock of E-fuels. There are again several hydrogen electrolysis technologies. Commercially available, low-temperature processes include alkaline electrolysis (AEC) and proton exchange membrane electrolysis (PEM). High-temperature electrolysis (SOEC) is less well developed [Concawe 2020].

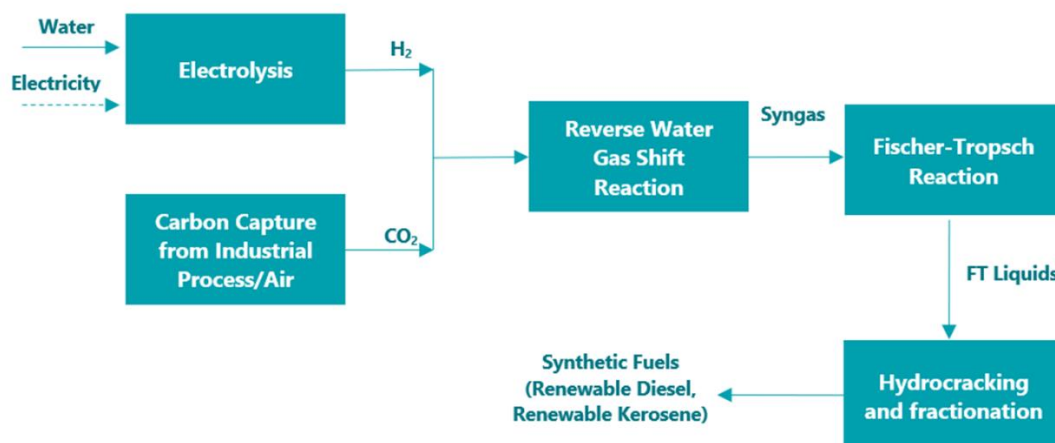
###### **4.4.1.2. Process**

The main E-fuels conversion routes consist of hydrogen reacting with captured CO<sub>2</sub> to produce clean syngas consisting of hydrogen and carbon monoxide. Oxygen is a by-product of this electrolysis process. Power consumption by the electrolyser is one of the main limiting factors on the volume of fuels that can be produced [Nordic Energy Research 2020].

Due to the limited experiences with CO<sub>2</sub>-based feed gases for FT synthesis and the early stage of FT catalyst development for direct CO<sub>2</sub> conversion, operational and planned plants exclusively rely on a shift from CO<sub>2</sub> to CO using a RWGS reactor (the

reverse of reaction 3 in 4.2.1.2) or co-electrolysis [Dieterich et al 2020]. The process is illustrated in the figure below.

**Figure 4** Schematic of E-Fuels production (from captured CO<sub>2</sub> and electrolytic hydrogen)



The RWGS reaction approach is considered to be suitable as it can be implemented with any locally available renewable energy source to contribute to a closed carbon loop [Daza and Kuhn 2016]. RWGS reactors use catalysts (e.g. supported metal catalysts, oxide catalysts). Noble metal catalysts have been shown to result in higher reaction rates, but their high prices and limited availability could make them unviable for implementation at a wide scale [González-Castaño et al 2021]. Developments of the process are focussing on designing cost-effective catalysts that can achieve high CO selectivity and high production rates [Daza and Kuhn 2016]. Recent research has also shown that energy consumption can be reduced by up to 54% using the intensified RWGS-Chemical Looping (RWGS-CL) process when compared to the conventional process [Wenzel 2018]. The TRL of the commercial use of the RWGS reaction is estimated to be 7 [Detz 2019].

The syngas produced can then be processed using the FT process (discussed in 4.1.1.2) to produce different type of fuels: e-gasoline, e-diesel and e-jet.

Common processes for fuel synthesis include FT and methanol synthesis. Plants using these processes are in operation and produce, for example, methane and methanol from carbon monoxide and hydrogen. Examples of these plants include a power-to-methanol production plant operated by Carbon Recycling International (CRI) producing a commercial scale renewable methanol, called Vulcanol, at 4,000 tonnes/year. Another example is A 20 MW facility to be installed by Sunfire and operated from 2023 by Norsk e-Fuel in Norway, which will produce 8,000 tonnes of 'e-crude' liquid fuel/year from renewable energy and carbon dioxide [Royal Society 2019].

#### 4.4.1.3. Products

Syngas can be processed to produce different type of fuels: e-gasoline, e-diesel and e-jet.

#### 4.4.1.4. Changes to refineries required

There is considered to be a moderate synergy with existing refining assets.

Refineries would require new RWGS reactors or electrolyzers and FT systems. Raw FT product is converted to fuel by co-processing in refinery hydrocracker or by transformation of refinery unit to 100% bio-feed. The refinery can use its own CO<sub>2</sub> emissions as feed for integrated e-fuel plants.

Common processes for fuel synthesis include FT and methanol synthesis. Very large-scale plants using these processes are in operation and produce, for example, methane and methanol from carbon monoxide and hydrogen.

#### **4.4.2. Technology and Supply-Chain Readiness**

The production of E-fuels at scale is also currently limited by the availability of low-cost sustainable electricity to power the generation of hydrogen, the module scale-up of the electrolyzers and by the generation of syngas. It is likely that centres of production will emerge where such energy sources are abundant (e.g., wind on the west coast of Africa and solar in desert regions), particularly if DAC of CO<sub>2</sub> is employed. E-fuels are therefore likely to be exported around the world from these centres of production [Royal Society 2019].

Producing low-carbon hydrogen through the electrolysis of water will become more commercially viable as the price of renewable electricity falls and the electrolyzers become more efficient.

Competing demand for renewable electricity is an important consideration. EU transport energy demand for renewable energies in 2050 will exceed current EU electricity production by a factor of between 1.7 and 3. The transport sector will thus become a major electricity market of the future. Aside from road transport, from 2030 onwards, the E-fuels demand from maritime transport and aviation is expected to grow dramatically, resulting in a sharp increase in the demand for renewable electricity. Renewable energy must therefore be ramped up as soon as possible [LBST and Dena 2017].

The FT process required for the production of E-fuels is established at scale. Similar conversion technologies are used in a several commercial gas-to-liquid plants to produce low sulphur diesel from natural gas or coal, and to a lesser extent from biomass as discussed in 4.2.

The RWGS process has not yet been developed at industrial scale. Further research is needed to optimize the reactor design using modern approaches [González-Castaño et al 2021].

#### **4.4.3. Environmental Impacts**

##### **4.4.3.1. Air Emissions**

Oxygen is produced as a by-product of the electrolysis process. There is potential for this oxygen to be used by co-located industrial facilities that require oxygen (e.g. iron and steel, copper pulp and paper) [Nordic Energy Research 2020].

The off-gas from the FT process can be recycled by using it as a combustion fuel to heat the syngas preparation process [Hannula et al 2020]. It can also be used for on-site energy recovery [Baldino et al 2019].

A lot of the literature on emissions associated with E-fuels focuses on the emissions to air associated with the carbon capture stage. Primary energy use increases when applying CO<sub>2</sub> capture technologies because CO<sub>2</sub> capture and pressurisation requires



energy. Due to the increased fossil fuel combustion, an increase in the air pollutant emissions like NO<sub>x</sub> may be observed [EEA 2011].

One side effect of the amine scrubbing process is that a small fraction of the amine solvent is released to the atmosphere where it can lead to a variety of environmental side effects [IASS 2013]. Amine-based solvents used for post-combustion CO<sub>2</sub> capture are produced from basic chemicals like ammonia, methanol and ethylene oxide. MEA is distilled from a mixture of MEA, DEA and TEA (mono-, di- and tri-ethanolamine) and produced in a batch mode from ethylene oxide and ammonia. Amines and degradation products can be emitted from the stack, potentially causing environmental impacts. MEA (2-aminoethanol) is emitted in small quantities (1 to 4 ppmv) due to entrainment in the scrubbed flue gas. This corresponds to 40 to 160 t/yr for a plant capturing 1 Mt per annum, but is possibly lower for capture facilities with mitigation measures implemented [Koornneef et al 2011].

#### **4.4.3.2. Water emissions (including process effluent volumes)**

The RWGS reaction produces water that must be removed *in situ*, although it is understood that this process has not yet been commercially verified [González-Castaño et al 2021].

The FT reaction also produces water as a by-product. The aqueous product fraction (recovered during condensation which is also required to recover the produced syncrude) contains water and a small amount of oxygenated hydrocarbon residues, and is treated as wastewater [Hannula et al 2020].

#### **4.4.3.3. Water (re)use**

Water is essential in any E-fuel scheme as the main feedstock for the production of e-hydrogen. It is also an important means of heat integration. Synthesis of 1 litre of liquid E-fuel in a water-cooled plant requires a water import of 3.7 - 4.5 l as feedstock. If all water produced is recycled back to the electrolyser, the net intake of water is 1.3 - 2.0 l per litre of e-fuel [Shell, 2018]. Many areas with favourable conditions for Photo-Voltaic (PV) solar and wind power generation have available land for e-fuels deployment but lack continuous sources of fresh water needed for the electrolysis step when producing e-fuels. Seawater desalination plants are one of the options to provide freshwater where water resources are limited [Concawe 2020].

#### **4.4.3.4. Waste**

The literature review yielded no information on solid waste production from the E-fuels pathway.

#### **4.4.4. Data gaps and limitations**

The literature review yielded little quantitative information on environmental parameters associated with E-fuel production. Where information on inputs, such as energy, was found, this was not broken down into different stages of the process. No Licensor was able to participate in the industry survey. As a result, it has not been possible to quantify the environmental parameters relevant to production of E-fuels.

The lack of quantified information in the literature is considered likely to be a result of the early development stage of the technology (RWGS process not yet developed at industrial scale and FT process optimized for large scale) and the low number of



operational plants. This may also partly explain why licensors were not able to participate in the survey. Other reasons suggested why Licensors were not able to participate included:

- The high workload of Technology Licensors, which prioritise profitable activities;
- The high level of detail of the data requested; and
- The fact that some Licensors might not be willing to share data relevant to their technology due to confidentiality and Intellectual Property concerns.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions with regard to the level of information available for each LCP can be drawn from the literature review and industry survey carried out:

- Generally speaking, the information obtained on lipids hydrotreatment enables a relatively complete evaluation of technical and environmental parameters. There are operational plants for which data was obtained from the literature and industry survey. One limitation was that only information relevant to hydrotreatment of lipidic feedstock in a dedicated unit was obtained. This may be due to the difficulty in evaluating the emissions from the lipidic feedstock in co-processing cases, and to the early stage of development of co-processing of lipids and fossil fuels in FCC and Hydrocracking Units.
- The literature review yielded minimal quantified information on the gasification-FT synthesis LCP, largely because the facilities using biomass and waste feedstocks in operation around the world are mostly at pilot scale. It is anticipated that further data will be available in coming years. The robustness and usefulness of the data collected are limited by the factors such as the moisture content of input wet biomass is not being specified, making it difficult to compare specific environmental data with other cases, and a lack of information on water contaminants in the water process effluent stream were not provided or obtained from the literature.
- The literature review for the hydrotreatment-hydrocracking of HTL and pyrolysis oils LCP yielded general commentary on emissions but little quantified information on environmental parameters. Data relevant to the environmental impact of biomass pyrolysis process was obtained from Licensors enabling a fairly comprehensive evaluation of technical details and environmental parameters with regards to pre-treatment and pyrolysis, although downstream processing is a gap. This is considered to be the result of the relatively early stage of technological development.
- The literature review yielded little quantitative information on environmental parameters associated with E-fuel production. No Licensor was able to participate in the industry survey. As a result, it has not been possible to quantify the environmental parameters relevant to production of E-fuels. The lack of quantified information in the literature is considered likely to be a result of the early development stage of the technology (RWGS process not yet developed at industrial scale and FT process optimized for large scale) and the low number of operational plants.

The following main recommendations are made in relation to the gaps and limitations identified above:

- Lipids hydrotreatment - Effluents from co-processing of lipidic biomass in existing hydrotreaters can be estimated as weighted average between a conventional feedstock hydrotreater and a dedicated lipids hydrotreating Unit, due to the similarity of the processes. Effluents from co-processing of lipids in HC/FCC Units can be estimated using conventional feedstock values and including some qualitative indications on expected effluent quantity and quality.

- Biomass gasification-FT synthesis - Given the importance of input biomass moisture content, it is important that commentary is provided on the sensitivity of emissions to this factor. This will include data quality and ranges of emissions that may be expected under different scenarios.
- Hydrotreatment-hydrocracking of pyrolysis- or HTL oils - Effluents from co-processing of pyrolysis/HTL oil in downstream Units will be estimated using conventional feedstock values and including some qualitative indications on expected effluents quantity and quality.
- E-fuel - On the basis of the limited information obtained, it will only be possible to estimate CO<sub>2</sub> emissions and water effluent production.

## 6. GLOSSARY

BOD5	Biological oxygen demand after 5 days
BTL	Biomass to Liquid
bpd	Barrels per day
BTEX	Benzene, toluene, ethylbenzene and xylenes
COD	Chemical oxygen demand
DAF	Dissolved Air Flotation
DT	Delta T (temperature difference)
FCC	Fluid catalytic cracking
FT	Fischer Tropsch process
GHG	Greenhouse Gas
HCL	Hydrogen Chloride
HCN	Hydrogen Cyanide
HOI	Hydrocarbon oil index
HP	High Pressure
HTL	Hydrothermal Liquefaction
LCP	Low Carbon Pathways (Concawe's LCP programme)
LP	Low Pressure
LPG	Liquid Petroleum Gas
MP	Medium Pressure
N/A	Not Available
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Ammonium
NM VOC	Non-methane volatile organic compounds

NO <sub>x</sub>	Nitrogen Oxides
NO <sub>2</sub>	Nitrogen dioxide
PAH	Polycyclic Aromatic Hydrocarbons
PFD	Process Flow Diagram
PM	Particulate matter
QMS	Quality management system
ReCAP	Project initiated in 2014 by the IEA Greenhouse Gas R&D Programme (IEAGHG), in collaboration with GASSNOVA, SINTEF and Concawe, to evaluate the performance and cost of retrofitting CO <sub>2</sub> capture in an integrated oil refinery
RFI	Request for information
RTP	Rapid Thermal Processing
RWGS	Reverse Water Gas Shift
SO <sub>2</sub>	Sulphur dioxide
Sox	Sulphur oxides
SOEC	Solid Oxides Electrolysis Cells
TRL	Technology readiness level
TSS	Total suspended solids
WGS	Water Gas Shift

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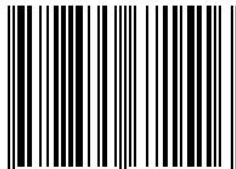
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**Concawe**  
Boulevard du Souverain 165  
B-1160 Brussels  
Belgium

Tel: +32-2-566 91 60  
Fax: +32-2-566 91 81  
e-mail: [info@concawe.eu](mailto:info@concawe.eu)  
<http://www.concawe.eu>

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