INTERNATIONAL COOPERATION FOR
SUSTAINABLE AVIATION BIOFUELS

Overview of the VC Biocrude oils to SAF

<March 2024>

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This project has received funding from the European Union’s Horizon Europe research and innovation programme under grant agreement No. 101122303

Table 1: Document information

Document Information	
Project name:	ICARUS
Project title:	International cooperation for sustainable aviation biofuels
Project number:	101122303
Start date:	01/10/2023
Duration:	6 months

Table 2: Dissemination level of this report

Dissemination level of this report	
PU	Public x
PP	Restricted to other programme participants (including the Commission Services)
RE	Restricted to a group specified by the consortium (including the Commission Services)
CO	Confidential, only for members of the consortium (including the Commission Services)

ACKNOWLEDGMENT & DISCLAIMER

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EXECUTIVE SUMMARY

The transition from fossil fuels to sustainable alternatives is imperative for mitigating climate change impacts and transitioning to a low-carbon economy. Bio-crude derived from hydrothermal liquefaction (HTL) offers a promising pathway for renewable energy; however, significant upgrading is necessary to align with the standards of conventional liquid fuels. The present deliverable addresses critical challenges, methodologies, and advancements in bio-crude upgrading, while also providing insights into the regulatory framework governing Sustainable Aviation Fuels (SAF).

Bio-crude upgrading plays a vital role in improving its compatibility with refining processes and enhancing its quality for fuel production. Catalytic Hydrodeoxygenation (HDO) stands out as a leading technique, utilizing catalysts to remove heteroatoms. Nonetheless, challenges such as hydrogen consumption and catalyst longevity persist. This report comprises an extensive literature review on innovative catalytic hydrotreatment approaches for biocrudes. It explores operational conditions, reactor configurations, feedstock, and catalyst types to optimize conversion performance and characterize upgraded biocrude effectively.

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1 Introduction

Reducing GHG emissions in the transport sector can be achieved without significant changes to existing infrastructure by increasing the use of renewable resources in current fuel production (Kim et al., 2020). Therefore, increased use of biofuels has the potential to help resolve the environmental and sustainability problems associated with the current use of petroleum-derived fuels. Among the most promising biofuels are second-generation biofuels, produced from lignocellulosic biomass, woody crops, agricultural residues and waste, and third-generation biofuels, produced from non-terrestrial organisms such as algae and yeast (Kargbo et al., 2021). These new generation biofuels do not have the disadvantages associated with first generation biofuels and are therefore the most favourable for future applications as liquid fuels in transport (Kargbo et al., 2021).

Bio-oil, defined as a complex mixture of valuable chemical compounds, is an energy vector that can be used directly as a fuel in less noble applications or improved in its characteristics for more advanced technological applications ((Azizi et al., 2018);(Nava Bravo et al., 2019);(Santillan-Jimenez et al., 2019)). Furthermore, the properties of the bio-oil obtained from HTL are strongly linked to the type of biomass converted and the process conditions, which include temperature and heating rate, residence time, ratio biomass : water, use of catalysts, as well as the procedures necessary to recover the products resulting from the process. Therefore, these operational parameters must be carefully studied.

The oil from high-pressure liquefaction (hydrothermal, alkali-catalyzed process) is a more deoxygenated product than fast pyrolysis bio-oil. As a result, it is more thermally stable and required less hydrogenation to produce fuels. Typically, bio-oil obtained from microalgae HTL has high nitrogen (5 – 8%) and oxygen (10 – 15%) contents compared to crude oil (J. Lu et al., 2021). This chemical profile indicates that bio-oils have generally negative fuel properties, including high levels of acidity, humidity and corrosivity, poor combustion performance and low H/C ratio, which makes their direct application as liquid fuel for transport difficult (diesel and aviation fuel). Therefore, upgrading bio-oil is a necessary step to resolve these limitations and improve its stability and fuel properties. The most used upgrading techniques include phase separation (to reduce the water content), hydrotreating (to reduce the viscosity, nitrogen and sulphur content), hydrodeoxygenation (to reduce the oxygen content), esterification (to reduce the acidity), hydro and catalytic cracking (to improve the H/C ratio and cetane number) and emulsification (to prevent phase separation) (Kazemi Shariat Panahi et al., 2019). This derivable is focused in the hydrodeoxygenation process.

2 Bio-oils production

2.1.1 Hydrothermal Liquefaction (HTL)

HTL is a thermochemical process in which biomass is decomposed and transformed into gas, liquid, and solid fractions in sub- or super-critical water and sometimes in the presence of organic solvents and/or catalysts (Elliott, 2007). The typical processing temperature ranges from 270 °C to 370°, while the pressure is between 4 and 22 MPa. When the temperature and pressure are close to the critical point (374 °C, 22 MPa), the properties of water change significantly, including density, di electric constant, permittivity, and polarity etc. In hydrothermal liquefaction processes, the target product is liquid bio-crude oil, and the objective of HTL is to obtain high yield and high quality biocrude. Different from petroleum, biocrude oil is a complex mixture of oxygenated compounds with a wide range of molar mass. Its quality can be characterized by its higher heating values (HHV), viscosity, density, acidity, stability, molar mass distribution, O/C or H/C ratios and chemical compositions, etc (J. Yang et al., 2019). Depending on downstream application, specific chemical composition and properties might be favoured.

Typically, biomass consists of four major organic heteropolymers: lignin, cellulose, hemicellulose, and extractives (tannins, fatty acids, resins, and inorganic salts) (Y. Lu et al., 2017). The composition depends on the type of feedstock. Thermal degradation of these organic polymers leads to the formation of hundreds of new compounds. Decomposition of hemicellulose and cellulose (at 200–350 ◦C) results in the formation of various oxygenates, including levoglucosan, anhydrosugars, alcohols, acids, aldehydes, ketones, furans, etc. Lignins on decomposition (at 280–500 ◦C) generate various phenolic compounds. Biocrudes are complex mixtures containing more than 400 compounds (Y. Lu et al., 2017) which makes the speciation and identification complicated. Therefore, a complete characterization of biocrude often need the use of more than one analysis technique (Badoga et al., 2022)

Hydrothermal liquefaction (HTL) followed by catalytic hydrotreating of the produced biocrude is increasingly gaining interest as an effective technology for the conversion of biomass into liquid biofuels. A strong advantage of HTL resides in its great flexibility towards the feedstock, since it can treat a large number of different organic substrates, ranging from dry to wet residual biomass. Nevertheless, the characteristics of biocrudes from different typologies of organic materials result in different challenges to be met during the hydrotreating step, leading to differences in heteroatoms removal and in the typology and composition of the targeted products (Castello et al., 2019) .

2.1.2 Microbial oils

The rapid expansion of biofuel production highlights the urgency to find alternative lipid sources to meet future biofuel needs without compromising agricultural land and food availability. While plants can synthesize lipids suitable for biofuel, some crops yield minimal oil compared to their whole biomass, whereas certain photosynthetic and heterotrophic microorganisms offer higher oil content. To address the rising demand for biofuel, microbial oil production may arise as an alternative.

Microorganisms contain various lipids, designated single cell oils (SCO), suitable for biofuel production (Bautista L. F. et al., 2012). Microbial oils offer several advantages over traditional sources, including independence from climate limitations, lack of competition with food supply, independence from agricultural land, shorter process cycles and utilization of industrial waste or inexpensive materials. Moreover, genetic modification allows for targeted enrichment of specific fatty acids in microbial oils, reducing the need for additional chemical synthesis (Ledesma-Amaro, 2015). (Ochsenreither et al., 2016) Technologies converting sugars to hydrocarbons are promising for sustainable bio-jet fuel production, with biological fermentation offering streamlined processes without the need for chemical catalysts or high temperatures (Jiménez-Díaz et al., 2017)

Oleaginous microorganisms

Microalgae, bacteria and fungi represent the range of the most common oleaginous microbial species that can produce microbial oils through fermentation, namely submerged (SmF) or solid-state fermentation (SSF) (Bautista L. F. et al., 2012). Suitable feedstocks depend on the species and there are various such as glucose and other sugars, glycerol, lignocellulosic biomass and respective hydrolysates like xylose (in the case of *Rhodosporidium toruloides*), fruit and vegetables, organic waste, starch and fats (Walls & Rios-Solis, 2020).

Bacteria, with their high growth rates, offer potential as biofuel sources but often accumulate complex lipids like phospholipids and glycolipids instead of triglycerides. However, *Escherichia coli* has been engineered for biofuel production due to the extensive knowledge of its physiology and metabolism (Bautista L. F. et al., 2012) (Ma et al., 2018)

Heterotrophic microalgae, unlike photosynthetic species, can accumulate lipids without requiring light, making them suitable for cost-effective cultivation in fermenters with less variations on lipid production (Sabikhi Latha and Kumar M.H., 2012). Microalgae offer numerous advantages over land plants and other microorganisms, including high lipid productivity (lipid content can reach up to 90% of the dry weight), efficient nutrient extraction and rapid growth rates (Silva et al., 2023). Referring to autotrophic microalgae, diminished light intensity encourages the formation of polar lipids, whereas heightened light intensity supports the generation of non-polar lipids. Furthermore, under reduced nitrogen levels, microalgae shift their lipid composition from free fatty acids to triglycerides (Ma et al., 2018).

Most fungi accumulate nutritious lipids (DHA, EPA, ARA) and for that reason these microorganisms are less suited for direct biofuel production (Thevenieau & Nicaud, 2013). However, some strains can accumulate up to 86% of lipids (Bautista L. F. et al., 2012) in dry biomass and therefore have potential for such production.

Yeasts can also accumulate up to 90% of their cell dry weight as fatty acids, while non-oleaginous *S. cerevisiae* has been engineered to also accumulate significant fatty acid percentages (Ledesma-Amaro, 2015). These microorganisms deliver higher lipid accumulation coupled with faster culture expansion when compared to oleaginous fungi and microalgae (Thevenieau & Nicaud, 2013). (Silva et al., 2023).

It is worth mention that some aerobic Gram-positive bacteria, cyanobacteria and other Eubacteria can synthesize alkanes suitable for bio-jet fuel (Jiménez-Díaz et al., 2017) being these hydrocarbons promising replacements for fossil fuels, fitting into the current infrastructure with high energy density, which is ideal for aviation (Lehtinen et al., 2018). Furthermore, targeting the microbial production of isoprenoid-derived hydrocarbons like monoterpenes (C10) or sesquiterpenes (C15) as bio-jet fuel precursors is also possible through metabolic engineering (Walls & Rios-Solis, 2020). These structures have a carbon distribution and number similar to conventional jet fuel.

Notwithstanding, even if the production of lipids or hydrocarbons has constraints for direct use for bio-jet fuel due the extent of unsaturation, hydrogenation can be carried out to improve biofuel quality (Jiménez-Díaz et al., 2017).

The oleaginicity of these microorganism stems from ATP-citrate lyase utilization for citrate into acetyl-CoA conversion, essential for fatty acid production (Sabikhi Latha and Kumar M.H., 2012). Moreover, following nitrogen depletion, excess carbon substrate is assimilated and stored as lipids. Phosphorus, magnesium, zinc, and iron deprivation can also lead to lipid accumulation although less efficiently (Bautista L. F. et al., 2012).

Microbial oils often contain a greater abundance of lipids than triglycerides and free fatty acids, with a fatty acid profile resembling that of plant and animal oils, primarily consisting of C16 and C18 fatty acids, often with high unsaturation levels. Triglycerides rich in polyunsaturated fatty acids (PUFA) can also represent the predominant components of microbial oils.

Table 1, adapted from (Thevenieau & Nicaud, 2013) and (Jenkins, 2015) , summarizes information regarding lipid and specific fatty acid content for different oleaginous microorganisms comparing with sunflower and palm oils.

Table 1. Lipid and specific fatty acid content for different oleaginous microorganisms comparing with sunflower and palm oils (adapted from (Thevenieau & Nicaud, 2013) and (Jenkins, 2015).

Oil source	Lipid content (% w/w)	Fatty acid (% w/w)														
		C4-C10	C12:0	C14:0	C16:0	C16:1	C16:2	C16:3	C18:0	C18:1	C18:2	C18:3	C20:1	C22:6	C23:0	C24:0
Sunflower	45				7				5	19	18	1				
Palm	50	1	1	1	44				4	38	10	1				
Yeast:																
Cryptococcus albidus	60				12	1			3	73	12					
Lipomyces starkeyi	63				34	6			5	51	3					
Rhodosporidium toruloides	66				18	3			3	66					3	6
Rhodotorula glutinis	72				37	1			3	47	8					
Yarrowia lipolytica	36				11	6			1	28	51					
Rhizopus arrhizus	57				18				6	22	10	12				
Fungi																
Mortierella isabelline	50				29				3	55	3	3 (n-6)				
Mucor circinelloides	25				22				5	38	10	15 (n-6)				
Pythium ultimum	48	7			15				2	20	16	1	4			
Bacteria																
Rhodococcus opacus	19-26								3-19	6-74						
Pseudomonas aeruginosa	38*				18	1			3	34	5					
Microalgae																
Chlorella zofingiensis	28-32				23	7	2		2	36	18	8				
Crypthecodinium cohnii	23		3	13	23				3	8				50		
Chatoceros muelleri	31-68		6-20	18-40	5-40		0-8		0-25	0-4	0-5	0-5				

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Downstream processing

Concerning downstream processing, after fermentation, thermal treatment for enzyme inactivation, centrifugation, cell disruption and lipid extraction can constitute a common pathway to retrieve microbial oils.

Regarding cell disruption, mechanical methods like bead milling are efficient but may be less effective for bacteria, while high-pressure homogenization offers scalability but may struggle with filamentous fungi. From the different non-mechanical methods, microwaves, osmotic shock and application of electric pulsed electric field are approaches to consider. However, some of the aforementioned methods lead to temperature increase during processing which can affect lipid quality, leading to the need for gentle processing and mild temperatures employment in order to tackle concerns related with rancidity and lipid oxidation. Notwithstanding, combined pretreatments methods show promise in maximizing extraction efficiency while maintaining product quality.

Traditional methods like Soxhlet or Bligh and Dyer are commonly used for lipid extraction after cell disruption, but these have drawbacks such as high temperatures or the use of toxic solvents, respectively. Alternative approaches using supercritical or subcritical fluids like carbon dioxide offer safer and more efficient extraction without the risk of contamination or thermal degradation (Silva et al., 2023) (Ochsenreither et al., 2016)

3 Bio-crude upgrading

Bio-oil obtained from HTL has limitations in directly replacing crude oil as a precursor to liquid fuels. As a raw material for fuel production, bio-oil is a highly viscous and unstable substance composed of a complex mixture of hundreds of oxygenated compounds and organic acids that can be responsible for corrosion phenomena in mechanical components. Some of the organic compounds present in HTL-derived bio-oil, for example aldehydes, high molecular weight oligomers, acetic acid, glycols, phenols or levoglucosan, nevertheless have a significant economic value and some commercial value (He et al., 2018).Table 2 presents a comparison between the properties of crude oil and some bio-oils obtained by HTL from microalgae (350ºC, 60 min, 10% Biomass).

Table 2. Comparison between typical composition and energy content of crude oil and some microalgae bio-oils(Shuping et al., 2010);(Chaiwong et al., 2013) (Raikova S. et al., 2016).

Proprieties	**Light fuel oil**	**Heavy fuel oil**	**Bio-oil from Spirulina sp.**	**Bio-oil from Chlorella sp.**	**Bio-oil from Nannochloropsis sp.**
HHV (MJ/Kg)	47.0	42.5	36.8	35.1	34.5
C (%w/w)	84.0	85.0	73.3	70.7	68.1
H (%w/w)	14.0	11.0	9.2	6.8	8.8
N (%w/w)	1.0	0.3	7.0	5.9	19.0
O (%w/w)	1.0	1.0	10.4	14.8	4.1
Ashes (%w/w)	0.1	0.1	-	-	-

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Considering the typical composition of the bio-oils presented in Table 2, it's clear that an upgrading step in the process is needed to obtain a bio-oil with properties closer to crude oil. After this step, the final bio-oil can then be converted into biofuels through conventional refining processes. Thus, upgrading processes are considered post-treatments to the HTL process that improve the quality and compatibility of crude bio-oil and enable its refining into commercial biofuels.

The focal objective of the upgrading is to convert the oxygen rich, and high atomic weight lignin into hydrocarbons that can be an alternative for today's petroleum derived fuels. Numerous substances, for example, aromatics, olefins, and pitches, can be separated from the pyrolysis bio-oil for useful modern application.

Thermochemical treatments use heat, pressure, hydrogen and catalysts to change the composition and characteristics of the bio-oil. These processes are widely used in crude oil refining and have received great attention, both in industry and academia. However, differences in relation to petroleum limit the direct application of these techniques to improve the characteristics of crude bio-oil. Furthermore, the process is very temperature and pressure intensive which means that many specific applications are not yet cost *competitive (Panwar & Paul, 2021).*

The hydro catalytic treatment processes available for the bio-oil upgrading are hydrodeoxygeneation (HDO), hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM), and hydrogenation (HYD)(Gollakota et al., 2016).

The most well-established bio-oil upgrading technique currently is catalytic HDO. This catalytic process involves the removal of heteroatoms at high temperatures and pressures and is considered a very promising route for the widespread production of high-quality biofuels. To date, research in this area has focused on varying reaction conditions and the development of different types of catalysts (Zhang et al., 2021) Even so, although catalytic HDO has already demonstrated good results in bio-oil upgrading, some obstacles to its application still need to be overcome, particularly in terms of hydrogen consumption and the short lifetime of the catalysts used.

3.1.1 Bio-crude pretreatment

Understanding and improving biocrude pretreatments is crucial for the optimization of biofuel quality. Biocrude, predominantly produced through hydrothermal liquefaction (HTL), offers significant promise as a renewable energy source. Effective pretreatment strategies focus on removing contaminants such as particulate matter/solids, nitrogen, and sulphur compounds present in biocrude pose challenges to its direct utilization by impacting the efficiency and stability of subsequent upgrading processes. Therefore, continuous innovation in pretreatment methods is fundamental to enhance biocrude quality, making it a viable alternative to conventional fossil fuels.

HTL process typically converts more than 50% of the biomass (ash-free dry weight) to organic fraction crude bio-oil and approximately 70% of the carbon to crude bio-oil. HTL crude bio-oils in nature are usually semi-liquid, viscous, dark coloured, and have a smoky smell. Usually, the components present in the crude bio-oil are acids, alcohols, aldehydes, esters, ketones, phenols, and guaiacol, besides a few hydrocarbon and nitrogen containing species. Also, the viscosity of crude bio-oils can be up to 4 orders of magnitude higher than that of diesel and biodiesel. Moreover, heating values are also slightly lower than those of conventional fuels and biodiesel.

These properties make direct application of HTL crude bio-oils as conventional transportation fuels difficult, apart from marine applications. The crude bio-oil generated from HTL is known to be unstable at room temperature and can also contain significant weight percent of nitrogen and oxygen, besides some amount of sulphur. The quality of crude bio-oil produced is primarily dependent on the feedstock being processed and hence feedstocks that are hydrocarbon rich in nature, such as oily/refinery sludge and plastic waste, typically produce crude bio-oil which is low in ash content and has very low heteroatom content and negligible inherent moisture content. This, in turn, makes the oil easily upgradeable.

On the other hand, crude bio-oil produced from feedstock such as algae, municipal solid waste (MSW) or food waste tends to have a relatively higher ash and inherent moisture content as well as higher heteroatom content. Even though HTL is a feed-flexible technology and can process various feedstock, the crude bio oil obtained from these varies with their properties and chemical composition (Xu et al., 2017)

Removal of particulate matter/solids

Solid particle removal from bio-oils (produced through HTL) is a critical step in ensuring the quality and functionality of the resulting biofuels. HTL transforms a wide range of biomasses into crude bio-oil which is comparable to fossil crude oil, but the presence of solid particles can hinder subsequent upgrading processes as stated before. Several processes approach this problem by applying one of the unit operations below.

- A commonly employed approach for solid particle removal from HTL bio-oils involves centrifugation-first strategy. This method focuses on separating solid products, such as coke, from bio-oil. Following centrifugation, further filtration processes can be implemented to ensure the removal of finer solid particles. The effectiveness of this approach lies in its simplicity and adaptability, allowing for scalable application in HTL bio-oil production processes. (Mujahid et al., 2020a)
- Microfiltration represents another viable technique for the removal of char particles from bio-oils. The challenge, however, is the lack of well-established technology to efficiently remove particles smaller than 10 µm. Despite this, ongoing research aims to develop liquid-phase applications that can effectively filter out these fine particulates, ensuring a purer bio-oil suited for upgrading or direct use. (Javaid et al., 2010) (Douglas C. Elliott, 2016).
- A two-step separation process specifically tailored for HTL bio-oil involves initial separation techniques followed by more refined methods to isolate the bio-oil from condensed products from the HTL process. This method is particularly useful when dealing with bio-oils derived from complex feedstocks such as microalgae, where the distinct characteristics of the input biomass can significantly influence the nature of the solid particles present. An example of this is the separation of light and heavy fractions of the bio-oil; the light part could be separated mechanically, and the heavy part is formed by solvent extraction and subsequent evaporation (Grigorenko et al., 2018)
- The utilization of biomass filter aids has been researched for its potential in enhancing the efficiency of solids removal from bio-oil. This approach involves using biomass-derived materials as filter aids to facilitate the efficient extraction of residual solids; filter aids can also be used to pre concentrate biomass prior to HTL and then be processed in the HTL step as well. The spent biomass filter aids, enriched with the extracted solids can then be processed, or discarded, depending on the specific requirements of the operation (Ronny W. Lin, 2015) (Biller et al., 2018)(Johannsen et al., 2019).
- Ceramic ultrafiltration membranes, operated in crossflow mode, present an advanced option for the separation of particles and oil-in-water mixtures resulting from the HTL process. The application of such membrane technologies allows for a cleaner separation of biocrudes and water by-products, contributing to an enhanced purity of the bio-oil and reduced water content, which is crucial for the stability (reduced water activity) and quality of the final product (Sayegh et al., 2022).

Table 3 consolidates some advantages and disadvantages found for each approach to the problem of solid particle removal from HTL crude bio-oils.

Table 3: Summary of approaches to solid matter removal from HTL crude bio-oils.

Process	Advantages	Disadvantages	Source
Centrifugation & Filtration	- Capable of recovering high yields of bio-oil - Simple and scalable	- May not effectively remove the finest particles	(Mujahid et al., 2020b)
Microfiltration	- Can target specific sizes of particles for removal - Beneficial for improving bio-oil purity	- Lack of established technologies for particles <10µm - Potential for high operational costs	(Elliot et al., 2016; Javaid et al., 2010),
Two-step separations	- Enhances bio-oil purity by employing sequential refinement - Effective for complex feedstock bio-oils (microalgae)	- Potentially resource-intensive due to multiple processes	(Grigorenko et al., 2018)
Biomass filter aids	- Utilizes biomass-derived materials, enhancing sustainability - Efficient in aiding the filtration process	- Requirement for subsequent disposal or processing of spent filter aids	(Biller et al., 2018; Johannsen et al., 2019; Lin, 2015)
Advanced membranes technologies	- High effectiveness in particle and oil separation - Reduced fouling compared to other membranes	- Costs associated with ceramic membranes can be high - Potential for ceramic membrane fouling in long-term operations	(Sayegh et al., 2022)

Nitrogen removal

Removing nitrogen from crude bio-oils produced via Hydrothermal Liquefaction (HTL) is a critical step in ensuring the quality and utility of the resulting bio-oil. Nitrogen in HTL bio-oils can significantly impact their use as a sustainable energy source, reducing the energy content and increase in emissions of nitrogen-containing compounds.

HTL generally produces bio-oil with a high energy content and recovery rate. However, the presence of nitrogen can affect the higher heating value (HHV) of bio-oil, potentially lowering its energy efficiency and making it less suitable as a renewable fuel source. During the HTL process, particularly when using feedstocks with high nitrogen content, such as microalgae, macroalgae, sludge, manure, and food waste, significant amounts (20-40%) of the nitrogen from the raw biomass can be retained in the bio-oil. This includes the presence of aromatic nitrogenated compounds, which are typically harder to remove and may pose challenges in downstream processing and utilization; during utilization of the biofuel, the emissions of NOx compounds is correlated with the presence of nitrogen in the substrate or the depth to which it was denitrogenated (Leng et al., 2020).

This text delves into an assortment of methods devised for nitrogen removal from HTL crude bio-oils, namely hydrotreating (hydrodenitrogenation), liquid-liquid phase partitioning, solvent deasphalting, adsorptive denitrogenation, chemical conversion followed by separation, and to a less extent, microbial conversion.

Hydrodenitrogenation

Hydrodenitrogenation (HDN) is an industrially significant process used for the removal of nitrogen from oils. It is considered the most applied method for nitrogen removal from oil in industrial settings. In HDN, nitrogen-containing compounds present in crude oils are subjected to a catalytic process that involves the breaking of nitrogen-carbon bonds under high temperature and pressure conditions. This process is vital in refining crude oils as nitrogen compounds can have detrimental effects on product quality and industrial processes if not removed effectively.

Unlike some other hydroprocessing reactions like hydrodesulfurization or hydrodeoxygenation, hydrodenitrogenation is not a selective process solely targeting nitrogen removal. During HDN, not only nitrogen removal occurs, but parallel reactions such as hydrodemetalation, hydrodesulfurization, hydrodeoxygenation, hydrodearomatization, and olefin saturation also take place simultaneously. Nitrogen is particularly challenging to remove compared to sulfur and oxygen in oils due to the nature of nitrogen bonds in compounds like pyridines, which require breaking both double and single bonds for effective denitrogenation. This complexity makes hydrodenitrogenation a crucial step in oil refining processes.

In the realm of hydrotreating processes, hydrodenitrogenation plays a central role as the "base case" technology against which other nitrogen removal methods are evaluated. Any alternative method for nitrogen removal must demonstrate clear advantages over HDN to be considered for industrial application. With approximately 30 different hydrotreating processes available for licensing, the importance of hydrodenitrogenation in the oil refining industry is evident, highlighting its key role in ensuring the quality and efficiency of refined oil products.

The types of catalysts commonly used in hydrodenitrogenation include tungsten and molybdenum sulfides supported on alumina, often modified with cobalt or nickel as hydrogenation promoters. These catalysts play a crucial role in facilitating the removal of nitrogen from oils during the refining process. The ranges of conditions for hydrodenitrogenation can vary depending on the feed material and the extent of hydrotreating required. Typically, the start-of-run inlet temperature ranges from 250 to 350 °C, pressure from 1.5 to 15 MPa, space velocity from 0.7 to 12 h^{-1}, and hydrogen-to-liquid feed ratio from 250 to 6000 normal $m^3 \cdot m^{-3}$. However, for high-nitrogen-content oils like coal-derived oils, more severe conditions may be necessary for effective nitrogen removal (Prado G. et al., 2017) (Zhao et al., 2017).

Table 4 gives a brief compilation of example of the sets of conditions and classes of catalyst employed in the denitrogenation operations.

Table 4: Examples of catalyst/conditions employed in Hydrodenitrogenation of fossil oils and bio-oils

Substrate	Conditions	Catalysts	N_2 evolution	ref
Gas oil from bitumen	9.4MPa/400ºC	NiMo/Al2O3 + 2.7 wt % B	97% N converted	(Ferdous et al., 2006)
Liaohe Chinese coker gas oil	6MPa/420ºC	NiW/CYCTS	80% N removed	(Wei et al., 2015)
straight-run gas oil	5MPa/330ºC	CoMo/Al2O3	92% N removed	(Pinheiro et al., 2009)
HTL Biocrude Algae/sludge (10-15% O&N)	310-400ºC 8MPa (H2 init.) t=4h	-	(1st stage) 2-4% N (2nd stage) 0-0.6%	(Haider et al., 2020)
Algae biocrude (Nanno. O.) 3.6%N	(2 stages) 300-400ºC	cNiMo/γ-Al2O3	1.95% N final	(Zhao et al., 2016)
Algae biocrude (Nanno) Initial = 3.73% N	(2 stages 350ºC, 6MPa	NiMo/γAl2O3 (+ RG-20B as guard)	First 1.27% N Sec 0.016%	(Zhao et al., 2017)
Algal biocrude 5.52% N	120-170 ºC and 405 ºC) 13.6 MPa of H_2	KF-1001, 4% Co, 15% Mo (MoS_2)	3.88% N	(Elliott et al., 2013)

Adsorptive denitrogenation

Adsorptive denitrogenation is a process that involves a solid material, known as an adsorbent, to remove nitrogen-containing compounds from oil. The adsorbent selectively attracts and retains nitrogen compounds through chemical or physical interactions on its surface as the oil passes over it. Chemical interactions involve the formation of chemical bonds between the adsorbent and the compounds, while physical interactions rely on forces like van der Waals or electrostatic forces to retain the compounds. The strength of retention and selectivity in adsorptive denitrogenation depends on the type of interaction between the adsorbent and nitrogen compounds, impacting the effectiveness of nitrogen removal.

Various types of adsorbents are used for denitrogenation, including silica gel, activated alumina, activated carbon, metal-organic frameworks, ion-exchange resins, zeolites, and polymers. These adsorbents exhibit different capacities for nitrogen removal and selectivity based on their surface properties and chemical composition. Adsorption processes for denitrogenation typically involve two vessels containing adsorbents operating in parallel to enable continuous operation. During the adsorption mode, nitrogen-containing compounds are removed from the oil by adsorption onto the adsorbent, leading to a lower nitrogen content in the oil at the outlet. The regeneration mode involves desorbing the nitrogen compounds from the adsorbent for reuse, often achieved through temperature increase or chemical reactions based on the nature of adsorption.

Typical conditions in adsorptive denitrogenation can vary based on the specific system and adsorbent used. Temperature can range from ambient temperature to around 50-80°C, depending on the adsorbent and oil feedstock. This process is usually operated at atmospheric pressure. The contact time varies based on the efficiency of nitrogen removal and the capacity of the adsorbent. A brief compilation with the adsorbents with higher nitrogen removal efficiencies is given in Table 5 (Prado G. et al, 2017)

Table 5: Adsorbents used and typical conditions for adsorption removal of nitrogen.

Type of adsorbent	Adsorbent	conditions	N conversion/removal	ref
Silica gel	Silica gel	Room temp	Up to 99.6% N removed	(Feng, 2004; Mushrush et al., 2011; H. Yang et al., 2004)
Activated carbons (MAXSORB-II/MGC-B/OG-20A)	MAXSORB-II MGC-B OG-20A	0.14MPa, 30ºC	41 to 77% N removed	(Sano et al., 2004)
MOFS	Mil-101(Cr)	403K for12h remaining time 298K	90% N removed	(Laredo et al., 2016)

Chemical conversion and separation.

Chemical conversion followed by separation in the context of nitrogen removal from oils includes transforming nitrogen-containing compounds into different chemical forms through reactions such as oxidation, N-alkylation, complexation with metal salts, and conversion in high-temperature water. These chemical conversion processes modify the nitrogen compounds to facilitate their separation from the oil. After the chemical conversion step, separation techniques are employed to remove the modified nitrogen compounds from the oil, resulting in a denitrogenated oil product. By altering the chemical structure of nitrogen-containing compounds, followed by effective separation, this approach aims to reduce the nitrogen content in oils and improve their quality and properties. (Prado G. et al, 2017)

The typical conditions, catalysts/additives, and solvent systems used in chemical conversion followed by separation for nitrogen removal from oils can vary based on the specific process and desired outcomes. Typically, temperature ranges from ambient temperature to elevated temperatures depending on the specific chemical reactions involved. The process can be operated at atmospheric pressure or slightly above to maintain the desired reaction conditions. Catalysts may include molybdenum and tungsten-based catalysts supported on alumina or other metal oxides, and additives like metallic ions or complexing agents can be used to enhance the removal of nitrogen compounds.

For the separation step, organic solvents, acidic solvents, and ionic liquids are commonly used for chemical conversion and separation processes. Deep eutectic solvents have also been explored as an alternative to ionic liquids for their denitrogenation capabilities.

These components work together to facilitate the transformation of nitrogen-containing compounds in oils through chemical reactions and subsequent separation to achieve effective denitrogenation. (Prado G. et al, 2017)

A summary of the nitrogen conversion/removal percentages achieved by different type of chemical conversion followed by separation denitrogenation (only the best results are presented in each category) is presented in Table *6*:

Table 6: Types of operations under chemical conversion followed by separation approaches to denitrogenation.

Approach	Conditions/agent	N removal	ref
Oxidation	(*t*-ButOOH as oxidant+16%MoO_3/Al_2O_3, separation process was adsorption by silica gel,60ºC, 30min).	up to **94.1% N removed**	(Ishihara et al., 2005)
Oxidative photoirradiation	(30% H_2O_2 as polar solv., 50ºC,36h).	up to **93% denitrogenation yield**	(Shiraishi et al., 2000)
n-alkylation	(alkylating agent CH3/AgBF4 , 30ºC, 11h, N_2 atmosphere).	up to **96% N conversion/removal**	(Shiraishi et al., 2001)
Metal complexation	**(**metal salt=20% $FeCl_3$, rt, 20 min.	up to **98.9% N conversion/removal**	(Feng, 2004)
Supercritical water	(400ºC, 30min, 20% vol)	up to 62.5% N removed	(He & Li, 2009)

Biological conversion

Microbial conversion, in the context of nitrogen removal or denitrogenation of oils, involves the use of different strains of microorganisms to degrade nitrogen-containing compounds present in the oil. These microorganisms, through their metabolic activities, can enzymatically transform nitrogen compounds into simpler forms or completely mineralize them into harmless substances. The denitrogenation pathways may vary for each compound and microbial strain, but a common mechanism involves aerobic degradation where oxygenase inserts oxygen into the substrate to produce hydroxylated intermediates, followed by ring cleavage. Compounds like quinoline, indole, and pyrrole are known to be readily degraded by microbial activity, while more complex compounds like carbazole may pose greater challenges due to their chemical structure.

One of the key advantages of microbial conversion for denitrogenation is its environmentally friendly nature, as it relies on natural biological processes to remove nitrogen compounds from oils. However,

a drawback of this method is that it can lead to the degradation of the carbon skeleton of the oil molecules, potentially reducing the energetic value of the fuel. Researchers are exploring genetic modifications of microorganisms to develop strains that can selectively target and remove nitrogen without significantly affecting the carbon structure, aiming to enhance the efficiency and applicability of microbial conversion for denitrogenation of oils. (Prado G. et al., 2017; Vazquez-Duhalt et al., 2002).
In the biological conversion of oils for nitrogen removal, different strains of microorganisms are utilized. Some typical conditions and strains used include:

- _Comamonas sp. TKV3-2-1_: Used for the degradation of quinoline in light crude oil. (Sugaya et al., 2001)
- _Rhodococcus erythropolis ATCC 4277_: biodenitrogenation of heavy gas oil nitrogen conversion removal of up to 43.2%. (Maass et al., 2015)
- _HY9 strain_: Applied for nitrogen removal from diesel oil, with increased efficiency observed when used in conjunction with the surfactant Tween80 of up to 19.3% N conversion/removal (Tang & Hong, 2014).

These strains demonstrate varying capabilities in denitrogenation, with some showing high conversion rates of nitrogen compounds in oils, highlighting the potential of microbial conversion as an environmentally friendly approach for nitrogen removal (Benedik et al., 1998).

Liquid-liquid phase partitioning

In the context of nitrogen removal, liquid-liquid phase partitioning involves the separation of nitrogen-containing compounds between the oil phase and a second immiscible liquid phase. This process relies on the differences in solubility parameters between the oil, nitrogen compounds, and the second liquid phase used for extraction. Liquid-liquid extraction processes are based on the principle of "like dissolves like," where the solubility parameter of the extracting liquid compared to the oil must favor the dissolution of nitrogen compounds. By exploiting these solubility differences, nitrogen-containing compounds can be selectively extracted into the second liquid phase, facilitating their removal from the oil.
The choice of solvent is crucial in liquid-liquid extraction, considering factors such as the nature of nitrogen compounds to be extracted, recoverability of the solvent, and purpose of nitrogen removal.
A general liquid-liquid phase partitioning denitrogenation would contain the following steps:

- Mixing the two liquid phases to facilitate extraction
- Phase separation of the two liquid phases
- Recovery and recycling of the solvent used for extraction
- Manipulating operating parameters like mixing intensity, time, and temperature to enhance mass transport.

The typical conditions for temperature are up to around 80°C, depending on the solubility of nitrogen compounds in the solvent. Pressure can vary from atmospheric pressure to moderate pressures to maintain the liquid phases in the desired state. Solvent-to-oil ratio is often adjusted to optimize the extraction efficiency and selectivity for nitrogen compounds.
The typical second liquid or solvent used in liquid-liquid phase partitioning for nitrogen removal includes organic solvents (methanol, acetic acid, or mixed solvents like methanol/water), which can selectively extract nitrogen compounds based on polarity and chemical interactions; acidic solvents, used to remove basic nitrogen compounds through acid-base reactions prior to extraction, and Ionic liquid, A newer class of solvents that have been explored for their denitrogenation capabilities due to their unique chemical properties.
These solvents are chosen based on their ability to selectively extract nitrogen-containing compounds from crude oil while considering factors like recoverability, selectivity, and overall process efficiency. (Prado G. et al, 2017)

Solvent deasphalting

Solvent deasphalting is a common process in oil refining that operates based on the principle of liquid-solid phase partitioning. In this process, a light paraffinic solvent is mixed with the oil to induce a change in solubility parameters and characteristics, leading to the formation of a separate solid phase known as the asphaltenes fraction. The choice of solvent and method used to trigger liquid-solid phase partitioning influences the yield and composition of the asphaltenes fraction separated from the oil. Solvent deasphalting is effective in removing heavier components like asphaltenes, which tend to contain higher concentrations of heteroatoms, such as nitrogen, compared to the bulk oil phase.

Typical conditions for solvent deasphalting are temperature ranges from around 60 to 200°C, depending on the specific solvent and oil feedstock and moderate pressures. Solvent-to-oil ratio is adjusted to optimize the efficiency of separating the asphaltenes fraction from the oil and light paraffinic solvents are commonly used due to their ability to induce liquid-solid phase partitioning effectively. Solvent deasphalting is a crucial process in refining heavy oil fractions, allowing for the removal of undesirable components like asphaltenes and heteroatoms, including nitrogen, to improve the quality and properties of refined oil products. (Prado G. et al., 2017)

Comparison of several routes available for Denitrogenation

Table 7 summarizes the advantages and disadvantages of different methods of removing nitrogen.

Table 7: Comparison of the main methods for nitrogen removal along with technology development state

Method	Advantages	Disadvantages	Technology readiness
Hydrotreating	- Industrially proven method for nitrogen removal - Effective in removing nitrogen as ammonia	- Not a selective nitrogen removal process - Other hydroprocessing reactions occur simultaneously	industrially proven and widely used
Liquid-Liquid Phase Partitioning	- Selective extraction of nitrogen-containing compounds based on solubility parameters - Potential for efficient separation of nitrogen compounds	- Limited by solubility parameters and selectivity of extracting liquid - Process complexity and solvent recovery challenges	requires further optimization for industrial application
Solvent Deasphalting	- Effective in removing heavier components like asphaltenes containing nitrogen - Can improve oil quality by reducing nitrogen content	- Not capable of deep nitrogen removal from oil - Process may not eliminate all nitrogen-containing compounds	requires further optimization for industrial application
Adsorption	- Selective adsorption of nitrogen-containing compounds based on interactions with adsorbent - Potential for high selectivity and capacity	- Regeneration of adsorbent for reuse can be challenging - Adsorbent capacity and selectivity may vary based on the type of adsorbent	requires further optimization for industrial application
Chemical Conversion and separation (2 step)	- Transformation of nitrogen compounds to facilitate separation - Potential for modifying chemical structure of nitrogen compounds	- Process complexity and optimization required for effective conversion and separation - May require specific catalysts and conditions	requires further optimization for industrial application

Microbial Conversion	- Potential for biological removal of nitrogen compounds from oils - Environmentally friendly approach	- Limited application and research compared to other methods - Effectiveness may vary based on microbial strains used	low

Without doubt, hydrodenitrogenation (hydrotreatment) is the most mature and established technology today, for nitrogen removal/reduction from oils and HTL crude bio-oils. Advancing nitrogen removal methods from HTL crude bio-oils is paramount for uplifting the bio-oil quality to meet fuel standards. Other diverse strategies ranging from adsorptive denitrogenation, to innovative approaches like using activated carbon-pretreated solvents and ST-HTL, exhibit potential in addressing the nitrogen content dilemma. The evolving landscape of HTL technology and nitrogen removal processes underscores the importance of interdisciplinary research in achieving sustainable bio-oil production.

3.1.2 Catalytic cracking

Deoxygenation of bio-oil is normally accomplished through catalytic cracking and hydroprocessing routes such as hydrotreatment, hydrodeoxygenation, and hydrocracking. Catalytic cracking is the process of thermal breakdown of larger complex compounds into simpler ones at high temperature (350–600 ◦C) and atmospheric pressure in the presence of catalysts. The process is accompanied by deoxygenation via gases production, such as CO, CO_2 and lighter hydrocarbons. Hydroprocessing involves the use of high hydrogen pressure and temperature (350-500 ◦C) which converts heavier oxygenated bio-oil into oxygen-free simpler compounds in presence of catalysts (Ni, NiMo, Pt, Ru supported on Al_2O_3, SiO_2, ZrO_2, etc.). The use of hydrogen improves product yield and quality removing the O, N as well as S, if present in bio-oil, in the form of H_2O, NH_3 and H_2S respectively (Saber et al., 2016). Several reactions involving hydrogenation, hydrocracking, hydrodeoxygenation occur during the process. In hydrotreatment, breaking of C–O, C–N, C–S bonds are the main reactions while in hydrocracking mainly occurs the breakage of C–C bond (Saber et al., 2016).

Upgrading methods such as hydrotreatment, hydrocracking, catalytic cracking, etc. are more efficient because their products have similar properties of petroleum fuels. However, the main disadvantages of these methods are high operating cost due to the use of expensive catalyst, coke formation causing fast catalyst deactivation, costly reactors and high-pressure requirement which limits their commercial application.

3.1.3 Hydrodeoxygenation (HDO)

Upgrading biomass-derived oils to hydrocarbon fuels requires oxygen removal and molecular weight reduction. As a result, there is typically a formation of an oil phase product and a separate aqueous phase product by hydroprocessing. To minimize hydrogen consumption in hydroprocessing, hydrodeoxygenation (HDO) must be emphasized, without saturation of the aromatic rings.

Hydrodeoxygenation (HDO) is a modified method of catalytic cracking which is used to remove oxygen under the influence of a catalyst and high pressure of hydrogen. This process can decrease oxygen content by converting it into CO_2 and H_2O from different types of oxygenated groups such as aldehydes, acids, phenols, esters, and ketones. HDO uses catalysts typically used for hydrodesulfurization (HDS), such as nickel-molybdenum supported on aluminum oxide (NiMo/Al2O3) or cobalt-molybdenum supported on aluminum oxide (CoMo/Al2O3), and hydrogen at moderate temperatures (300–600°C) to remove oxygen from bio-oil (Sorunmu et al., 2020).

3.1.3.1 Operation conditions

HDO (also called hydrotreatment) generally involves the conversion of carbonyl and carboxyl functional groups into alcohols at moderate conditions (100 − 300◦C), accompanied by subsequent reactions at higher temperatures (350 − 400◦C). The process includes the combination of different reactions of hydrogenation, hydrogenolysis, decarboxylation, decarbonylation and dehydration, depending on the specific process conditions(Zacher et al., 2014). The most important operational parameters in relation to the yield and properties of the bio-oil resulting from the process include temperature, hydrogen pressure, residence time and the use of solvents. Table 8 shows the typical range of values and the main effects that the variation of these parameters has on the bio-oil after upgrading.

Table 8. Typical values and main effects associated with main HDO operating conditions (adapted from(Dabros et al., 2018) (Panwar & Paul, 2021)

Parameter	Range of values	Efects
Temperature	250ºC and 400ºC (higher efficiency between 300 and 350ºC)	Temperatures above 450ºC are not favorable for upgrading due to the exothermic nature of the HDO process and the increased formation of coke deposits and consequently catalysts deactivation.
H_2 Pressure	10-30MPa	High pressures ensure good solubility of H_2 in the reaction medium and promote the stabilization of unstable precursors derived from bio-oil (i.e., high molecular weight intermediate compounds). These conditions reduce the formation of solid deposits and increase the lifetime of the catalysts; some studies have demonstrated that lower H_2 pressures can achieve good deoxygenation efficiencies with catalysts
Solvent	Use of H_2 donor solvents such as methanol, ethanol, propan-2-ol, tetralin and formic acid.	The use of solvents influences the heterogeneous catalysts activity in HDO through competition for active centres. The possible formation of oxides on the surface of the catalysts and of intermediate compounds specific to each solvent can interfere with the activation energy of the process. The promotion of parallel hydrolysis and esterification reactions is also a problem.
Residence time	Residence times between 0.5 – 8 h (defined as the contact time between the raw material and the catalyst).	High feeding rates and hourly mass space velocity. Short residence times result in low HDO efficiencies.

In addition to these parameters, HDO also requires the use of stable and versatile catalysts, typically of a heterogeneous nature (e.g., metals, acidic and bifunctional catalysts). Catalytic HDO is a well-known process in the petroleum industry, where it is used to remove the oxygen content present in crude oil (generally < 1%). However, as the oxygen content in bio-oil is much higher, the needs of the process are also different.

3.1.3.2 Catalysts for HDO

Several studies have been carried out on the technical and economic feasibility of the process, focussing on the development of more efficient, robust and lower price catalysts. Catalysts such as Pd, Pt, Ru, PtCo, PtNi, NiMoCx, Mo_2C, CoMo, Mo_2N, HZSM-5, modernite zeolite, Y-zeolite, etc. are emerging as most effective catalysts for deoxygenation and cracking processes (Gupta et al., 2021). Solid acid catalyst is another group of catalysts reported to be used in HDO. Simple oxides (Al_2O_3, SiO_2, ZrO_2), mixed oxides (SiO_2-Al_2O_3, ZrO_2-Al_2O_3, ZrO_2-SiO_2, MgO-Al_2O_3), zeolites (HZSM-5, HY, HB, mordernite), activated carbons and carbon supported materials (mesoporous carbon, activated carbon, carbon nanotubes) are the most common solid acid catalysts utilized in hydrodeoxygenation of bio-oil. Presence of Lewis and Bronsted acidic sites acts as an active catalytic site for deoxygenation of oxygen-containing compounds present in bio-oil. Degree of deoxygenation depends on the availability as well as the strength of the acidic sites. In addition, extensive research has been performed in the development of bi-functional and multifunctional catalysts. These catalysts include both acidic as well as metallic functionality with high activity for HDO reactions. Biochar (byproduct of pyrolysis process) based catalysts produced after certain physical and chemical modifications, also exhibit high activity in bio-oil deoxygenation and are of great interest in order to make the whole process more economic and integrated (Gupta et al., 2021).

However, sulphide CoMo/Al_2O_3, NiMo/Al_2O_3 systems are the most frequently used catalyst for hydrotreating of bio-oils. Oxygen is removed as water, sulphur is removed as H_2S and nitrogen is removed as NH_3 (Zhang et al., 2021).

The other reactions involved are hydrogenation, hydrogenolysis, decarboxylation, decarbonylation, dehydration and polymerization (Zhang et al., 2021). The Hydrodeoxygenation reaction reduces the oxygen content, while simultaneously increasing the hydrogen content of the bio-oil. HDO occurs at temperatures above 350 °C. Hydrogenation is usually involved in hydrotreatment because of the non-destructive and simple hydrogenation nature of the method, which means that increases the product yield without changing the boiling range. The most challenging is not the oxygen but the nitrogen removal, that is the most difficult to be removed. So, more research, specially focused, on more efficient catalyst in N2 removal is being conducted. Furthermore, the pre-removal of N2 before the HTL process is being considered.

The specific reaction mechanism depends on the type of catalyst used (including the particle size of the active phase, promoters and supports), the operating conditions and the presence of inhibitors. Still, (Dabros et al., 2018) recently detailed the mechanisms involved in the process when the objective is to produce biofuels, an understanding that has proven necessary for the development of HDO on an industrial scale. In the case of conventional HDO, for example, the kinetics have been studied through the application of “lumped” models, which has helped its evolution (Dabros et al., 2018). In general, catalysts used in HDO can be classified into five categories: sulfides, oxides, noble metals, phosphides, and others (carbides and nitrides) (Zhang et al., 2021). Table 9 presents an overview of the main catalytic materials used.

Table 9. Comparison between catalysts used in HDO (Mayorga et al., 2020).(Zhang et al., 2021)

Parameter	Active Phase		
	Monometallic and bimetallic sulfides	Metal carbides, nitrides and phosphides	Reduced metals such as Pd, Co, Ni, Pt, W, Fe, and other noble metals
Cost	low	intermediate	high
Selectivity	HDO	HDO	DCX (decarboxylation)
Bifunctionality	Saturated plane and active sites (S-H) for hydrogenation Vacant sites for C-O activation	Oxygen modifies sites (-OH) providing an acid function Vacant sites for C-O activation	Metal sites for hydrogenation Support can give acid sites
Activation energy for dissociation of H2	0.55-0.97 eV MoSx 0.34-0.52 eV CoMoSx 0.32-0.74 eV NiMoS	0.00 eV MoP(001)	0.19 eV Pt (111) 0.12 eV Pd(111) 0.00 eV Ru (0001)
Deactivation routes	Surface oxidation Coke generation Leaching of S	Surface oxidation Loss of C / N / P Coke formation	Sintering Sulfur poisoning Coke generation
Notes	Co, Ni, Mo, CoMo and NiMo sulfides supported on SiO2 or Al2O3 are commonly used and well known in the petroleum industry	Non-noble metal phosphides, nitrides and carbides have been widely tested for economic reasons. Developments in the area are still at a very early stage.	Noble metals generally have higher deoxygenation efficiencies compared to Mo-based sulfides.

As shown in Table 9, decarboxylation reactions are favoured by metallic catalysts such as Co, Pd, Pt, Ni, Rh, Mo and Ru. Generally, Co is the material that presents the highest catalytic activity. On the other hand, HDO reactions are predominate when are used metals based on C, Fe and W or bimetallic materials with sulphur such as Ni/MoS_2, $CoMoS_2$ and $NiWS_2$. Furthermore, saturation of double bonds occurs more easily with the use of Pd and Pt catalysts (Ameen et al., 2017) (Mayorga et al., 2020). The hydrotreatment of bio-oils has also shown good results with metal catalysts supported on zeolites or carbonaceous materials (especially in very acidic media where conditions create structural problems for zeolites and aluminas) (Mayorga et al., 2020).

Several researchers have carried out studies applying different catalysts for the upgrading of bio-oil by HDO. However, most studies use bio-oils produced by pyrolysis and/or originating from lignocellulosic biomass. Furthermore, studies are also typically carried out in laboratory-scale batch reactors (4 –

500mL), with a great lack of information regarding the continuous operation of reactors. Batch tests, for example, typically involve equilibrium-limited reactions, which is not necessarily the case in continuous flow reactors. (López Barreiro et al., 2016). So, there is a clear need for more research using more data obtained in HDO of real bio-oils, instead of using model compounds. Even though, there are already some studies that use bio-oil from microalgae in upgrading experiments, but only in batch mode. Table 10 presents a series of results regarding the most significant response parameters of the process (reduction in the O/C ratio, increase in the H/C ratio, reduction in N and increase in PCS) obtained with microalgal biomass and different heterogeneous catalysts.

Table 10. Overview of the characteristics of bio-oils obtained from microalgae biomass under varying HDO conditions (Costanzo et al., 2015) (Li & Savage, 2013)(López Barreiro et al., 2016) (Masoumi & Dalai, 2021)

Microalgae bio-oil	**HDO process conditions**	**Catalyst**	**O/C Reduction (%)**	**H/C increase (%)**	**N reduction (%)**	**PCS Increase (%)**
Nannochloropsis sp.	400 °C; 4 h; 6,3 mmol H2; 10% m/m catalyst dosage	HZSM-5	71.1	3.2	56.6	13.8
	400°C; 4h; 6.3 mmol H2; 50% m/m catalyst dosage		69.8		68.2	13.0
	450 °C; 4 h; 6,3 mmol H2; 50% m/m catalyst dosage		90.1			10.4
	500 °C; 4 h; 6,3 mmol H2; 5% m/m catalyst dosage		95.9			14.1
	500 °C; 4 h; 6,3 mmol H2; 50% m/m catalyst dosage		89.7			4.9
	500 °C; 0,5 h; 6,3 mmol H2; 50% m/m catalyst dosage		92.3			6.8
Consortium (*C. surokiniana* + *C. minutíssima* + *S. bíjuga)*	350 °C; 4 h; 22,1 mmol H-1 g cat-1 H2; 10% m/m catalyst dosage	Ru/C	28.4	1.1	1.7	7

Nannochloropsis sp.	400 °C; 2 h; 3,0 MPa H2; 5% m/m catalyst dosage	Mo2C	78.4	3.0	16.7	23.7
		NiMoC-CH4/H2	40.7		3.7	9.3
		NiMoC-H2	74.3		9.3	21.0
		NiMoC-N2	78.0	3.6	22.2	24.3
		NiMoC – co-impregnated	85.5	7.2	27.8	28.1
S. almeriensis	400 °C; 4 h; 3,4 MPa H2; 20% m/m catalyst dosage	Pt/Al2O3	83.0	5.0	26.3	15.4
		HZSM-5	73.7		12.3	12.1
N. gaditana	400°C; 4h; 3,2MPa H2; 20% m/m catalyst dosage	Pt/Al2O3	86.3	2.4	50.0	16.8
		HZSM-5	76.7		50.0	14.3

Zeolites are very efficient catalysts to produce alkanes and aromatic hydrocarbons, being of lower price than metallic catalysts based on Pt and Pd. (Li & Savage, 2013). Some studies have confirmed the effective catalytic activity of zeolites in the upgrading bio-oil from Nannochloropsis sp. through the use of HZSM-5 under different conditions and catalyst dosages (Table 6). The researchers reported high removal rates of oxygenated compounds, corresponding to a 95.9% reduction in the O/C ratio and a 14.1% increase in HHV at 500°C (5% m/m catalyst dosage). Also, the nitrogen content effectively decreased, reaching a maximum of 69.9% at 500°C, but with a catalyst dosage of 50% m/m (Li & Savage, 2013).

Transition metal carbides are also very active for the HDO process due to their unique electronic structure and high thermal stability. In relation to bio-oils rich in aliphatic and oxygenated cyclic compounds, catalysts such as NiMo have shown good performance due to their ability to promote decarboxylation reactions and to break C-O bonds, simultaneously they present lower coke depositions and energy consumption when compared with catalysts based on noble metals. Moreover, (Masoumi & Dalai, 2021) investigated the use of NiMo carbides supported on activated carbon derived from microalgae as a catalyst for the HDO process. The results showed reductions in the O/C ratio between 40.7 and 85.5%, with the maximum value being achieved with a co-impregnated NiMoC catalyst. This catalyst also corresponded to a reduction in N content of 27.8% and an increase of 28.1% in terms of HHV. This authors also observed a positive correlation between the performance of the catalyst and the size of its pores and active phase. On the other hand, (López Barreiro et al., 2016) studied the influence of two catalysts (Pt/Al2O3 and HZSM-5) on HDO of crude bio-oil from biomass of*S. almeriensis* and *N. gaditana*. The researchers observed a higher influence of temperature than of the catalysts chosen for the process on the upgrading efficiency, but it was still possible to conclude that Pt/Al2O3 led to better results in both bio-oils (reduction in the O/C ratio of 83.0% and 86.3% for bio-oils originating from *S. almeriensis* and *N. gaditana*, respectively). Despite these results, it was clear in this study that the level of upgrading was not sufficient to convert bio-oils into fuel, with the need to develop more research into upgrading technologies for bio-oils derived from microalgal biomass (López Barreiro et al., 2016).

Globally, the diversity of reaction systems, catalysts and experimental conditions difficult the comparisons between available works. However, based on the literature review it can be considered that residence times of 4h, temperatures of 400°C and the use of catalysts such as Pt, CoMo or zeolites are currently the “standard” operating conditions for the removal of heteroatoms in bio-oils. microalgal origin.

4 Standards applied to the production and use of SAF

The production and use of Sustainable Aviation Fuels (SAF) are governed by various national and international standards and policies aimed at reducing the aviation sector’s carbon footprint. These standards are critical for ensuring that SAF meets specific sustainability, safety, and performance criteria, making it a viable alternative to conventional jet fuel. This production and use is very country-specific; a brief description of the policies in place in the MIC countries (Europe, United States, Canada, India, Brazil): This info on policies is summarized in the following Table 11.

In Europe, the ReFuelEU Aviation regulation is at the forefront of SAF standardization. It aims to promote the uptake of SAF by normalizing its use across main airports in the European Union. The European Union Aviation Safety Agency (EASA) is instrumental in facilitating the adoption of these fuels, with SAF currently being subjected to a maximum blending ratio of 50% with fossil-based jet fuel, contingent upon the feedstock-production pathway considered. This regulatory environment ensures that SAF meets rigorous sustainability criteria, helping to lower aviation emissions significantly.

The United States has announced a goal (SAF Grand Challenge) to amplify the production of SAF, intending to reach at least 3 billion gallons per year by 2030. This target is part of a broader strategy to decarbonize the aviation sector, supported by policies that incentivize the SAF production, distribution, and use. Standards governing SAF in the US place a strong emphasis on sustainability and emissions reduction, driving technological innovation and collaboration across the biofuel and aviation industries.

Canada's approach includes a mixture of industry-led initiatives and governmental regulations aiming to bolster the SAF sector. The Canadian Council for Sustainable Aviation Fuels (C-SAF) exemplifies industry collaboration, while regulations, such as those outlined in British Columbia, require renewable fuel to constitute a minimum percentage of jet fuel supply, setting a clear path for SAF integration into the market. These efforts show Canada's commitment to reducing aviation emissions through a comprehensive SAF strategy.

India is set to mandate the use of 1% SAF for domestic airlines by 2025. This initiative underscores the country's dedication to reducing aviation emissions and its willingness to incorporate SAF into its aviation sector. Such a mandate not only highlights the environmental priorities of the Indian government but also reflects the global shift towards more sustainable aviation practices. As this policy unfolds, India is poised to make substantial contributions to the international efforts in mitigating climate change impacts.

In Brazil, a SAF mandate is scheduled to take effect in January 2027, with the intent to cut airline emissions by incorporating SAF into the Brazilian energy matrix. The National Sustainable Aviation Fuel Program (PROBIOQAV) aims to promote SAF production and usage, setting standards for sustainability and emission reduction. This program is a critical component of Brazil's strategy to address aviation's environmental impacts, demonstrating leadership in adopting renewable energy solutions in the aviation sector.

Table 11: SAF policies being enforced in the Mission Innovation Countries.

Country /Area	Policy	Commitments	refs
Europe	EU Renewable Energy Directive (RED II)	Mandates increasing the share of renewable energy in the EU's energy mix, including a sub-target for advanced biofuels and SAF. It sets sustainability criteria for biofuels used in the aviation sector.	(1)
	European Commission's ReFuelEU Aviation Initiative	Proposes a SAF blending mandate starting at **2% in 2025**, gradually increasing to **63% by 2050**, to boost the supply and demand for SAF in aviation across EU member states.	
Canada	Clean Fuel Standard (CFS)	Aims to reduce the carbon intensity of fuels used in Canada, including aviation fuels. It encourages the use of lower carbon fuels, energy sources, and technologies. Industry-led initiatives and governmental regulations, including British Columbia's mandates to increase renewable fuel percentage in jet fuel, aimed at scaling up SAF usage.	(2)
India	SAF Mandate for Airlines	A forthcoming mandate for the use of 1% SAF in domestic airlines by 2025 to align with emissions reduction goals.	(3)
Brazil	National SAF Program (PROBIOQAV)	A policy targeting the inclusion of SAF into the Brazilian energy matrix from January 2027 to curb airline emissions.	(4)
US	Sustainable Aviation Fuel Grand Challenge	Aims to produce 3 billion gallons of SAF per year by 2030 and reduce aviation emissions by 20% by 2035. The initiative involves collaboration between various federal agencies to support SAF development and deployment.	(5)

(1) https://www.easa.europa.eu/en/domains/environment/sustainable-aviation-fuels-saf
https://transport.ec.europa.eu/index_en
https://energy.ec.europa.eu/index_en
(2) https://www.canada.ca/en/environment-climate-change/services/managing-pollution/energy-production/fuel-regulations/clean-fuel-regulations.html
(3) https://satat.co.in/satat/#/
(4) https://www.gov.br/anp/pt-br/assuntos/renovabio
(5) https://www.energy.gov/eere/bioenergy/sustainable-aviation-fuel-grand-challenge

5 Sources

Ameen, M., Azizan, M. T., Yusup, S., Ramli, A., & Yasir, M. (2017). Catalytic hydrodeoxygenation of triglycerides: An approach to clean diesel fuel production. In *Renewable and Sustainable Energy Reviews* (Vol. 80, pp. 1072–1088). Elsevier Ltd. https://doi.org/10.1016/j.rser.2017.05.268

Azizi, K., Keshavarz Moraveji, M., & Abedini Najafabadi, H. (2018). A review on bio-fuel production from microalgal biomass by using pyrolysis method. In *Renewable and Sustainable Energy Reviews* (Vol. 82, pp. 3046–3059). Elsevier Ltd. https://doi.org/10.1016/j.rser.2017.10.033

Badoga, S., Gieleciak, R., Alvarez-Majmutov, A., Xing, T., & Chen, J. (2022). An overview on the analytical methods for characterization of biocrudes and their blends with petroleum. In *Fuel* (Vol. 324). Elsevier Ltd. https://doi.org/10.1016/j.fuel.2022.124608

Bautista L. F., Vicente G., & Garre V. (2012). Biodiesel from microbial oil Advances in Biodiesel Production, Woodhead Publishing Series in Energy, Pages 179-203. https://doi.org/10.1533/9780857095862.2.179

Benedik, M. J., Gibbs, P. R., Riddle, R. R., & Willson, R. C. (1998). Microbial denitrogenation of fossil fuels. *Trends in Biotechnology*, *16*(9), 390–395. https://doi.org/10.1016/s0167-7799(98)01237-2

Biller, P., Johannsen, I., dos Passos, J. S., & Ottosen, L. D. M. (2018). Primary sewage sludge filtration using biomass filter aids and subsequent hydrothermal co-liquefaction. *Water Research*, *130*, 58–68. https://doi.org/10.1016/j.watres.2017.11.048

Castello, D., Haider, M. S., & Rosendahl, L. A. (2019). Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks. *Renewable Energy*, *141*, 420–430. https://doi.org/10.1016/j.renene.2019.04.003

Chaiwong, K., Kiatsiriroat, T., Vorayos, N., & Thararax, C. (2013). Study of bio-oil and bio-char production from algae by slow pyrolysis. *Biomass and Bioenergy*, *56*, 600–606. https://doi.org/10.1016/j.biombioe.2013.05.035

Costanzo, W., Jena, U., Hilten, R., Das, K. C., & Kastner, J. R. (2015). Low temperature hydrothermal pretreatment of algae to reduce nitrogen heteroatoms and generate nutrient recycle streams. *Algal Research*, *12*, 377–387. https://doi.org/10.1016/j.algal.2015.09.019

Dabros, T. M. H., Stummann, M. Z., Høj, M., Jensen, P. A., Grunwaldt, J. D., Gabrielsen, J., Mortensen, P. M., & Jensen, A. D. (2018). Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis. In *Progress in Energy and Combustion Science* (Vol. 68, pp. 268–309). Elsevier Ltd. https://doi.org/10.1016/j.pecs.2018.05.002

Elliot, D. c., Hart, T. R., Neuenschwander, G. G., Oyler, J. R., Rotness, L. J. Jr., Schmidt, A. J., & Zacher, A. H. (2016). *System and process for efficient separation of biocrudes and water in a hydrotermal liquefaction system* (Patent US9404063).

Elliott, D. C. (2007). Historical developments in hydroprocessing bio-oils. In *Energy and Fuels* (Vol. 21, Issue 3, pp. 1792–1815). https://doi.org/10.1021/ef070044u

Elliott, D. C., Hart, T. R., Schmidt, A. J., Neuenschwander, G. G., Rotness, L. J., Olarte, M. V., Zacher, A. H., Albrecht, K. O., Hallen, R. T., & Holladay, J. E. (2013). Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. *Algal Research*, *2*(4), 445–454. https://doi.org/10.1016/j.algal.2013.08.005

Feng, Y. (2004). A Study on the Process Conditions of Removing Basic Nitrogen Compounds from Gasoline. *Petroleum Science and Technology*, *22*, 1517–1525.

Ferdous, D., Dalai, A. K., & Adjaye, J. (2006). Comparison of product selectivity during hydroprocessing of bitumen derived gas oil in the presence of NiMo/Al2O3 catalyst containing boron and phosphorus. *Fuel*, *85*(9), 1286–1297. https://doi.org/10.1016/j.fuel.2005.11.018

Ronny W. Lin (2015). *(54) SOLIDS REMOVAL FROM BIO-OILUSING.* (*US 2015/0110680 A1)*

Gollakota, A. R. K., Reddy, M., Subramanyam, M. D., & Kishore, N. (2016). A review on the upgradation techniques of pyrolysis oil. In *Renewable and Sustainable Energy Reviews* (Vol. 58, pp. 1543–1568). Elsevier Ltd. https://doi.org/10.1016/j.rser.2015.12.180

Grigorenko, A. V., Vlaskin, M. S., Kotelev, M. S., & Ivanov, E. V. (2018). Two-step separation of bio-oil from condensed products of hydrothermal liquefaction of microalgae. *Journal of Physics: Conference Series*, *1111*(1). https://doi.org/10.1088/1742-6596/1111/1/012057

Gupta, S., Mondal, P., Borugadda, V. B., & Dalai, A. K. (2021). Advances in upgradation of pyrolysis bio-oil and biochar towards improvement in bio-refinery economics: A comprehensive review. In *Environmental Technology and Innovation* (Vol. 21). Elsevier B.V. https://doi.org/10.1016/j.eti.2020.101276

Haider, M. S., Castello, D., & Rosendahl, L. A. (2020). Two-stage catalytic hydrotreatment of highly nitrogenous biocrude from continuous hydrothermal liquefaction: A rational design of the stabilization stage. *Biomass and Bioenergy*, *139*. https://doi.org/10.1016/j.biombioe.2020.105658

He, Z., & Li, L. (2009). *Simultaneous metal, sulfur and nitroen removal using supercritical water* (Patent WO2009085436A1).

He, Z., Xu, D., Liu, L., Wang, Y., Wang, S., Guo, Y., & Jing, Z. (2018). Product characterization of multi-temperature steps of hydrothermal liquefaction of Chlorella microalgae. *Algal Research*, *33*, 8–15. https://doi.org/10.1016/j.algal.2018.04.013

Ishihara, A., Wang, D., Dumeignil, F., Amano, H., Qian, E. W., & Kabe, T. (2005). Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process. *Applied Catalysis A: General*, *279*(1), 279–287. https://doi.org/https://doi.org/10.1016/j.apcata.2004.10.037

Javaid, A., Ryan, T., Berg, G., Pan, X., Vispute, T., Bhatia, S. R., Huber, G. W., & Ford, D. M. (2010). Removal of char particles from fast pyrolysis bio-oil by microfiltration. *Journal of Membrane Science*, *363*(1–2), 120–127. https://doi.org/10.1016/j.memsci.2010.07.021

Jenkins, R. (2015). *Renewable liquid transport fuels from microbes and waste resources*.

Jiménez-Díaz, L., Caballero, A., Pérez-Hernández, N., & Segura, A. (2017). Microbial alkane production for jet fuel industry: motivation, state of the art and perspectives. In *Microbial Biotechnology* (Vol. 10, Issue 1, pp. 103–124). John Wiley and Sons Ltd. https://doi.org/10.1111/1751-7915.12423

Johannsen, I., Biller, P., & Ditlev Mork Ottosen, L. (2019). *A method for biomass assisted separation of particulate matter from a liquid stream and upgrading of the combined solids* (Patent EP3421575A1). European Patent Office.

Kargbo, H., Harris, J. S., & Phan, A. N. (2021). "Drop-in" fuel production from biomass: Critical review on techno-economic feasibility and sustainability. In *Renewable and Sustainable Energy Reviews* (Vol. 135). Elsevier Ltd. https://doi.org/10.1016/j.rser.2020.110168

Kazemi Shariat Panahi, H., Tabatabaei, M., Aghbashlo, M., Dehhaghi, M., Rehan, M., & Nizami, A. S. (2019). Recent updates on the production and upgrading of bio-crude oil from microalgae. *Bioresource Technology Reports*, *7*. https://doi.org/10.1016/j.biteb.2019.100216

Kim, Y., Thomas, A. E., Robichaud, D. J., Iisa, K., St. John, P. C., Etz, B. D., Fioroni, G. M., Dutta, A., McCormick, R. L., Mukarakate, C., & Kim, S. (2020). A perspective on biomass-derived biofuels: From catalyst design principles to fuel properties. *Journal of Hazardous Materials*, *400*. https://doi.org/10.1016/j.jhazmat.2020.123198

Laredo, G. C., Vega-Merino, P. M., Ascención Montoya-de la Fuente, J., Mora-Vallejo, R. J., Meneses-Ruiz, E., Jesús Castillo, J., & Zapata-Rendón, B. (2016). Comparison of the metal–organic framework MIL-101 (Cr) versus four commercial adsorbents for nitrogen compounds removal in diesel feedstocks. *Fuel*, *180*, 284–291. https://doi.org/https://doi.org/10.1016/j.fuel.2016.04.038

Latha Sabikhi, & M.H. Sathish Kumar. (n.d.). *Fatty Acid Profile of Unconventional Oilseeds - ScienceDirect*.

Ledesma-Amaro, R. (2015). Microbial oils: A customizable feedstock through metabolic engineering. In *European Journal of Lipid Science and Technology* (Vol. 117, Issue 2, pp. 141–144). Wiley-VCH Verlag. https://doi.org/10.1002/ejlt.201400181

Lehtinen, T., Virtanen, H., Santala, S., & Santala, V. (2018). Production of alkanes from CO2 by engineered bacteria. *Biotechnology for Biofuels*, *11*(1). https://doi.org/10.1186/s13068-018-1229-2

Leng, L., Zhang, W., Peng, H., Li, H., Jiang, S., & Huang, H. (2020). Nitrogen in bio-oil produced from hydrothermal liquefaction of biomass: A review. In *Chemical Engineering Journal* (Vol. 401). Elsevier B.V. https://doi.org/10.1016/j.cej.2020.126030

Li, Z., & Savage, P. E. (2013). Feedstocks for fuels and chemicals from algae: Treatment of crude bio-oil over HZSM-5. *Algal Research*, *2*(2), 154–163. https://doi.org/10.1016/j.algal.2013.01.003

Lin, R. W. (2015). *Solids removal from bio-oil using biomass filter aid* (Patent US8952210B2).

López Barreiro, D., Gómez, B. R., Ronsse, F., Hornung, U., Kruse, A., & Prins, W. (2016). Heterogeneous catalytic upgrading of biocrude oil produced by hydrothermal liquefaction of microalgae: State of the art and own experiments. *Fuel Processing Technology*, *148*, 117–127. https://doi.org/10.1016/j.fuproc.2016.02.034

Lu, J., Zhang, Z., Zhang, L., Fan, G., Wu, Y., & Yang, M. (2021). Catalytic hydrothermal liquefaction of microalgae over different biochars. *Catalysis Communications*, *149*. https://doi.org/10.1016/j.catcom.2020.106236

Lu, Y., Li, G. S., Lu, Y. C., Fan, X., & Wei, X. Y. (2017). Analytical Strategies Involved in the Detailed Componential Characterization of Biooil Produced from Lignocellulosic Biomass. In *International Journal of Analytical Chemistry* (Vol. 2017). Hindawi Limited. https://doi.org/10.1155/2017/9298523

Ma, Y., Gao, Z., Wang, Q., & Liu, Y. (2018). Biodiesels from microbial oils: Opportunity and challenges. In *Bioresource Technology* (Vol. 263, pp. 631–641). Elsevier Ltd. https://doi.org/10.1016/j.biortech.2018.05.028

Maass, D., Todescato, D., Moritz, D. E., Oliveira, J. V., Oliveira, D., Ulson de Souza, A. A., & Guelli Souza, S. M. A. (2015). Desulfurization and denitrogenation of heavy gas oil by Rhodococcus erythropolis ATCC 4277. *Bioprocess and Biosystems Engineering*, *38*(8), 1447–1453. https://doi.org/10.1007/s00449-015-1386-7

Masoumi, S., & Dalai, A. K. (2021). NiMo carbide supported on algal derived activated carbon for hydrodeoxygenation of algal biocrude oil. *Energy Conversion and Management*, *231*. https://doi.org/10.1016/j.enconman.2021.113834

Mayorga, M. A., Cadavid, J. G., López, C. A., Suárez, O. Y., Bonilla, J. A., López, M., Trujillo, C. A., & Durán, H. A. (2020). Definition of the catalyst family for the production of green diesel by hydrotreatment in situ of triglycerides. *Chemical Engineering Transactions*, *80*, 241–246. https://doi.org/10.3303/CET2080041

Mujahid, R., Riaz, A., Insyani, R., & Kim, J. (2020a). A centrifugation-first approach for recovering high-yield bio-oil with high calorific values in biomass liquefaction: A case study of sewage sludge. *Fuel*, *262*. https://doi.org/10.1016/j.fuel.2019.116628

Mujahid, R., Riaz, A., Insyani, R., & Kim, J. (2020b). A centrifugation-first approach for recovering high-yield bio-oil with high calorific values in biomass liquefaction: A case study of sewage sludge. *Fuel*, *262*, 116628. https://doi.org/https://doi.org/10.1016/j.fuel.2019.116628

Mushrush, G. W., Quintana, M. A., Bauserman, J. W., & Willauer, H. D. (2011). Post-refining removal of organic nitrogen compounds from diesel fuels to improve environmental quality. *Journal of Environmental Science and Health, Part A*, *46*(2), 176–180. https://doi.org/10.1080/10934529.2011.532433

Nava Bravo, I., Velásquez-Orta, S. B., Cuevas-García, R., Monje-Ramírez, I., Harvey, A., & Orta Ledesma, M. T. (2019). Bio-crude oil production using catalytic hydrothermal liquefaction (HTL) from native microalgae harvested by ozone-flotation. *Fuel*, *241*, 255–263. https://doi.org/10.1016/j.fuel.2018.12.071

Ochsenreither, K., Glück, C., Stressler, T., Fischer, L., & Syldatk, C. (2016). Production strategies and applications of microbial single cell oils. In *Frontiers in Microbiology* (Vol. 7, Issue OCT). Frontiers Media S.A. https://doi.org/10.3389/fmicb.2016.01539

Panwar, N. L., & Paul, A. S. (2021). An overview of recent development in bio-oil upgrading and separation techniques. In *Environmental Engineering Research* (Vol. 26, Issue 5). Korean Society of Environmental Engineers. https://doi.org/10.4491/eer.2020.382

Pinheiro, A., Hudebine, D., Dupassieux, N., & Geantet, C. (2009). Impact of oxygenated compounds from lignocellulosic biomass pyrolysis oils on gas oil hydrotreatment. *Energy and Fuels*, *23*(2), 1007–1014. https://doi.org/10.1021/ef800507z

Prado, G. H. C., Rao, Y., & De Klerk, A. (2017). Nitrogen removal from oil: A review. In *Energy and Fuels* (Vol. 31, Issue 1, pp. 14–36). American Chemical Society. https://doi.org/10.1021/acs.energyfuels.6b02779

Raikova S., Le C. D., Wagner J. L. V.P., Ting V. P., & Chuck C. J. (2016). *Biofuels for Aviation*. https://www.sciencedirect.com/science/article/abs/pii/B9780128045688000093

Saber, M., Nakhshiniev, B., & Yoshikawa, K. (2016). A review of production and upgrading of algal bio-oil. In *Renewable and Sustainable Energy Reviews* (Vol. 58, pp. 918–930). Elsevier Ltd. https://doi.org/10.1016/j.rser.2015.12.342

Sano, Y., Choi, K.-H., Korai, Y., & Mochida, I. (2004). Adsorptive removal of sulfur and nitrogen species from a straight run gas oil over activated carbons for its deep hydrodesulfurization. *Applied Catalysis B: Environmental*, *49*(4), 219–225. https://doi.org/https://doi.org/10.1016/j.apcatb.2003.12.007

Santillan-Jimenez, E., Pace, R., Morgan, T., Behnke, C., Sajkowski, D. J., Lappas, A., & Crocker, M. (2019). Co-processing of hydrothermal liquefaction algal bio-oil and petroleum feedstock to fuel-like hydrocarbons via fluid catalytic cracking. *Fuel Processing Technology*, *188*, 164–171. https://doi.org/10.1016/j.fuproc.2019.02.018

Sayegh, A., Merkert, S., Zimmermann, J., Horn, H., & Saravia, F. (2022). Treatment of Hydrothermal-Liquefaction Wastewater with Crossflow UF for Oil and Particle Removal. *Membranes*, *12*(3). https://doi.org/10.3390/membranes12030255

Shiraishi, Y., Hirai, T., & Komasawa, I. (2000). Photochemical Denitrogenation Processes for Light Oils Effected by a Combination of UV Irradiation and Liquid−Liquid Extraction. *Industrial & Engineering Chemistry Research*, *39*(8), 2826–2836. https://doi.org/10.1021/ie990917a

Shiraishi, Y., Tachibana, K., Taki, Y., Hirai, T., & Komasawa, I. (2001). A Novel Desulfurization Process for Fuel Oils Based on the Formation and Subsequent Precipitation of S-Alkylsulfonium Salts. 2. Catalytic-Cracked Gasoline. *Industrial & Engineering Chemistry Research*, *40*(4), 1225–1233. https://doi.org/10.1021/ie000548e

Shuping, Z., Yulong, W., Mingde, Y., Kaleem, I., Chun, L., & Tong, J. (2010). Production and characterization of bio-oil from hydrothermal liquefaction of microalgae Dunaliella tertiolecta cake. *Energy*, *35*(12), 5406–5411. https://doi.org/10.1016/j.energy.2010.07.013

Silva, J. de M. e., Martins, L. H. da S., Moreira, D. K. T., Silva, L. do P., Barbosa, P. de P. M., Komesu, A., Ferreira, N. R., & Oliveira, J. A. R. de. (2023). Microbial Lipid Based Biorefinery Concepts: A Review of Status and Prospects. In *Foods* (Vol. 12, Issue 10). MDPI. https://doi.org/10.3390/foods12102074

Sorunmu, Y., Billen, P., & Spatari, S. (2020). A review of thermochemical upgrading of pyrolysis bio-oil: Techno-economic analysis, life cycle assessment, and technology readiness. In *GCB Bioenergy* (Vol. 12, Issue 1, pp. 4–18). Blackwell Publishing Ltd. https://doi.org/10.1111/gcbb.12658

Sugaya, K., Nakayama, O., Hinata, N., Kamekura, K., Ito, A., Yamagiwa, K., & Ohkawa, A. (2001). Biodegradation of quinoline in crude oil. *Journal of Chemical Technology & Biotechnology*, *76*(6), 603–611. https://doi.org/https://doi.org/10.1002/jctb.423

Tang, K., & Hong, X. (2014). Application of Bacterium HY9 Strain for Diesel Oil Denitrogenation. *Petroleum Science and Technology*, *32*(20), 2466–2472. https://doi.org/10.1080/10916466.2013.838263

Thevenieau, F., & Nicaud, J. M. (2013). Microorganisms as sources of oils. In *OCL - Oilseeds and fats, crops and lipids* (Vol. 20, Issue 6). https://doi.org/10.1051/ocl/2013034

Vazquez-Duhalt, R., Torres, E., Valderrama, B., & Le Borgne, S. (2002). Will Biochemical Catalysis Impact the Petroleum Refining Industry? *Energy & Fuels*, *16*(5), 1239–1250. https://doi.org/10.1021/ef020038s

Walls, L. E., & Rios-Solis, L. (2020). Sustainable Production of Microbial Isoprenoid Derived Advanced Biojet Fuels Using Different Generation Feedstocks: A Review. In *Frontiers in Bioengineering and Biotechnology* (Vol. 8). Frontiers Media S.A. https://doi.org/10.3389/fbioe.2020.599560

Wei, Q., Wen, S., Tao, X., Zhang, T., Zhou, Y., Chung, K., & Xu, C. (2015). Hydrodenitrogenation of basic and non-basic nitrogen-containing compounds in coker gas oil. *Fuel Processing Technology*, *129*, 76–84. https://doi.org/https://doi.org/10.1016/j.fuproc.2014.08.001

Xu, Y., Li, Y., Wang, C., Wang, C., Ma, L., Wang, T., Zhang, X., & Zhang, Q. (2017). In-situ hydrogenation of model compounds and raw bio-oil over Ni/CMK-3 catalyst. *Fuel Processing Technology*, *161*, 226–231. https://doi.org/10.1016/j.fuproc.2016.08.018

Yang, H., Chen, J., Fairbridge, C., Briker, Y., Zhu, Y. J., & Ring, Z. (2004). Inhibition of nitrogen compounds on the hydrodesulfurization of substituted dibenzothiophenes in light cycle oil. *Fuel Processing Technology*, *85*(12), 1415–1429. https://doi.org/https://doi.org/10.1016/j.fuproc.2003.09.008

Yang, J., (Sophia)He, Q., & Yang, L. (2019). A review on hydrothermal co-liquefaction of biomass. In *Applied Energy* (Vol. 250, pp. 926–945). Elsevier Ltd. https://doi.org/10.1016/j.apenergy.2019.05.033

Zacher, A. H., Olarte, M. V., Santosa, D. M., Elliott, D. C., & Jones, S. B. (2014). A review and perspective of recent bio-oil hydrotreating research. In *Green Chemistry* (Vol. 16, Issue 2, pp. 491–515). Royal Society of Chemistry. https://doi.org/10.1039/c3gc41382a

Zhang, M., Hu, Y., Wang, H., Li, H., Han, X., Zeng, Y., & Xu, C. C. (2021). A review of bio-oil upgrading by catalytic hydrotreatment: Advances, challenges, and prospects. In *Molecular Catalysis* (Vol. 504). Elsevier B.V. https://doi.org/10.1016/j.mcat.2021.111438

Zhao, B., Shi, Z., & Yang, X. (2017). Upgrading Algae Biocrude for a Low-Nitrogen-Containing Biofuel: Compositions, Intermediates, and Reaction Routes. *Industrial and Engineering Chemistry Research*, *56*(22), 6378–6390. https://doi.org/10.1021/acs.iecr.7b01405

Zhao, B., Wang, Z., Liu, Z., & Yang, X. (2016). Two-stage upgrading of hydrothermal algae biocrude to kerosene-range biofuel. *Green Chemistry*, *18*(19), 5254–5265. https://doi.org/10.1039/c6gc01413e