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# A review of fractional distillation to improve hydrothermal liquefaction biocrude characteristics; future outlook and prospects

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**Abstract:** *Hydrothermal liquefaction (HTL) is an efficient thermochemical method for biomass conversion into biocrude which could be operated with a wide range of feedstock resources. However, HTL biocrude characteristics including viscosity, density, heating value, composition and stability are not comparable with conventional products. The current focus for upgrading mainly relates to catalytic and hydrogenation processes; however, physical processes are cheaper and more reliable. Fractional distillation has potential as a cost-efficient physical technique for biocrude upgrading or even co-processing with crude oil in a refinery. This review summarises and discusses changes in physical and chemical properties of biocrude using fractional distillation. Distillation reduces the oxygen content of biocrude for heavy fractions more than 53% on average. It also decreases the sulphur and nitrogen content of biocrude up to 5-44 %. The potential role of distillation in preparing fuel suitable for diesel engines is investigated. The challenges and technical limitations in HTL biocrude application in industry are also discussed alongside with possible solutions and future research potential which addresses these challenges.*

## Highlights:

- The Hydrothermal liquefaction impact on biomass was investigated.
- The distillation studies in both Hydrothermal liquefaction and pyrolysis were categorised and studied.
- Distillation could be helpful in more accurate biocrude characterisation by separating the biocrude into simpler fractions.
- Distillation showed a possible impact on biocrude HHV, elemental content, viscosity and stability.
- Distillation may improve the current unacceptable biocrude diesel engine combustion both in emission and performance factors.

**Keywords:** biomass, hydrothermal liquefaction (HTL), upgrading, biofuel, distillation, diesel engines

**Abbreviations:** BSFC, brake specific fuel consumption; BTE, brake thermal efficiency; FTIR, Fourier-Transform Infrared Spectroscopy; GC-FID, gas chromatography with Flame Ionization Detector; GHG, greenhouse gases; HFO, Heavy fuel oil; HHV, higher heating value; HTL, hydrothermal liquefaction; LHV, lower heating value; MS, mass spectrometry; NMR, nuclear magnetic resonance, NO<sub>x</sub>, nitrogen oxides; PM, particulate matter; PN, particle number; SCWO, supercritical water oxidation; TAN, total acid number; TBP, true boiling point; TGA, thermogravimetric analysis.

**Word count:** 8230 without tables and 15130 with all tables.

## 1. Introduction

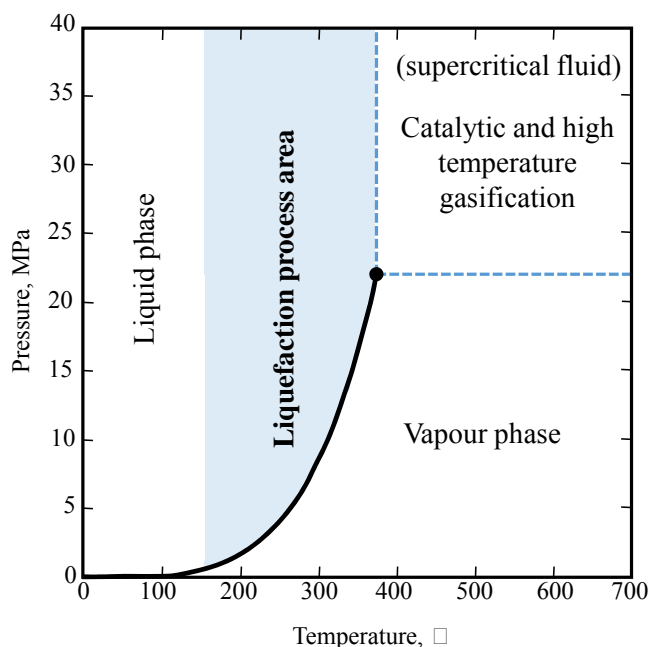
Currently, there are serious concerns about future energy supplies due to the increase in global primary energy consumption, which has increased by 1.8% p.a. over the 10 years to 2016 [1]. Although there are numerous renewable energy resources available such as solar and wind energy, alternative sources of liquid fuels are also required. Besides this, fossil fuels are being depleted; some studies suggest a global peak in conventional oil consumption will occur between 2030-2042 [2-5]. Importantly, fossil fuels contribute to greenhouse gas (GHG) emissions. Supplementing the fuel supply with renewable fuels would reduce the use of fossil fuels. Biomass is an appropriate and abundant source of energy which could play an essential role in resolving the depletion of fossil fuels and reducing environmental problems [6].

Biomass has different options to be applied for providing energy in the industry, such as combusting directly or firstly converting into liquid fuels. Liquid fuels are conveniently divided into three generations. First generation biofuels generated from arable sources, which can potentially compete with the food industry [7]. Lignocellulosic resources such as wood, agricultural residues and energy crops have constructed the second generation biofuels which do not compete with the food industry, although raw feedstocks are grown on arable land. Third generation biofuels refer to those derived from algae biomass and arable land is not essential in their production [7]. There are several methods for biomass conversion to liquid fuels including chemical, biochemical and thermochemical processes which includes hydrothermal liquefaction (HTL), gasification and pyrolysis [8-10].

Thermochemical methods to convert biomass to liquid fuels are receiving increasing interest due to several reasons. These methods are capable of converting biomass to a wide range of products including gas, different range of liquid biofuels and even biochar (the solid residue), which has several applications such as bioremediation and soil productivity improvement [11, 12]. In addition, thermochemical methods are relatively feedstock-agnostic, easily adaptable to process a range of moisture contents, and easy to operate [13-15]. Among thermochemical techniques, pyrolysis has been studied in significant detail and so it has subsequently progressed further [16]. Pyrolysis is a well-investigated process which converts biomass into pyrolytic biocrude, gas and biochar which normally operates at 400-700 °C and 0.1-0.2 MPa [17, 18]. However, the main problems with biocrude produced by pyrolysis are the high oxygen and water content resulting in low higher heating value (HHV). More importantly, the need for biomass moisture reduction prior to the pyrolyser is energetically expensive [19].

Hydrothermal liquefaction, in contrast, operates at lower temperatures of 200-500 °C and higher pressures of 5-30 MPa [13]. In these conditions, shown in Figure 1 [20], the water is in the liquid phase so there is no latent heat required to evaporate the in-situ water within the biomass. Also HTL could improve the solubility of organic compounds in the water due to decreasing water density near the critical point [20, 21]. These features make HTL preferable to pyrolysis for many feedstocks since it can convert a broader range of feedstocks with higher moisture content and there is no need for reducing the biomass moisture content before HTL. Also, the requirement for removing moisture is not only eliminated, but water acts as a process catalyst [21].

There are other processes similar to HTL which operate in more severe conditions including above the critical water temperature, namely supercritical water oxidation (SCWO) [22]. Nevertheless, SCWO has some issues for industrialisation due to corrosion and deposition [23].



**Figure 1.** Pressure-temperature phase diagram of water [adapted from 20]

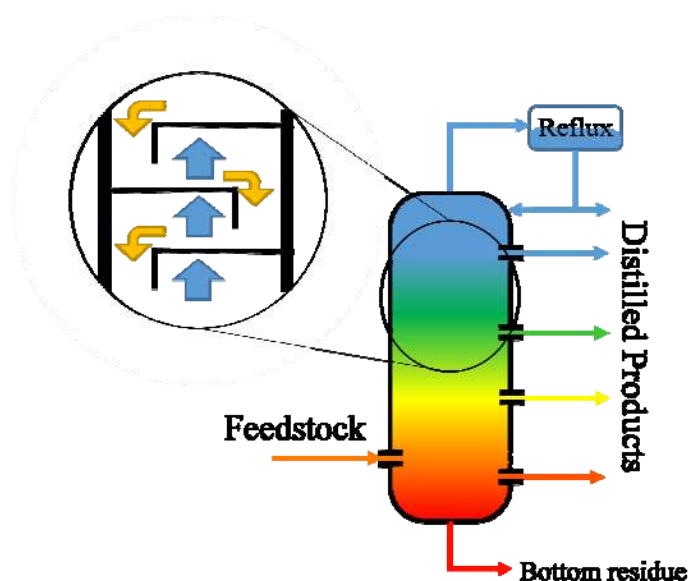
In addition to combustion quality, each fuel should be acceptable in regards to environmental concerns. Sulphur in fuels is one of the main concerns and contributes significantly to air pollution [24]. On the one hand, the sulphur content of crude oil is increasing. The sulphur content of crude oil input to refineries increased from 1.1 wt. % to

1.41wt. % between 1990-2017 (USA) [25] subsequently increasing refining costs. Meanwhile, the limits for sulphur content in refined fuel are becoming more restrictive. For instance, after 1 January 2020 in Australia, the sulphur content of shipping fuel oil must not exceed 0.5 wt.% [26]. To this end, a new upgraded green energy resource with less sulphur is needed [27].

The primary product of HTL (or pyrolysis) is biocrude which is a dense black liquid with a relatively high heating value; however, the co-products generated include gas, a water-soluble phase and biochar [21]. Before using biocrude as a drop-in biofuel, it typically needs upgrading. Upgrading improves the fuel's physical characteristics (viscosity, HHV, colour, density) and chemical characteristics (carbon, sulphur, hydrogen, nitrogen and oxygen content, chemical functional groups).

In the case of biocrude upgrading, it is helpful to consider petro-crude processing. Subsequently, biocrude upgrading processes are conceptually similar to petrocrude upgrading. Hence, upgrading processes include solvent extraction distillation, hydrogenation. Catalytic and thermal cracking which cracks heavier compounds into lighter products and transesterification which esterify biocrude to make it comparable with biodiesel. Table 1 briefly summarises the biocrude upgrading processes.

Fractional distillation is an energy efficient and economically feasible upgrading process which has been continuously developed since the first refineries were built in the late 19<sup>th</sup> century until now [28, 29]. In the conventional refineries, distillation is primarily a physical separation, without necessitating the use of a catalyst. Subsequently, there is no issue with catalyst poisoning caused by petrocrude or biocrude oxygenated compounds which makes conventional refining uneconomical [15]. Another advantage of exploring distillation for biocrudes is that there is potential for integrating biocrude into the current fuel supply chains. A schematic of a fractional distillation tower is shown in Figure 2.



**Figure 2.** A schematic of a fractional distillation column

**Table 1**

Biocrude upgrading processes overview.

	Upgrading process	Conditions	Catalyst applied	Energy consumption	Positive/negative features	Ref.
Separation	Distillation	Up to 250 °C* 100-0.01 kPa	No	Medium	+ Simple and reliable. + No need to catalyst. + Products separated with no need to further processing. - Needs energy and vacuum.	[30-32]
	Solvent extraction	Ambient	No	Low	+ Simple and reliable. + No need to catalyst. - Needs high amounts of solvent. - Solvent should be recovered.	[6, 33, 34]
Hydrogenation	Adding hydrogen donor solvents	Ambient	No	Low	+ Simple and reliable. + Improves the fuel stability. - Need adding solvent. - Solvent should be recovered.	[14, 35, 36]
	Mild hydrogenation	Below 300 °C Usually Less than 4 MPa	Yes	Medium	+ Prevent biochar formation. + Stabilise biocrude. - Consumes energy, hydrogen and catalyst. - Catalysts should be recovered.	[15, 37, 38]
	Hydro deoxygenation	Up to 350 °C 4-16 MPa	Yes	High	+ Effectively improve the biocrude quality. + Well saturates the biocrude by hydrogen. - Consumes lots of hydrogen and catalyst. - Catalysts should be recovered.	[39-41]
Cracking	Thermal cracking	Up to 550 °C Ambient pressure	No	High	+ Effectively convert heavy compounds into light ones. + No need to catalyst. - Consumes energy. - More biochar generation.	[42, 43]
	Catalytic cracking	Up to 500 °C Ambient pressure	Yes	High	+ Effectively convert heavy compounds into light ones. - Consumes energy and catalyst.	[44, 45]

Esterification	Ambient or supercritical conditions	Mostly used	Low/High**	- Catalysts should be recovered.	[46-48]
				+ Convert biocrude compounds to form esters similar to biodiesel. + Improve physical properties such as viscosity, HHV and density. - Catalysts (if any) should be recovered. - Alcohol should be used.	
*Operating temperature. Atmospheric equivalent temperature for vacuum distillation could be up to 400 °C.					
** Depends on esterification conditions.					

Fractional distillation could be employed to improve the quality of biocrude by separating components based on their boiling point with each fraction having properties that may be distinct from the original biocrude as well as other fractions [30]. Biocrude mixtures could be separated into liquefied petroleum gas (LPG), diesel, heavy fuel oil and other commercial fractions to produce a range of fuels [49]. However, to the best of our knowledge, there is little information available in the literature in which the effect of distillation on biocrude properties such as heating value, density, viscosity, stability and miscibility potential are comprehensively described. This review explored the potential of fractional distillation on HTL biocrude based on observation from fossil fuels refining and the modest amounts in HTL and pyrolysis literature to clarify the potential role of this important conventional process in biocrude upgrading. The challenges, research gaps and perspective for future research studies in this area will also be discussed.

## 2. HTL Biomass and biocrude origins and features

### 2.1. Composition of biomass used in HTL

Prior to studying the impact of distillation on biocrude, it is essential to understand the character of the biomass and biocrude. There are a plethora of research studies reporting HTL processing using hundreds of biomass feedstocks which could be categorized into several broad groups. Hardwood and softwood biomass resources such as aspen and pine which leads to second biofuel generation. Agricultural wastes and energy crops such as sugarcane bagasse and oil-palm petioles are feedstocks of first or second generation biofuels. Different wastes such as anaerobic sludge and garbage are important sources of biomass categorized into second generation biofuels, while different types of algae biomass resources comprise the third generation biofuels. Table 2 summarises the different types of biomass feedstock used for HTL, and Table 3 provides an average for these values.

**Table 2**  
Various biomass HTL feedstocks in the literature

Feedstock	Fibre analysis (wt. %)			Proximate analysis (wt. %)				Ultimate analysis (wt. %)					HHV (MJ/kg)	Ref.
	Cellulose	Hemicellulose	Lignin	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O		
<i>Wood</i>														
Aspen wood	47.1	19.6	22.1	-	-	-	0.5	50.4	6.2	0.2	-	43.2	-	[50]
Beech wood	44.2	33.5	21.8	-	-	-	0.5	50.2	6.2	0.4	-	42.6	19.1	[51]
Birch wood sawdust	-	-	-	6.5	83.5	16.3	0.2	47.6	6.3	0.0	-	45.9	16.9	[52]
Cypress wood	43.6	27.6	28.8	-	-	-	-	48.9	6.0	0.3	-	44.8	-	[53]
Eucalyptus globulus wood	39.7	21.4	25.7	6.5	-	-	0.1	-	-	-	-	-	-	[54]
Oak wood	38.1	23.0	32.0	7-15	-	-	2.0	50.2	7.0	-	-	42.8	21.4	[55]
Paulownia wood	-	-	-	-	-	-	-	45.5	6.3	0.0	-	48.2	15.8	[56]
Pine wood	37.0	38.0	22.0	-	-	-	0.3	49.3	6.2	0.3	0.1	44.2	16.3	[57]
Rubber tree	45.8	73.8	21.4	-	-	-	1.0	47.7	5.5	0.0	-	45.9	19.2	[58]
Spurse wood	-	-	-	6.2	86.3	13.4	0.2	50.1	6.4	0.1	0.1	43.5	20.5	[59]
Waste Furniture sawdust	32.6	37.2	22.2	7.1	79.4	12.7	0.8	47.4	5.7	0.2	-	46.7	15.8	[60]
Willow	-	-	-	-	-	-	-	47.9	6.0	0.0	-	-	-	[61]
<i>Agricultural waste</i>														
Bamboo shoot shell	-	-	-	-	-	-	-	45.0	6.2	1.8	-	47.0	15.7	[62]
Banana stem	37.9	71.2	12.3	-	-	-	12.9	38.2	5.3	0.3	-	43.4	15.7	[58]
Barely Straw	46.0	23.0	15.0	6.2	-	-	4.3	44.7	6.3	0.5	0.6	48.0	17.4	[63]
Blackcurrant pomace	-	-	-	59.6	-	-	4.3	50.3	6.8	1.9	0.2	36.8	18.5	[64]
Coconut husk	30.6	56.5	38.8	-	-	-	2.9	49.4	5.3	0.5	-	41.9	19.4	[58]
Coconut shell	26.5	79.3	35.5	-	-	-	1.2	52.0	6.2	0.2	-	41.0	20.3	[58]
Corn stalk	39.2	37.5	20.2	-	-	-	5.5	43.9	5.6	1.8	-	48.7	14.1	[65]
D. stramonium L. stalks	42.2	23.1	24.3	3.7	-	-	6.4	43.6	6.0	0.8	-	49.7	14.4	[66]
Oil palm empty fruit bunch fibres	23.7-65.0	20.6-33.5	14.1-30.4	2.4-14.3	70.1-83.9	9.0-18.3	1.3-13.6	43.8-54.8	4.4-7.4	0.25-1.2	0.1-1.1	38.3-47.8	17.0-19.3	[67]
Oil palm empty fruit fibres	-	-	-	-	-	-	-	47.9	6.1	0.7	-	45.4	19.3	[68]
Green landscaping waste branches	26.0	18.9	23.3	-	-	-	2.9	45.6	7.0	0.2	<0.1	47.2	17.0	[69]
Green landscaping waste leaves	20.9	16.2	20.1	-	-	-	7.7	45.1	7.4	1.2	<0.1	46.4	17.5	[69]
Hazelnut shell	25.2	28.2	42.1	-	-	-	1.4	50.8	5.6	1.4	-	40.9	19.3	[51]
Metroxylon sp. stem	36.6	69.9	25.9	-	-	-	4.6	45.6	5.6	0.2	-	44.0	18.6	[58]
Oil-palm husk	34.3	61.3	31.9	-	-	-	5.5	47.8	5.5	0.7	-	40.6	19.9	[58]
Oil-palm shell	52.1	75.7	48.9	-	-	-	17.0	50.2	6.1	0.6	-	38.0	20.5	[58]
Palm kernel shell	24.5	22.9	33.5	-	-	-	19.1	47.8	4.1	0.5	0.2	47.6	17.5	[70]
Palm mesocarp fiber	23.1	22.2	30.6	-	-	-	24.1	46.3	4.7	1.4	0.2	47.4	16.5	[70]



Feedstock	Fibre analysis (wt. %)			Proximate analysis (wt. %)				Ultimate analysis (wt. %)					HHV (MJ/kg)	Ref.
	Cellulose	Hemicellulose	Lignin	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O		
Pineapple leaf	32.2	63.2	18.7	-	-	-	6.0	48.8	6.2	1.1	-	37.9	19.4	[58]
Prangmites australis	43.3	15.5	27.1	7.0	-	-	17.9	-	-	-	-	-	-	[71]
Pre-treated Sorghum Bagasse	49.8	8.0	24.7	-	-	-	4.2	43.2	5.8	0.7	0.8	41.4	15.5	[72]
Raw empty fruit bunch	26.6	26.9	18.6	-	-	-	27.9	43.6	4.0	2.0	0.2	50.2	16.3	[70]
Rice husk	-	-	-	8.4	76.9	-	14.8	43.1	6.1	4.3	-	46.6	14.9	[73]
Rice Straw	-	-	-	6.0	71.6	6.6	15.8	39.8	5.5	0.8	0.2	53.6	15.2	[74]
Sorghum bagasse	37.7	17.0	13.8	11.0	-	-	0.9	-	-	-	-	-	-	[72]
Spent coffee grounds	-	-	-	4.0	82.3	-	1.4	50.4	7.2	2.1	-	40.3	20.2	[75]
Sugarcane bagasse	46.5	33.4	19.0	-	-	-	1.2	44.8	6.1	2.6	0.7	45.8	15.6	[76]
Sugarcane bagasse/black liquor	41.3	23.7	25.6	8.8	69.8	15.3	6.2	43.2	5.5	0.5	-	32.6	17.8	[77]
Sunflower stalk	62.6	13.4	18.0	6.0	-	-	3.7	-	-	-	-	-	-	[78]
Tea Waste	31.2	22.8	40.3	-	-	-	3.4	49.6	5.5	0.5	-	44.4	17.1	[51]
Verbascum stalk	50.3	17.6	31.4	5.3	-	-	2.4	-	-	-	-	-	-	[79]
Walnut shell	23.3	20.4	53.5	5-12	-	-	1.5	45.6	4.3	-	-	50.1	14.7	[55]
Wheat straw	-	-	-	7.9	77.3	9.5	5.3	40.5	5.6	0.9	0.1	52.9	-	[80]
<b>Energy crops</b>														
Acacia mangium	43.1	72.1	29.9	-	-	-	0.6	48.9	5.9	0.2	-	44.5	19.7	[58]
Cunninghamia lanceolata	42.5	-	32.4	-	-	-	0.3	50.0	6.4	0.2	-	43.5	18.2	[81]
Duckweed	Protein : 23.2, lipid: 9.2, Carb.: 26.1			13.2	58.7	9.8	18.3	35.4	4.8	3.7	1.0	32.3	13.1	[82]
Ferula orientalis L	41.3	22.6	26.1	5.7	-	-	4.9	44.7	6.1	0.8	-	48.5	16.2	[83]
Kenaf	42.6	81.3	10.3	-	-	-	1.9	44.6	5.7	0.1	-	47.7	17.8	[58]
Metroxylon sp. petioles	33.4	62.7	21.9	-	-	-	5.0	43.9	5.4	0.4	-	45.4	17.7	[58]
Miscanthus grass	-	-	-	6.1	75.8	15.2	2.9	44.6	5.7	0.1	-	49.1	-	[84]
Natural hay	31.4	31.4	12.0	5-12	-	-	7.8	40.6	4.2	1.0	-	54.2	13.2	[55]
Oil-palm petioles	37.0	71.7	20.9	-	-	-	4.0	43.6	5.1	0.2	-	47.1	18.2	[58]
Onopordum heteracanthum	40.3	24.1	27.8	5.7	-	-	5.2	44.9	6.6	1.7	-	46.8	16.3	[85]
Pinus banksiana	-	-	-	-	81.5	18.3	0.2	53.3	6.2	0.1	0.1	40.3	19.7	[86]
Posidonia oceanica	-	-	-	5.5	54.4	14.3	26.1	35.5	3.6	0.3	0.2	28.9	12.8	[87]
Typha latifolia	37.3	70.1	21.7	5.7	-	-	3.1	-	-	-	-	-	-	[88]
<b>Other wastes</b>														
Anaerobic Sludge	15.0	<1.0	54	-	-	-	31	-	-	-	-	-	-	[89]
Fat meat swine	-	-	-	8.8	65.9	25.3	0.0	77.2	13.8	0.4	0.1	8.6	39.3	[90]

Feedstock	Organic Components			Proximate Analysis				Ultimate Analysis					HHV	Ref.
	Protein	Lipid	Carbohydrates	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O		
carcasses														
Garbage	18.4	5.3	55	90.3	-	-	25.3	44.2	5.8	3.5	-	31.2	17.7	[91]
Lean Meat swine carcasses	-	-	-	70.3	67.6	3.9	0.0	17.4	10.2	3.2	0.4	68.7	8.8	[90]
Oil mill wastewater	-	13.9	-	88.0	58.7	8.5	22.5	54.9	7.0	1.4	n.d.	14.2	24.3	[92]
Pulp/paper sludge		85 (total organic matters)		-	-	-	15.0	45.6	5.2	7.2	1.7	25.3	18.3	[93]
Sewage sludge	8.0	1.1	44.2	75-80	51.3	2.0	46.7	26.0	3.9	4.5	1.0	15.5	11.6	[94]
Swine Manure	25	22	37	-	-	-	16.0	-	-	-	-	-	-	[89]
Wet organic waste matter		51 (total organic matters)		78.0	-	-	22.0	51.0	8.0	6.0	-	13.0	-	[95]
Algae														
Bacillariophyta sp.	29.6	8.2	27.0	88.6	52.4	12.4	35.2	31.9	4.5	5.2	1.1	22.0	13.4	[96]
Cyanobacteria sp.	35.2	<0.5	35.4	85.0	61.8	9.3	28.9	33.6	5.2	5.9	0.3	25.9	14.5	[96]
Dunaliella tertiolecta	50.3	17.8	21.7	25.5	53.1	11.6	9.8	39.0	5.4	2.0	-	43.9	-	[97]
Mixed-culture algal biomass	27.2	1.7	-	-	52.5	-	47.5	27.9	3.0	3.9	0.4	65.2	12.9	[98]
Nannochloropsis gaditana	32.2	13.4	-	-	-	-	12.4	47.6	7.5	6.9	0.5	25.1	23.1	[99]
Nannochloropsis occulta	57.0	32.0	8.0	7.2	-	-	26.4	57.8	8.0	8.6	-	25.7	17.9	[100]
Phaeodactylum tricornutum	37.5	21.9	-	-	-	-	24.6	38.0	4.8	5.2	0.7	-	-	[101]
Spirulina platensis	64.7	4.8	19.3	6.8	90.4	-	9.6	49.6	6.2	10.8	0.8	33.4	-	[102]
Synechococcus sp.	54.2	6.1	22.9	10.4	-	-	28.9	48.3	9.2	6.2	-	-	11.3	[103]
Synechocystis cf. salina	53.7	2.8	40.5	4.5	-	-	11.2	46.1	8.0	3.5	-	-	15.4	[103]
Green Algae														
Botryococcus branunii		98 (total organic matters )		90	-	-	2.0	63.1	11.7	2.8	-	22.4	-	[104]
Chaetomorpha linum	11.1	3.3	43.9	5.1	-	-	36.6	26.5	4.1	3.4	2.1	31.0	10.3	[33]
Chlorella pyrenoidosa	71.5	0.2	22.5	6.1	94.3	-	5.7	51.2	6.8	11.3	0.7	30.7	-	[102]
Chlorella sorokiniana	45.1	21.2	33.7	2.8	64.6	22.8	10.1	58.0	7.7	10.5	0.7	23.1	26.6	[105]
Chlorella vulgaris	55.0	25.0	9.0	8.5	-	-	7.0	52.6	7.1	8.2	0.5	32.2	23.2	[100]
Cladophora coelothrix	17.8	4.6	45.4	6.7	-	-	25.5	30.9	5.0	5.2	2.3	34.9	12.7	[33]
Cladophora glomerata	26.3	2.4	34.7	4.4	44.8	29.1	26.1	31.3	5.0	4.9	2.0	30.7	13.7	[106]
Derbesia tenuissima	21.6	10.4	26.9	6.4	-	-	34.7	29.2	4.8	4.5	2.8	27.4	12.4	[33]
Desmodesmus sp.	38-44	10-14	13-20	-	-	-	-	52.0	7.3	6.9	-	33.9	23.4	[107]

Feedstock	Organic Components			Proximate Analysis			Ultimate Analysis						HHV	Ref.
	Protein	Lipid	Carbohydrates	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O		
Enteromorpha prolifera	-	-	-	8.6	68.7	6.8	15.9	35.2	5.2	2.1	-	33.0	13.4	[108]
Oedogonium sp.	19.8	8.5	57.8	7.2	-	-	6.7	44.4	6.7	4.2	0.2	39.2	19.3	[109]
Oedogonium sp.	22.5	9.4	41.0	6.5	-	-	20.6	36.6	5.7	4.8	0.4	30.9	15.8	[33]
Scenedesmus almeriensis	30	13.1	-	-	-	-	20	38	5.6	5.5	0.5	30.4	16.8	[99]
Tetraselmis sp.	43.6	19.5	-	-	-	-	15.9	45.0	5.9	6.3	1.1	-	-	[101]
Ulva ohnoi	16.3	1.9	43.9	7.2	-	-	30.7	27.7	5.5	3.5	5.0	41.1	11.7	[33]
<b>Brown Algae</b>														
Alaria Esculenta	-	-	-	6.8	-	-	25.2	34.6	4.7	1.9	0.6	31.1	13.9	[110]
Fucus vesiculosus	10.7	1.2	-	-	-	-	36.0	34.3	5.2	2.0	2.8	19.7	16.0	[111]
Laminaria digitata	-	-	-	6.6	-	-	23.9	33.1	4.7	1.8	0.8	33.9	13.1	[110]
Laminaria hyperborea	-	-	-	5.6	-	-	16.6	35.8	5.1	1.5	0.9	39.1	14.2	[110]
Laminaria saccharina	-	-	-	-	69.3	14.1	16.6	39.4	5.1	3.0	0.6	52.0	14.5	[112]
Macrocystis pyrifera	-	-	-	-	42.4	33.4	18.5	27.3	4.1	2.0	1.9	34.8	16.0	[113]
Sargassum tenerrimum	-	-	-	5.7	61.5	11.9	26.5	32.1	4.7	0.9	1.6	60.7	12.0	[114]
Sargassum. patens	-	-	-	14.4	55.5	12.4	17.8	40.2	5.2	2.0	1.0	33.9	15.5	[115]
<b>Red Algae</b>														
Cyanidioschyzon merolae	56.5	2.0	-	67.1	-	-	7.1	48.1	5.1	9.0	1.2	36.5	18.1	[116]
Galdieria sulphuraria	45.1	3.2	42.3	67.4	-	-	9.4	42.4	3.9	9.4	1.4	42.9	16.4	[117]
Gracilaria gracilis	13.7	1.7	28.6	5.9	53.1	10.9	36.0	36.8	5.9	2.9	2.0	17.5	11.7	[106]
Porphyridium creuntum	43	8	40	5.1	-	-	24.4	51.3	7.6	8.0	-	33.1	14.7	[100]

**Table 3**  
Range of values for various biomass HTL feedstocks

Feedstock	Fibre analysis (wt. %)			Proximate analysis (wt. %)				Ultimate analysis (wt. %)					HHV (MJ/kg)
	Cellulose	Hemi-cellulose	Lignin	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O	
Wood	33-47 (41.0)	20-74 (34.3)	21-32 (24.5)	6-15 (8.8)	80-84 (81.4)	13-16 (14.5)	0.1-2 (0.6)	46-50 (48.7)	6-7 (6.2)	0-0.4 (0.2)	0.05-0.1 (0.08)	43-48 (44.8)	16-21 (18.1)
Agricultural waste	21-65 (37.0)	8-79 (34.1)	12-54 (27.3)	2-59 (10.4)	70-84 (76.0)	7-18 (11.7)	1-28 (7.7)	38-55 (46.1)	4-7 (5.8)	0.2-4 (1.1)	0.04-1.1 (0.4)	33-54 (44.5)	14-21 (17.3)
Energy crops	31-43 (38.8)	23-81 (54.5)	10-32 (22.6)	5-13 (7.4)	54-82 (67.6)	10-18 (14.4)	0.2-26 (6.2)	35-53 (44.2)	4-7 (5.5)	0.1-4 (0.7)	0.1-1 (0.4)	29-54 (44.0)	13-20 (16.6)
Feedstock	Protein	Lipid	Carb.	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O	HHV (MJ/kg)
Algae	11-72 (37.0)	0.2-32 (9.6)	8-58 (30.8)	3-90 (20.4)	42-94 (61.7)	7-33 (15.9)	2-47 (20.8)	26-63 (40.5)	3-12 (5.9)	0.9-11 (5.1)	0.2-5 (1.3)	18-65 (33.9)	10-27 (15.6)
Other wastes	8-25 (16.6)	1-22 (10.6)	37-55 (47.6)	9-90 (70.1)	51-68 (60.9)	2-25 (9.9)	0-47 (19.8)	17-77 (45.2)	4-14 (7.7)	0.4-7 (3.7)	0.05-2 (0.8)	9-69 (25.2)	9-39 (20.0)

Note: Average values are given in brackets

According to Table 2 and Table 3, the lignocellulosics biomass such as woods, agricultural wastes and energy crops are composed mainly of cellulose (37%-41%), hemicellulose (34%-55%) and lignin (23%-27%) which are polymers mainly made of organic compounds consisting carbon, hydrogen and oxygen atoms [21]. In addition, there are traces of other compounds such as fatty acids, alcohols, aliphatics, carboxylic acids, ketones, aromatics, aldehydes and other extractives and inorganic compounds [32, 118]. These kinds of biomass are extracted from forests, food industry wastes, different non-edible crops, and even wood processing industry wastes. However, the algae and waste biomass feedstocks are mainly significant amounts of protein (17%-37%) and lipid (10%-11%) as well as carbohydrates (31%-48%). Between lignocellulosics, woods have higher heating values and less ash; however, other factors such as availability, yield, cultivation time, transportation cost, end-user price and environmental issues should also be considered. The moisture content of feedstock varies considerably between different studies. This may be due to the different feed preprocessing conditions. For example algae or lignocellulosic feedstocks could be dried or processed as a slurry. However, waste feedstock is usually reported as received/wet.

## 2.2. Composition of HTL biocrude

The compounds detected in different HTL biocrude feedstocks include esters, phenolic compounds, aromatics and heterocyclic compounds, aldehydes, acids, ketones, alkanes and alkenes, alcohols and nitrogenates. Table 4 summarises the most common compounds in biocrudes with different feedstocks based on gas chromatography–mass spectrometry (GC-MS) analysis.

**Table 4**  
Chemical group detected by GC-MS for different biocrudes

Feedstock	GC-MS area percent range %									Ref.
	Esters	Phenolic	Aromatics and Heterocyclic	Aldehydes	Acids	Ketones	Alkanes and alkenes	Alcohols	Nitrogenates	
Wood	0-24	<b>11-62</b>	6-24	0-18	1-25	2-32	0-23	1-12	0-8	[50, 55, 56, 60, 61]
Agricultural wastes	2-39	<b>5-65</b>	4-35	0-17	2-38	1-17	0-13	1-33	0-8	[67, 72, 73, 77, 119, 120]
Energy crops	1-41	<b>7-70</b>	6-74	0-8	6-39	1-24	2-9	2-9	0-15	[83, 85, 86, 88]
Other wastes	<b>2-46</b>	0-20	0-43	0-9	<b>4-75</b>	0-24	1-7	0-18	<b>4-24</b>	[89, 90, 92, 94]
Algae	<b>2-63</b>	0-10	3-20	0-8	<b>3-66</b>	0-15	1-22	0-5	<b>2-41</b>	[89, 97, 98, 106, 121]

HTL process temperature, pressure, catalyst type and solvent can modify the biocrude quality [85, 97, 98, 102, 121-123]. The process conditions affect the biocrude compounds interactions and reaction pathways which have been widely discussed in the literature [107, 124, 125]. In addition, reaction kinetics and biocrude yield could be modified by changing the process conditions [100, 126, 127]. The type of solvent used in biocrude extraction is also affects the biocrude quality[128]. However, as might be expected the feedstock origin and its composition has a big role on the biocrude composition. Phenolic compounds are among the most common compounds in biocrudes from lignocellulosic biomass, while esters and acids are more common in biocrudes from other wastes and algae. The most common phenolic compounds in the lignocellulosic biomass biocrudes are phenol and phenolic derivatives including 2-methoxyphenol, 2-methylphenol, and 4-propylphenol. Phenolic compounds are the result of biomass lignin conversion by breaking carbonyl and C-C bonds and to some extent, carbohydrate and protein conversion [129-131]. Nevertheless, the phenolic derivatives, which are more resistant to hydro-deoxygenation [132], are more common than simple phenols in biocrude.

The most common acidic compounds in biocrude are carboxylic acids such as hexadecanoic acid and their ester derivatives such as hexadecanoic acid methyl ester. The high content of acids and esters in biocrude leads to an increase in total acid number (TAN) which is undesirable due to difficulty in storage and fuel instability [61]. In addition, the presence of alkyl chains such as alkyl and hydroxyl groups in some carboxylic acids leads to polymerisation reactions, which affect vehicle life [133]. Similar to the elemental analysis results (Table 2), the nitrogenates in algae and waste biocrudes are considerably higher in quantity (24-41 %) than in lignocellulosics (8-15 %) due to algae and waste feedstocks being richer in proteins [131]. The most common nitrogenates are furan, pyrrole and indole derivatives.

The wide range of compounds in biocrude reveals their complexity, which is a key issue for upgrading biocrude. There are other important problems with biocrude in comparison with conventional products including low HHV, high viscosity, high oxygen content, high heteroatoms content and instability. Fractional distillation as a physical method might play a role in some of these issues which will be discussed in the following sections.

### **3. The role of distillation in categorising and characterising biocrude**

Usually, petro-crude is classified by various bulk and physical properties such as density, viscosity, elemental content, smoke and pour points and true boiling point (TBP) distillation curve, which is obtained using various prescribed test methods [29]. These properties, which are known as assay data, are used by refineries to investigate the oil refining behaviour and design or select the best process for upgrading [134]. Distillation TBP data, using the ASTM D2892 standard method [135] is an essential procedure that extracts the boiling point range of petro-crude compounds in the shape of true boiling point curve. The TBP curve temperature range then could be divided into several sub-ranges, which makes commercial fractions such as gas, gasoline, diesel and fuel oil [29].

Currently, there is no TBP procedure specifically for biocrude distillation [49]; however, a similar TBP method for petro-crude has been applied for biocrude in several studies e.g. [49, 136-138]. In contrast with the bulk properties of biocrude such as viscosity, flash point and melting point which give a general view of biocrude, biocrude's fractional behaviour such as TBP curves would be truly useful for characterising biocrude [49]. For instance, according to the TBP curve, biocrude could be categorised into commercial fractions and be compared with equivalent petro-crude products in more detail in many cases such as heating values or nitrogen and sulphur contents [136]. Applying different biocrude fractions in the best possible processing units in a conventional refinery based on their heteroatom contents and other physical properties such as HHV for co-processing may optimise the whole process financially [32]. However, more studies are needed in this area.

Fractional distillation is a promising technique in the characterisation of HTL biocrude. Understanding the fuel combustion behaviour and chemical structure improve if fuel composition can be determined accurately [32]. For instance, understanding individual compounds that contain S and N may assist in developing approaches to remove them selectively. Unfortunately, the effort required to detect all the biocrude compounds individually may be greater than its value due to their complexity. However, distillation may be helpful in reducing the biocrude complexity by separating it into several fractions prior to GC-MS. This reduction in the number of compounds may assist GC-MS as the most popular biocrude characterisation technique since it has some limitations including large background signals due to the complex nature of the whole biocrude and low-efficiency separation [122, 139]. Distillation may assist chemical analysis by reducing the number of sample compounds,

thus instead of a complex whole biocrude, individual fractions such as gas and gasoline can be analysed separately [140]. There are other studies which have used Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) [139, 141] or solvent extraction [6] to separate biocrude and then characterise more, so the logic to analyse the separated biocrude is not insane. In addition, distillation may be cheaper than more complex spectroscopy methods. The distillation application for HTL biocrude characterisation upgrading in the literature will be discussed in the next section.

#### 4. Distillation studies in the HTL and pyrolysis biocrude

The number of studies that have explored biocrude distillation is limited. Table 5 highlights distillation research studies in the literature for both the HTL and pyrolysis processes. There are decidedly fewer studies that focus on upgrading fuel using distillation for HTL biocrude than that for pyrolysis biocrude; further research is needed to progress HTL biocrude upgrading by distillation.

**Table 5**  
Literature on distillation studies on pyrolysis and HTL biocrude

Process	Feedstock	Distillation conditions	Description	Ref.
<i>Simple distillation</i>				
HTL	Microalgae (Spirulina sp. and Tetraselmis sp.) HTL biocrude	70-360 °C 1.325 kPa	<ul style="list-style-type: none"> <li>The biocrude was vacuum distilled to improve the quality.</li> <li>The improvement in quality was substantial including 25 % increase in HHV and up to 95% deoxygenation of HTL biocrude.</li> </ul>	[30]
Pyrolysis	Rice husks pyrolysis oil	IBP-240 °C 101.325 kPa	<ul style="list-style-type: none"> <li>Combining atmospheric distillation and co-pyrolysis for commodity chemical production has been done.</li> <li>Study on the new compound generation within distillation using GC-FID.</li> </ul>	[28]
HTL and Pyrolysis	Duckweed HTL biocrude and pyrolysis oil	200-400 °C Pressure not reported	<ul style="list-style-type: none"> <li>Distillation was used to compare the upgrading impact of pyrolysis and HTL.</li> </ul>	[82]
Pyrolysis	Softwood and bark pyrolysis oil	60-100 °C 10 kPa Distillation time: 0.5-1 hour	<ul style="list-style-type: none"> <li>Distillation was performed for the extraction of low MW compounds.</li> <li>Distillation reduced the corrosiveness of distillation residue by lowering TAN (25%) due to reduce water content, so distillation improved the stability and the destructive potential of biocrude for further catalytic processing.</li> <li>Distillation increased the HHV of 60-80 °C fraction (at 10 kPa) biocrude by second times (8.3 to 19.6 MJ/kg).</li> <li>Short path vacuum distillation is an effective method for biocrude improvement and blending with conventional</li> </ul>	[142]



Process	Feedstock	Distillation conditions	Description	Ref.
			fuels.	
Pyrolysis	Rice husks pyrolysis oil	IBP-80 °C (AET~IBP-197 °C @ 1 atm [143]) 0.2 kPa	<ul style="list-style-type: none"> <li>Total distillation yield was 61%.</li> <li>Distillation increased the lower heating value (LHV) of vacuum distilled biocrude at 80 °C by two times from 17.42 MJ/kg to 34.2 MJ/kg.</li> <li>Distillation decreased the water content of distilled biocrude from 25.2wt. % to 0.01wt. %.</li> <li>Distillation reduced the corrosiveness of distilled biocrude by increasing pH from 2.8 to 6.8.</li> </ul>	[31]
Pyrolysis	Switchgrass feedstock tail-gas reactive pyrolysis (TGRP) oil	IBP-235 °C Not reported pressure	<ul style="list-style-type: none"> <li>Extraction of valuable chemicals in TGRP biocrude using distillation.</li> <li>Distillation of TGRP oils leads to the generation of more organic compounds than biocrude by three times.</li> <li>Naphthalene was purified up to 65%.</li> <li>Distillation curve for TGRP was calculated theoretically.</li> </ul>	[144]
HTL	Spirulina sp.	IBP-340 °C 1 kPa	<ul style="list-style-type: none"> <li>Microalgae HTL biocrude was hydrotreated and the oxygen content completely removed.</li> <li>Distillation was performed in order to investigate the nitrogen distribution in hydrotreated biocrude.</li> <li>More nitrogen content was reported in the heavy fractions.</li> </ul>	[145]
Pyrolysis	Unknown pyrolysis oil	20-80 °C (AET~103-173 °C @ 1 atm [143]) 5 kPa	<ul style="list-style-type: none"> <li>Distillation was performed in the presence of an alcohol and solid catalyst to improve the distillate properties.</li> <li>The moisture of distilled biocrude at 80 °C reduced from 31.6wt. % to 4.9wt. %.</li> <li>The HHV of distilled biocrude increased from 20.6 to 27.7 MJ/kg.</li> </ul>	[146]
<b><i>Bench-scale column type distillation</i></b>				
Pyrolysis	Corn stover pyrolysis oil	IBP-250 °C 50 kPa	<ul style="list-style-type: none"> <li>The phenolic compounds (53%) separated using distillation (in the heavy fraction).</li> <li>Distillation decreased the water content (97%), corrosiveness (69-79% reduction in TAN) and increased the HHV (3-4.5%).</li> </ul>	[147]
Pyrolysis	Rice husks pyrolysis oil	20-55 °C 101.3 kPa	<ul style="list-style-type: none"> <li>Low temperature distillation performed to separate ethyl ester.</li> <li>The moisture of biocrude decreased from 33wt. % to 0.52-5.03 wt. % The HHV increased from 14.3 to 21.5-24.5.</li> </ul>	[148]
Pyrolysis	Loblolly Pine pyrolysis oil	IBP-400 °C 20 kPa	<ul style="list-style-type: none"> <li>A two-stage distillation procedure was performed to extract phenolic compounds in biocrude.</li> <li>Eugenols and guaiacols concentrated from 10wt% to 35wt% using distillation.</li> <li>The distillation yield was 60-80%.</li> <li>The moisture content of heavy fractions improved significantly using distillation by 87-90 %.</li> </ul>	[149]
HTL	Swine manure glycerol assisted HTL biocrude	232-500 °C 101.325 kPa	<ul style="list-style-type: none"> <li>Biocrude was chemically and physically characterised.</li> <li>The biocrude was separated into nine distillates.</li> <li>The HHV of the heaviest fraction increased from 36.41 to 45.38 with the aim of distillation.</li> </ul>	[150]

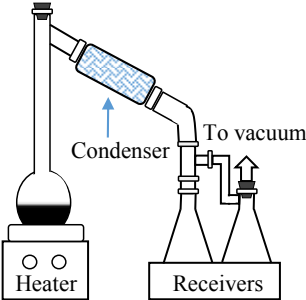
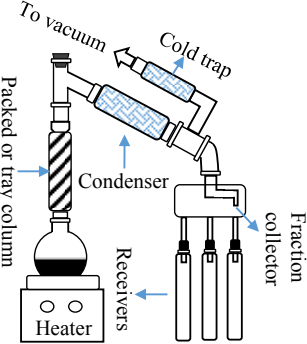
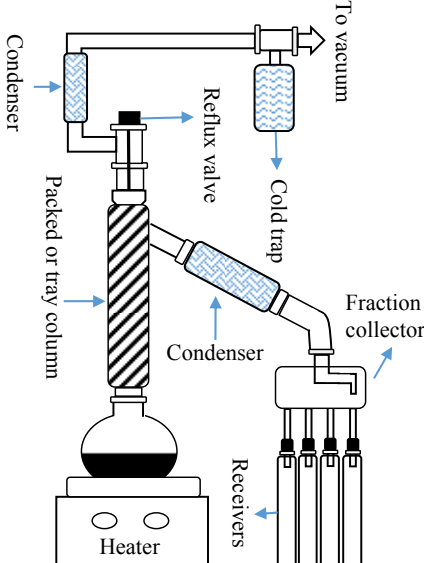
Process	Feedstock	Distillation conditions	Description	Ref.
HTL	Swine manure and food processing waste HTL biocrude	198-310 °C 101.325 kPa	<ul style="list-style-type: none"> <li>Distillation and transesterification was performed for upgrading purpose instead of other conventional methods such as hydrogenation.</li> <li>Energy recovery in the distillation and transesterification method was twice in comparison with hydrotreating.</li> <li>The upgraded distillates showed the comparable properties with diesel.</li> </ul>	[151]
Pyrolysis	Microalgae pyrolysis oil	IBP-200 °C 103.325-0.09 kPa	<ul style="list-style-type: none"> <li>The microalgae biocrude was upgraded using two atmospheric fractional distillation and vacuum distillation techniques to examine their sustainability to be used as a fuel.</li> <li>Vacuum distillation had cleaner separation; however, fractional distillation had more yield.</li> <li>Distillation of biocrude, definitely improved the properties of distillates in HHV (increase by 0.1-6.7%), TAN (99% reduction for light fractions).</li> </ul>	[152]
<b>Large-scale column type distillation</b>				
HTL	Hardwood HTL biocrude	100-375 °C 0.013 kPa	<ul style="list-style-type: none"> <li>Biocrude was chemically and thermophysically characterised using fractional distillation.</li> <li>The improvement in biocrude quality using distillation was highly promising such as decreasing nitrogen content in the all fractions.</li> </ul>	[49]
Pyrolysis	Mesua ferrea L. seed oil processed oil	35-370 °C 0.013 kPa	<ul style="list-style-type: none"> <li>The feed distillate into four conceptual lumps including gasoline, kerosene, diesel and wax and the fuel characterisations of the different distillates conformed petro-crude products.</li> <li>The yield of distillation was 62wt. %. Distillation increased the HHV from 40 to 44 for diesel fraction.</li> </ul>	[136]
Pyrolysis	Sewage sludge pyrolysis oil	65-374 °C Not reported pressure	<ul style="list-style-type: none"> <li>Pyrolysis oil was divided into five fractions.</li> <li>Distillation decreased the water content (up to 75%), and increased the HHV (up to 46%).</li> <li>Distillation decreased the oxygenated compounds and sulphur content in heavy fraction by 58 % and 64 %, respectively.</li> <li>The oil and some fractions had the potential to be used instead of No. 2 fuel standard in China.</li> </ul>	[137]
HTL	Microalgae (Tetraselmis sp. and Arthrospira platensis) HTL biocrude	IBP-370 °C 0.27 kPa	<ul style="list-style-type: none"> <li>Biocrude-petrocrude, 10%-90% blend, was distilled and characterised chemically.</li> <li>The upgrading features such as HHV were also studied.</li> </ul>	[138]
Pyrolysis	Brown alga Saccharina Japonica pyrolysis oil	25-160 °C (AET~108-263 °C @ 1 atm [143]) 5.33 kPa	<ul style="list-style-type: none"> <li>For chemical characterisation, biocrude was divided into three different fractions.</li> <li>The distillation yield was 83 wt%.</li> <li>Aliphatic and aromatic compounds and ketones, acid and ethers were separated using distillation.</li> <li>The organic section of distilled biocrude was blended using</li> </ul>	[153]

Process	Feedstock	Distillation conditions	Description	Ref.
			fuel oil to improve its characteristics and showed genuinely high position to be used either alone or in the mixture.	

There are more studies which have reported pyrolysis biocrude distillation in comparison with HTL biocrude distillation. The power of distillation in assisting precise chemical analysis was revealed in studies where a comprehensive chemical characterisation analysis was performed using distillate products. The distillation studies performed with HTL and pyrolysis biocrude could be categorised into two major groups. The first group is simple distillation which usually uses lab-scale distillation apparatus in which biocrude is separated into two or three distillates. Although there are studies with more than three distillate cuts [28, 144], nevertheless this kind of distillation is not optimal for separating biocrude into multiple distillates due to the lack of equilibrium stages due to the lack of trays or packing. In simple distillation, the lightest distillate or water phase contains mostly water-soluble polar compounds and the heavier distillates contain more non-polar shows quality improvement in comparison with biocrude [30, 31]. The second group uses packed or tray column for performing fractional distillation mostly according to ASTM D2892 in which biocrude is divided into several fractions based on TBP and could be operated and categorised into large and bench scale. Table 6 presents an overview of the different distillation apparatuses used in the literature.

**Table 6**

General overview of different distillation apparatus on biocrude conducted in research studies.

Description	Simple distillation	Column type distillation	
		Bench scale distillation	Large scale distillation
Schematic view			
Biocrude loading (g)	25-150	10-200	1000-1200
Number of ideal stages	N/A	1-5	10-15
Number of fractions	2-6	2-9	6-11
Notes	<ul style="list-style-type: none"> <li>+ Easy to operate</li> <li>+ Cheap</li> <li>- Problem in fractionation</li> <li>- Not ideal for multiple fractions</li> </ul>	<ul style="list-style-type: none"> <li>+ Fractionation capability</li> <li>+ Best apparatus for small scale</li> <li>- Expensive</li> <li>- Hard to operate</li> </ul>	<ul style="list-style-type: none"> <li>+ Fractionation capability</li> <li>+ Capability to perform large scale</li> <li>- Expensive</li> <li>- Hard to operate</li> </ul>
Ref.	[28, 30, 31, 82, 142, 144-146]	[147-152]	[32, 49, 136-138, 153]

For fractional distillation involving several fractions, the analysis is more challenging and the same techniques for biocrude analysis could be applied. The most common techniques for analysis biocrude are GC-MS, Fourier-Transform Infrared Spectroscopy (FTIR), CHNS elemental analysis and thermogravimetric analysis (TGA). There are other analytical methods which are applied in some studies for biocrude characterisation including (NMR) spectroscopy [153-155], GC with Flame Ionization Detector (GC-FID) quantitative analysis [142], Fourier-Transform Ion Cyclotron Resonance (FT-ICR) [141] and two dimensional GC-MS (GCxGC-MS) [32, 49] with improvements in separation and detection accuracy. In addition to chemical characterisation, the impact of distillation on biofuel upgrading [146, 148, 156] was investigated as well as biofuel stability improvement [31, 148], extracting commodity chemicals [144, 149, 157], and even blending with petro-crude [142, 153] which will be discussed in the following sections.

## **5. Effect of distillation on the biocrude elemental content**

### **5.1. Biomass and biocrude elemental status before distillation**

The five essential atoms in biocrude are C, H, N, S and O, although carbon and oxygen are the most common in biocrude by wt. %. Table 7 shows the elemental composition of different biocrude feedstocks. The mean values of each element are shown in Table 8. There are very few available data for sulphur and nitrogen contents of biocrude since the heteroatoms distribution in biocrude was not the main focus of research in HTL studies. However, due to the recent strict environmental regulations, the heteroatom content of biocrude will need studying in more detail. The heteroatom content of biocrude and recent studies in this area will be discussed further in the following sections.

**Table 7**

Elemental composition, yield and HHV of different biomass feedstocks after HTL processing

Feedstock	Yields (%)	Process conditions	Ultimate analysis (wt. %)					Catalyst	Max HHV (MJ/kg)	Ref.	
			C	H	N	S	O				
<i>Wood</i>											
Beech wood	28.4	377°C, 0.01 wt. % DM, 25 min	75.1	6.0	0	-	19.1	-	34.9	[51]	
Birch wood sawdust	40.0	300°C,10 wt. % DM, 30 min, 90bar	66.5	6.1	0.1	-	27.3	KOH	26.3	[52]	
Hard wood	27.5	400°C,0.8 wt. , 300 bar	75.2	8.2	0.5	-	15.8	Alkaline cat.	34.3	[50]	
Oak wood	-	320°C, 20wt. % DM, 30 min	69.4	6.3	-	-	24.2	-	27.5	[55]	
Paulownia wood	36.3	340°C, 14wt. % DM,10 min	73.5	7.1	0	-	19.4	10%Fe	31.5	[56]	
Pine wood	40.0	300°C, 10wt. % DM, 0 min, 85bar	68.0	7.1	-	-	24.9	NaBO <sub>3</sub> ·H <sub>2</sub> O	28.6	[158]	
Rubber tree	30.7	300°C, 10wt. % DM, 30 min, 100bar	72.5	7.3	0.1	-	20.1	Na <sub>2</sub> CO <sub>3</sub>	31.5	[58]	
Spurse wood	25.8	377°C, 1 wt. % DM, 25 min	75.4	6.1	0	-	18.8	-	33.9	[51]	
Waste furniture sawdust	34.9	280°C, 14 wt.% DM, 15 min	73.9	7.1	0	-	19.0	K <sub>2</sub> CO <sub>3</sub>	31.8	[60]	
Willow	29.8	400°C, 20wt. % DM, 20 min, 330 bar	74.7	9.6	1.4	-	-	-	-	[61]	
<i>Agricultural waste</i>											
Bamboo shoot shell	6.7	150°C, 14wt. % DM, 120 min	47.1	10.6	1.1	-	41.1	H <sub>2</sub> SO <sub>4</sub>	23.8	[62]	
Banana stem	20.6	300°C, 10wt. % DM, 30 min, 100bar	74.6	7.3	0.8	-	17.3	Na <sub>2</sub> CO <sub>3</sub>	32.9	[58]	
Barely straw	31.8	320°C, 12wt. % DM, 20 min	68.0	8.0	0.7	-	23.4	K <sub>2</sub> CO <sub>3</sub>	30.2	[63]	
Blackcurrant pomace	29	300°C, 5wt. %, 60 min	73.3	9.6	3.4	0.1	13.6	-	35.9	[64]	
Cellulose	-	320°C, 20wt. % DM, 30 min	67.4	5.3	-	-	27.3	-	24.6	[55]	
Coconut husk	27.9	300°C, 10wt. % DM, 30 min, 100bar	73.0	6.1	0.2	-	20.6	Na <sub>2</sub> CO <sub>3</sub>	29.8	[58]	
Coconut shell	34.3	300°C, 10wt. % DM, 30 min, 100bar	70.4	6.4	0.2	-	22.9	Na <sub>2</sub> CO <sub>3</sub>	30.2	[58]	
Corn stalk	28.3	300°C, 10wt. % DM, 30 min, 100bar	72.8	6.1	0.5	-	20.6	-	29.7	[58]	
D. stramonium L. stalks	53.9	300°C, 75 min, 300 bar	74.2	8.1	0.4	-	18.4	ZnO	33.4	[66]	
Green landscaping waste branches	43.2	300°C, 9wt. % DM, 30 min 82-85 bar	69.1	6.7	0.4	<0.01	23.8	-	28.7	[69]	
Green landscaping waste leaves	33.7	300°C, 9wt. % DM, 30 min 82-85 bar	70.4	7.7	1.3	<0.01	20.6	-	31.3	[69]	
Hazelnut shell	22.1	377°C, 0.01 wt. % DM, 25 min	75.2	5.8	0.1	-	18.9	-	32.9	[51]	
Metroxylon sp. stem	28.5	300°C, 10wt. % DM, 30 min, 100bar	72.2	6.6	0.4	-	20.8	Na <sub>2</sub> CO <sub>3</sub>	28.1	[58]	
Oil palm empty fruit fibres	-	275°C, 42wt. % D22.M, 60 min	75.3	9.6	0.4	-	14.7	-	29.4	[68]	
Oil-palm husk	27.2	300°C, 10wt. % DM, 30 min, 100bar	73.5	7.2	1.4	-	17.9	Na <sub>2</sub> CO <sub>3</sub>	32.0	[58]	
Oil-palm shell	35.9	300°C, 10wt. % DM, 30 min, 100bar	79.9	8.1	0.8	-	11.2	Na <sub>2</sub> CO <sub>3</sub>	31.0	[58]	
Pineapple leaf	-	300°C, 10wt. % DM, 30 min, 100bar	73.8	7.5	1.9	-	16.8	Na <sub>2</sub> CO <sub>3</sub>	32.4	[58]	
Pre-treated sorghum bagasse	61.8	300°C, 20wt. % DM, 60 min	73.2	7.7	0.5	0.2	15.0	K <sub>2</sub> CO <sub>3</sub>	33.1	[72]	

Feedstock	Yields (%)	Process conditions	Ultimate analysis (wt. %)					Catalyst	Max HHV (MJ/kg)	Ref.
			C	H	N	S	O			
Rice husk	31.5	260°C, 20wt. % DM, 20 min, 40-150 bar	63.6	7.5	2.7	-	26.2	-	27.6	[73]
Rice stalk	55.0	325°C, 9wt. % DM, 60 min	-	-	-	-	-	-	29.0	[119]
Rice straw	47.8	320°C, 9wt. % DM, 15 min	63.0	8.0	0.7	-	28.4	-	28.6	[74]
Spent coffee grounds	47.3	275°C, 5 wt. % DM, 10 min, 20 bar	71.2	7.1	3.0	-	18.7	-	31.0	[75]
Sugarcane bagasse	16.5	250°C, 9wt. % DM, 15 min	64.4	7.4	0.5	0.1	27.5	-	27.4	[76]
Sugarcane bagasse/black liquor	55.4	350°C, 5 wt. % DM, 30 min, 10 bar	67.0	7.4	0.7	-	25.0	-	30.0	[77]
Tea waste	22.6	377°C, 0.01 wt. % DM, 25 min	71.6	5.6	0.0	-	22.8	-	33.6	[51]
Walnut shell	-	320°C, 20wt. % DM, 30 min	71.2	6.3	-	-	22.5	-	28.5	[55]
<b>Energy Crops</b>										
Acacia mangium	31.7	300°C, 10wt. % DM, 30 min, 100bar	71.7	6.5	0.4	-	21.5	Na <sub>2</sub> CO <sub>3</sub>	29.8	[58]
Cunninghamia lanceolata	20.1	360°C, 7 wt. % DM, 10 min	75.1	5.8	0.0	-	19.2	-	30.2	[81]
Duckweed	21.2	350°C, 40wt. % DM, 30 min, 220 bar	71.9	7.7	87.4 (g/L)	-	4.5	Ru/C	34.5	[82]
Ferula orientalis L.	45.5	300°C, 10wt. % DM, 10 min	56.6	7.8	0.2	-	35.3	Na <sub>2</sub> CO <sub>3</sub>	24.0	[83]
Kenaf	27.7	300°C, 10wt. % DM, 30 min, 100bar	72.9	6.5	0.3	-	20.3	Na <sub>2</sub> CO <sub>3</sub>	30.4	[58]
Metroxylon sp. petioles	23.4	300°C, 10wt. % DM, 30 min, 100bar	73.1	6.7	0.8	-	19.5	Na <sub>2</sub> CO <sub>3</sub>	31.0	[58]
Miscanthus	38	410°C, 7wt. % DM, 60 min, 285-305 bar	77.0	6.9	0.1	-	16.0	-	-	[84]
Natural hay	-	320°C, 20wt. % DM, 30 min	74.5	7.4	-	-	18.1	-	31.4	[55]
Oil-palm petioles	23	300°C, 10wt. % DM, 30 min, 100bar	70.4	6.4	0.6	-	22.6	Na <sub>2</sub> CO <sub>3</sub>	29.0	[58]
Onopordum heteracanthum	35.5	290°C, 12wt. % DM, 75 min	63.2	7.2	2.3	-	27.4	-	26.8	[85]
Pinus banksiana	40	300°C, 7wt. % DM, 40 min, 50 bar	71.4	8	0	-	20.6	-	31.8	[86]
<b>Other wastes</b>										
Anaerobic sludge	9.4	300°C, 20wt. % DM, 30 min, 120 bar	66.6	9.2	4.3	1.0	18.9	-	32.0	[89]
Fat meat swine carcasses	62.2	250°C, 60 min,	75.0	13.7	4.5	0.4	8.4	NaOH	32.4	[90]
Garbage	27.6	340°C, 10 wt. % DM, 30 min, 180 bar	73.6	9.1	4.6	-	12.7	Na <sub>2</sub> CO <sub>3</sub>	36.0	[91]
Oil mill wastewater	58	280°C, 12 wt. % DM, 30 min	75.5	11.9	0.5	n.d.	13.4	-	37.9	[92]
Pulp/paper sludge	46.9	280°C, 9 wt. % DM, 60 min	76.8	8.9	3.4	-	10.9	K <sub>2</sub> CO <sub>3</sub>	36.7	[93]
Sewage sludge	34.9	220°C, 10 wt. % DM, 30 min, 34-35 bar	58.4	8.0	8.6	0.9	24.1	-	27.0	[94]
Swine manure	24.2	340°C, 20 wt. % DM, 15 min, 7 bar	72.6	9.8	4.5	-	13.2	-	36.1	[159]
<b>Algae</b>										
Bacillariophyta sp.	18.2	350°C, 9 wt. % DM, 60 min	76.1	9.1	5.6	0.9	8.3	-	36.5	[96]
Cyanobacteria sp.	21.1	350°C, 9 wt. % DM, 60 min	76.0	9.1	6.3	1.2	7.4	-	36.5	[96]
Dunaliella tertiolecta	64.7	320°C, 9 wt. % DM, 30 min	71.8	9.1	5.4	-	13.6	-	35.0	[97]
Mixed-culture algal biomass	47.8	300°C, 25 wt. % DM, 90 min	65.7	8.8	3.9	-	21.7	-	30.0	[98]
Nannochloropsis gaditana	52.6	350°C, 9 wt. % DM, 15 min, 20 bar	76.1	10.3	4.5	0.4	8.8	-	38.0	[99]
Nannochloropsis occulta	23	350°C, 10 wt. % DM, 60 min	74.7	10.6	4.3	0	10.4	HCOOH	39.0	[100]

Feedstock	Yields (%)	Process conditions	Ultimate analysis (wt. %)					Catalyst	Max HHV (MJ/kg)	Ref.
			C	H	N	S	O			
Phaeodactylum tricornutum	54.3	375°C, 7 wt. % DM, 5 min	73.4	9.1	5.8	1	7.8	-	35.9	[101]
Spirulina algae	32.6	300°C, 20wt. % DM, 30 min, 120 bar	68.9	8.9	6.5	0.9	14.9	-	33.2	[89]
Spirulina platensis	53.7	360°C, 9wt. % DM, 20 min,	69.6	12.5	7.5	0.5	9.9	-	39.8	[121]
Synechococcus sp.	-	-	69.9	9.4	5.3	-	-	-	34.2	[103]
Synechocystis cf. salina	-	-	70.9	8.6	4.6	-	-	-	33.4	[103]
<b>Green Algae</b>										
Botryococcus branunii	57	300°C, 13wt. % DM, 60 min, 20 bar	84.2	14.9	0.3	-	0	-	50	[104]
Chaetomorpha linum	16.6	350°C, 7wt. % DM, 8 min, 90 bar	70.9	7.7	6.8	0.1	11.4	-	32.5	[33]
Chlorella sorokiniana	30.7	240°C, 10wt. % DM, 20 min, 90 bar	71.5	9.8	5.7	0.4	12.7	-	36	[105]
Chlorella vulgaris	31	240°C, 10wt. % DM, 20 min, 90 bar	74.0	9.6	7.7	0.9	7.8	-	37.5	[105]
Cladophora coelothrix	20	350°C, 7wt. % DM, 8 min, 90 bar	71.6	8.0	7.1	0.9	10.6	-	35.3	[33]
Cladophora glomerata	16.9	350°C, 9wt. % DM, 15 min,	70.4	8.4	4.0	2.0	12.3	-	33.1	[106]
Derbesia tenuissima	33.4	350°C, 7wt. % DM, 8 min, 90 bar	73.0	7.5	6.5	0.7	10.6	-	33.2	[33]
Desmodesmus sp.	49.0	375°C, 8wt. % DM, 5 min,	74.5	8.6	6.3	-	10.5	-	-	[107]
Enteromorpha prolifera	28.4	290°C, 25wt. % DM, 20 min	69.2	6.8	3.9	-	20.1	-	29.5	[108]
Oedogonium sp.	35.6	350°C, 7wt. % DM, 8 min, 70 bar	71.7	7.4	5.3	0.4	13.8	-	32.2	[109]
Oedogonium sp.	26.2	350°C, 7wt. % DM, 8 min, 90 bar	72.1	8.1	6.3	0.8	10.4	-	33.7	[33]
Scenedesmus almeriensis	51.5	350°C, 9 wt. % DM, 15 min, 20 bar	74.9	9.1	5.9	0.7	9.6	-	36.2	[99]
Scenedesmus sp.	33.6	350°C, 25 wt. % DM, 60 min	75.6	10.1	4.0	-	10.3	-	29.8	[160]
Tetraselmis sp.	45.6	375°C, 7 wt. % DM, 5 min	74	9.0	6.1	0.9	7.7	-	36	[101]
Ulva ohnoi	30.1	350°C, 7wt. % DM, 8 min, 90 bar	72.6	8.2	5.8	0.4	11	-	33.8	[33]
<b>Brown Algae</b>										
Alaria esculenta	17.8	350°C, 22 wt. % DM, 15 min	73.8	8.0	3.8	0.8	14	-	33.8	[110]
Fucus vesiculosus	22	350°C, 9 wt. % DM, 15 min	72.1	8.2	3.5	1	15.2	-	33.4	[111]
Laminaria digitata	17.6	350°C, 22 wt. % DM, 15 min	70.5	7.8	4.0	0.7	17	-	32.0	[110]
Laminaria hyperborea	9.8	350°C, 22 wt. % DM, 15 min	72.8	7.7	3.7	0.8	14.9	-	33.0	[110]
Laminaria saccharina	13	350°C, 22 wt. % DM, 15 min	74.5	7.9	3	0.6	14	-	33.9	[110]
Sargassum. patens c. agardh	32.1	340°C, 9 wt. % DM, 15 min, 30 bar	64.6	7.4	2.5	0.7	22.0	-	27.1	[115]
<b>Red Algae</b>										
Cyanidioschyzon merolae	22.7	300°C, 10 wt. % DM, 30 min,	76.8	5.1	5.7	0.9	11.5	KOH	33.7	[116]
Galdieria sulphuraria	20.5	240°C, 10wt. % DM, 20 min, 90 bar	69.7	8.7	7.2	1.3	13.2	-	33.9	[105]
Gracilaria gracilis	15.7	350°C, 9wt. % DM, 15 min,	71.6	10.2	7.1	1	13.1	-	36	[106]
Porphyridium creuntum	20.1	350°C, 10 wt. % DM, 60 min	72.5	9.1	5.7	0.4	13.3	HCOOH	36.3	[100]



**Table 8**

Mean values of elemental composition, yield and HHV of different biocrudes

Feedstock	Yield	Ultimate analysis (wt. %)					HHV (MJ/kg)
		C	H	N	S	O	
Wood	33-40 (25.8)	67-75 (72.4)	6-9 (7.1)	0-0.5 (0.1)	-	16-27 (21.0)	26-35 (31.1)
Agricultural waste	7-62 (34.6)	47-80 (70.2)	5-11 (7.3)	0-3 (1.0)	0.01-0.2 (0.1)	11-41 (21.4)	24-36 (30.2)
Energy crops	20-46 (30.6)	57-77 (70.7)	6-8 (7.0)	0-2 (0.5)	-	5-35 (20.5)	24-35 (30.0)
Algae	10-65 (31.3)	65-82 (72.6)	5-14 (8.8)	1-8 (5.3)	0-2 (0.8)	4-22 (12.0)	27-47 (34.7)
Other wastes	9-62 (37.6)	58-77 (71.2)	8-14 (10.1)	0.5-9 (4.3)	0.4-1 (0.7)	8-24 (14.5)	27-38 (34.0)

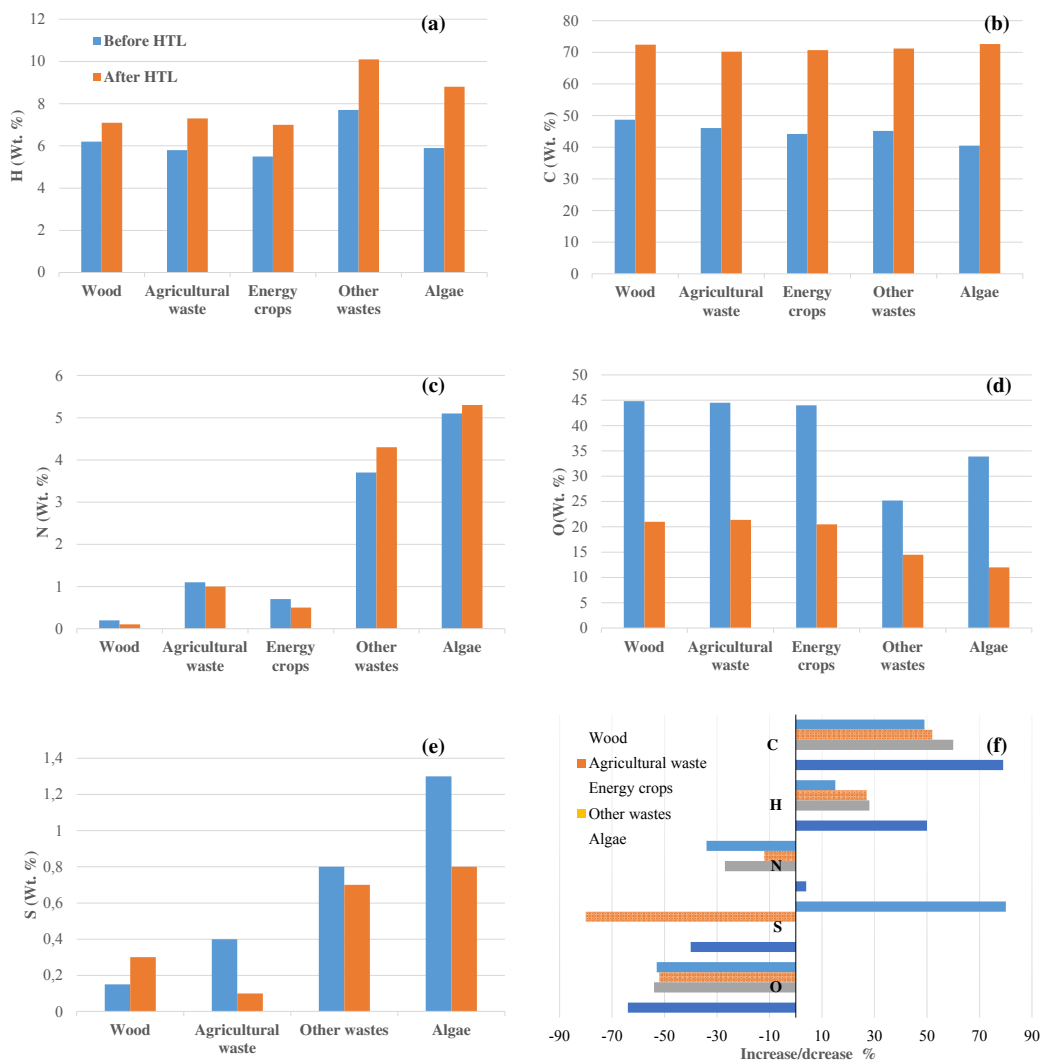
Note: Mean values are given in brackets

The average carbon content of different studies for each biomass type varies between 70-73 wt. %, while the mean oxygen content in biocrude in each biomass type varies between 12-21 wt. % (see Table 8). The high oxygen content of biocrude is a key difference between biocrude with petrocude and the main reason for the relatively low heating value of biocrude. The oxygen content could give an indication of the amount of oxygenated compounds abundance in the biocrude. The more oxygenated the biocrude, the higher the polarity and therefore poor miscibility with petrocude. Furthermore, a biocrude with more oxygenated compounds is generally more unstable [14, 161-163].

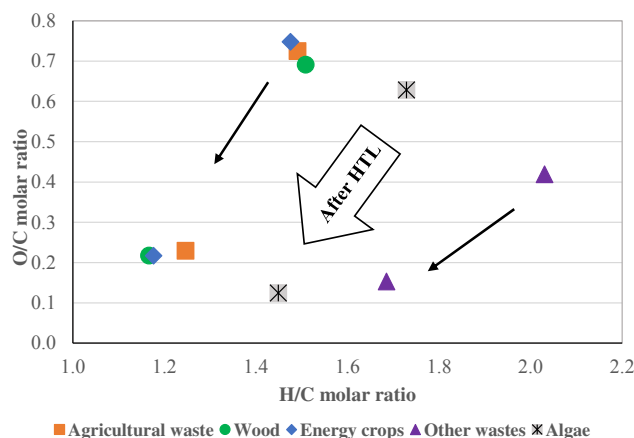
The O/C and H/C atomic ratio are two important factors for fuel assessment. A lower O/C ratio after the HTL process means more de-oxygenation has occurred. Also, a higher H/C ratio means lower aromatic content [122].

Figures 3 and 4 summarises the elemental analysis and Van Krevelen diagram for five different biomass resources based on Table 2. The amount by which O/C ratio reduced with HTL was in the order algae (80 %) > energy crops (71 %) > wood (69 %) > agricultural wastes (68 %) > other wastes (63 %) which shows better de-oxygenation in algae and energy crops. The amount by which H/C ratio reduced with HTL was in the order wood (23 %) > energy crops (20 %) > other wastes (17 %) > agricultural wastes  $\cong$  algae (16 %) which shows woods and energy crops have larger increases in aromatic content in comparison with raw

biomass. Nevertheless, this does not necessarily show the aromatic content order between different biocrudes feedstocks as shown previously in Table 4.



**Figure 3.** (a-e) Average elemental analysis of different feedstock types before (blue bars) and after (orange bars) HTL process. (f) Increase/decrease percent in the average elements' content before and after HTL process.



**Figure 4.** Van Krevelen diagram for different feedstock types before and after HTL process.

## 5.2. Oxygen content changes after distillation

The reduction in oxygen content increases the potential for biocrude to be used directly as a fuel for power generation unit operations (such as boilers, gas turbines and furnaces) without any further upgrading [31]. For simple distillation, the oxygen content for heavy fractions are always lower following distillation. In some cases significant changes in oxygen content up to 93% has been reported [30, 31]. The change in oxygen content of the light fractions has not been reported commonly. However, a decrease [82] and no change [145] in oxygen content are reported in the literature. The current studies in simple distillation mostly focused on lignocellulosic and algae feedstocks, although waste biomass resources have not been thoroughly investigated.

A similar change in oxygen content was also noted for studies using column type fractional distillation. The oxygen content reduces by 12-75% for all heaviest fractions which shows distillation could be a powerful technique for biocrude deoxygenation. In addition, oxygen reduction is reported in some light fractions up to 61 % [49, 137, 147, 153], although in some studies, oxygen content increased in the lightest fraction [32, 136, 149, 152] which shows the oxygen content behaviour for distillate depends on other related factors such as number of distillates, or distillation operating pressure and temperature which should be studied in more detail. However, in general the oxygenated compounds in light fractions are mostly light alcohols, esters, ketones and phenols such as propanol, ethyl acetate, hexanone and 4-methylanisole. While the oxygenated compounds in heavier fractions are high boiling point acids, ketone and phenolic compounds. Table 9 and Table 10 summarises the percent changes in biocrude properties after distillation. On average, the oxygen content increases for lighter

fractions and decreases for heavier fractions which means distillation is a successful method for separating most oxygenated compounds into lighter distillate fractions. In addition, distillation has a bigger effect on the oxygen content than carbon and hydrogen content.

**Table9**  
The distillation impact on properties of biofuels

Feedstock		Ultimate Analysis (wt. %)					HHV (MJ/kg)	Viscosity (cSt)	Density (kg/m³)	Ref.
		C	H	N	S	O				
Simple distillation										
Duckweed HTL biocrude	Biocrude	71.9	7.7	87.4 (g/L)	-	4.5	34.5	-	-	[82]
	Lightest fraction in distillation	68.7	9.1	18.5 (g/L)	0.32 (g/L)	3.8	35.5	-	-	
	Heaviest fraction in distillation	80	10.7	17.7 (g/L)	0.70 (g/L)	2	42	-	-	
Duckweed pyrolysis biocrude	Biocrude	75.1	9.1	58 (g/L)	-	4.5	37.6	-	-	
	Lightest fraction in distillation	69	8.5	22.4 (g/L)	0.23 (g/L)	4.6	34.6	-	-	
	Heaviest fraction in distillation	78.9	10	21.5 (g/L)	1.01 (g/L)	2.4	40.5	-	-	
Spirulina sp. HTL biocrude	Biocrude	70.5	10.1	5.4	1.1	12.9	35.3	-	-	[30]
	Lightest fraction in vacuum distillation	NR	NR	NR	NR	NR	NR	NR	NR	
	Heaviest fraction in vacuum distillation	83.8	9.5	4.6	0.6	1.5	40.4	-	-	
Tetraselmis sp. HTL biocrude	Biocrude	68.5	8.4	4.7	1.1	17.3	32.1	-	-	
	Lightest fraction in vacuum distillation	NR	NR	NR	NR	NR	NR	NR	NR	
	Heaviest fraction in vacuum distillation	85.2	8.2	4.8	0.7	1.1	40	-	-	
Rice husks pyrolysis biocrude	Biocrude	41.7	7.7	0.3	0.0	50.3	17.4	-	1190	[31]
	lightest fraction in vacuum distillation	NR	NR	NR	NR	NR	NR	NR	NR	

	Feedstock	Ultimate Analysis (wt. %)					HHV (MJ/kg)	Viscosity (cSt)	Density (kg/m <sup>3</sup> )	Ref.
		C	H	N	S	O				
	heaviest fraction in vacuum distillation	76	12.2	0.4	0	9.2	34.2	-	1270	
Bench scale column type distillation										
Swine manure HTL biocrude	Biocrude	-	-	-	-	-	36.4	9.71 cP	-	[150]
	Lightest fraction in atmospheric distillation	33.1	10.9	1.4	1.5	53.2	18.8	2.78 cP	-	
	Heaviest fraction in atmospheric distillation	81	10.7	2.2	1.6	4.5	45.4	6.85 cP	-	
Loblolly pine pyrolysis biocrude	Biocrude	70.2	7.2	0.3	-	22.4	-	169	1218	[149]
	Lightest fraction in vacuum distillation	12.3	10.2	-	-	77.5	-	-	1008.7	
	Heaviest fraction in vacuum distillation	72.8	8.6	-	-	18.4	-	-	1210	
Corn Stover pyrolysis biocrude	Biocrude	76.9	8.9	1.9	0.51	11.7	35.4	-	-	[147]
	Lightest fraction in atmospheric distillation	75.6	9.6	2.6	0.37	11.8	-	-	-	
	Lightest fraction in vacuum distillation	77.3	9.4	3.0	0.23	11.2	-	-	-	
	Heaviest fraction in atmospheric distillation	78.1	8.7	2.5	0.09	10.6	37	-	-	
	Heaviest fraction in vacuum distillation	77.6	8.5	2.7	0.08	10.1	36.5	-	-	
Nannochloropsis oculata pyrolysis biocrude	Biocrude	72.2	9.7	6.0	0.2	11.9	38.6	3.6	-	[152]
	Lightest fraction in atmospheric distillation	69	9.9	4.6	0.4	16.1	40.0	0.6	-	
	Lightest fraction in vacuum distillation	66.3	9.4	4.1	0.2	19.9	40.5	0.7	-	
	Heaviest fraction in atmospheric distillation	79.7	8.4	5.6	0.1	6.3	40.6	-	-	
	Heaviest fraction in vacuum distillation	77.1	9.7	5.5	0.1	7.5	38.9	-	-	
Large scale column type distillation										
Hard wood HTL biocrude	Biocrude	83.9	10.4	0.4	-	5.3	40.4	12	970.3	[49]
	Lightest fraction in vacuum distillation	84.4	13.5	BDL	-	2.1	43.9	-	792	

	Feedstock	Ultimate Analysis (wt. %)					HHV (MJ/kg)	Viscosity (cSt)	Density (kg/m <sup>3</sup> )	Ref.
		C	H	N	S	O				
Aspen wood HTL biocrude	Heaviest fraction in vacuum distillation	88.2	10.5	BDL	-	1.3	41.8	-	995	[32]
	Biocrude	76.4	8.4	-	-	15.2	34.3	-	-	
	Lightest fraction in vacuum distillation	67.6	13.5	-	-	18.9	33.8	-	-	
	Heaviest fraction in vacuum distillation	77.8	9.2	-	-	13.0	35.5	-	-	
Mesua ferrea L. seed hydro-processed biocrude	Biocrude	87.7	10.5	0.2	0.03	1.6	40.3	9.6	876.3	[136]
	Lightest fraction in vacuum distillation	76.2	10.5	0.1	0.02	13.2	40.5	0.6	758.1	
	Heaviest fraction in vacuum distillation	86.9	12.2	0.1	0.01	0.8	47.7	10.2	884.8	
Sewage sludge pyrolysis biocrude	Biocrude	57.9	8.3	4.0	1.0	29	25.1	7.0	971	[137]
	Lightest fraction in distillation	68.0	8.6	4.9	1.1	17.5	31.9	0.8	839	
	Heaviest fraction in distillation	73.7	9.2	4.7	0.3	12.2	34.8	5.1	947	
Saccharina japonica pyrolysis biocrude	Biocrude	16.2	10.2	<0.3	<0.3	63.9	-	-	-	[153]
	Lightest fraction in vacuum distillation	1.4	10.1	-	-	85.6	-	-	-	
	Heaviest fraction in vacuum distillation*	60.4	9.2	-	-	27.4	-	-	-	

BDL: Below the detection limit.

NR: Not reported

\*: Mean values are reported

**Table 10**  
Average impact of distillation on biocrude elemental and physical properties

Feedstock and fraction type		Ultimate Analysis changes %					Physical properties changes %			Ref.
		C	H	N	S	O	HHV	Viscosity	Density	
Simple distillation										
Duckweed HTL biocrude	Light	-6.3	+5.8	-70.1	-	-6.7	-2.5	-	-	[82]
	Heavy	+8.2	+24.4	-71.3	-	-51.1	+14.7	-	-	
Spirulina sp. HTL biocrude	Light	-	-	-	-	-	-	-	-	[30]
	Heavy	+18.9	-5.9	-14.8	-45.5	-88.4	+14.5	-	-	
Tetraselmis sp. HTL biocrude	Light	-	-	-	-	-	-	-	-	[30]
	Heavy	+24.4	-2.4	+2.1	-36.4	-93.6	+24.6	-	-	
Rice husks pyrolysis biocrude	Light	-	-	-	-	-	-	-	-	[31]
	Heavy	+82.3	+58.4	+33.3	+33.3	-81.7	+96.3	-	+6.7	
Bench-scale column type distillation										
Swine manure HTL biocrude	Light	-	-	-	-	-	-48.5	-71.4	-	[150]
	Heavy	-	-	-	-	-	+24.6	-29.5	-	
Loblolly pine pyrolysis biocrude	Light	-82.5	+41.6	-	-	+246.4	-	-	-17.2	[149]
	Heavy	+3.8	+19.8	-	-	-17.8	-	-	-0.7	
Corn Stover pyrolysis biocrude*	Light	-0.6	+6.7	+49.7	-41.2	-1.7	-	-	-	[147]
	Heavy	+1.2	-3.4	+39.0	-83.3	-11.5	+3.8	-	-	
Nannochloropsis oculata pyrolysis biocrude*	Light	-6.3	-0.5	-27.5	+27.3	+51.3	+4.3	-82.1	-	[152]
	Heavy	+8.6	-6.7	-7.5	-56.8	-42.0	+3.0	-	-	
Large scale column type distillation										
Hard wood HTL biocrude	Light	+0.7	+29.4	-	-	-60.6	+8.6	-	-18.4	[49]
	Heavy	+5.2	+0.7	-	-	-75.3	+3.3	-	+2.6	
Aspen wood HTL biocrude	Light	-11.5	+60.7	-	-	+24.3	-1.5	-	-	[32]
	Heavy	+1.8	+9.5	-	-	-14.5	+3.5	-	-	
Mesua ferrea L. seed hydro-processed biocrude	Light	-13.2	-0.1	-35.0	-20.0	+105.8	+0.5	-93.3	-13.5	[136]
	Heavy	-0.9	16.2	-40.0	-60.0	-50.3	+18.4	+5.5	+1.0	
Sewage sludge pyrolysis biocrude	Light	+17.6	+4.1	+22.7	+12.6	-39.7	+27.1	-88.6	-13.6	[137]
	Heavy	+27.3	+11.1	+17.6	-64.2	-58.1	+38.7	-27.1	-2.5	
Saccharina japonica pyrolysis biocrude	Light	-91.6	-1.4	-	-	+34.0	-	-	-	[153]
	Heavy	272.8	-9.8	-	-	-57.1	-	-	-	
Average changes	Light	-21.5	+16.3	-12.0	-5.3	+39.2	-1.7	-83.8	-15.7	-
	Heavy	+37.8	+9.3	-5.2	-44.7	-53.5	+22.3	-17.0	+1.4	-

\*: Mean values for vacuum and atmospheric distillation are reported

### **5.3. Carbon content changes after distillation**

For simple distillation, the carbon content of the heavy fractions from biocrude typically increases. Carbon content is reported to increase by 24 % and 82 % [30, 31] following the distillation of biocrudes from algae and rice husks which leads to higher HHV [31]. In addition, increasing carbon content to 83-87 wt. % makes it comparable with petrocrude [30].

For column type fractional distillation, the carbon content of biocrude is generally higher in heavy fractions as distillation efficiently separates heavier compounds with higher carbon numbers and boiling points into heavier fractions. In other words, distillation separates low boiling point hydrocarbons from aromatic compounds and high carbon number long chain unsaturated hydrocarbons end up in the heavier fractions [32]. Mante, Dayton [149] distilled loblolly pine pyrolysis biocrude into four fractions and compared the elemental contents of distillates. The carbon content of biocrude increased from 70.2 wt. % to 72.8 wt. % for the heaviest fraction. On the other hand, for the lightest fractions of biocrudes, both increases [49, 137, 153] and decreases [32, 136, 147, 149, 152] in carbon content were reported. The possible explanation for this fact is that the distillation working pressure and the distillates numbers or temperature intervals in different studies do not follow a specific direction due to the lack of pre-defined distillation procedure for biocrude in contrast with petrocrude. Subsequently, the temperature interval of a light fraction in a specific study could be equal to a medium range fraction in another vice versa. However, most studies reported decreasing carbon content which proves again the presence of long-chain hydrocarbons in heavier fractions. On average, for both simple and column type distillation, the carbon content increases for heavy fractions and decreases for light fractions by 38 % and 22 %, respectively (see Table 9).

### **5.4. Hydrogen content changes after distillation**

The hydrogen content is normally higher in biocrude distillate from simple distillation in most cases [30, 31, 153]. Changes in the H/C ratio is a more valuable comparison for fuels. High H/C indicates the existence of short chain hydrocarbons [49]. A 18-20 % decrease in H/C ratio for two types of algae biocrudes was reported by Eboibi, Lewis [30] for distilled biocrude at 360 °C and 1 atm. The increase in carbon content was more than the increase in hydrogen content which could have been due to more unsaturated compounds going into the distillate fractions which is not favourable.



Studies using column type fractional distillation also reported a reduction in the H/C ratio for light distillates for most studies. In the case of the heaviest fraction (similar to simple distillation) the H/C ratio for most studies was lower than the original content in biocrude. However, there are some reports in which distillation increased the H/C ratio for both the light and heavy fractions [82, 136, 149]. This result shows the high dependency of H/C ratio on the feedstock type and distillation conditions. However, in all cases the H/C ratio of heavy fractions are less than in light fractions which shows that the aromatic and unsaturated compounds are concentrated (in heavier fractions) [122]. Distillation increases the hydrogen percentage of both the light and heavy fractions. However, due to the decreasing H/C ratio, a hydrogenation step might be required for some heavy fractions.

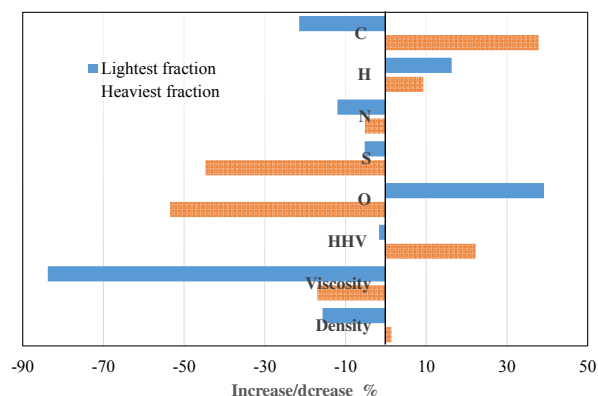
### **5.5. Other major heteroatom changes after distillation**

Due to environmental concerns, the content of unwanted heteroatoms such as nitrogen and sulphur should be reduced as much as possible. Subsequently, the impact of distillation on nitrogen and sulphur reduction as an upgrading technique is significant. The current distillation studies are mostly focused on upgrading biocrude for transportation fuels and less focused on environmental issues. Consequently, there are very few papers which have reported both nitrogen and sulphur changes in all fractions after distillation [136, 137, 145]. Table 9 shows a brief review of the available data relating to nitrogen and sulphur.

Nevertheless, the nitrogen content is reported more frequently than sulphur content due to the fact that the average sulphur content of biocrude is usually lower (see Table 7). Some studies have not reported the sulphur content of biocrude or distillates due to the sulphur content being lower than the detection limit of the measuring instrument [49, 153].

A significant reduction in nitrogen content was reported by Eboibi, Lewis [30] using simple distillation of microalgae biocrude. The aqueous phase contained around 65% of the nitrogen and may be extracted and used as a fertiliser [164]. The metal analysis over nine different elements (including Ca, Cu, Fe, K, Mg, Mn, Na, Ni and Zn) showed around 58-99 % reduction in distillate biocrude in comparison with plain biocrude which is beneficial due to the problems related to the process and environment[30]. Most recently, Haider, Castello [145] studied the distribution of nitrogen for hydrotreated microalgae biocrude by separating the biocrude into two different fractions using small scale distillation. The results showed that around 63-68% of nitrogen compounds were located in the heavy fractions. There are other studies which have reported an increase [137, 147] or a decrease [49, 82, 152]

of nitrogen content after distillation in all fractions. Figure 5 reveals the overall changes in physical properties and ultimate analysis after distillation based on current distillation studies. In average, the nitrogen content of biocrude decreases for light (12%) and heavy (5%) distillate fractions, respectively.



**Figure 5.** Overall changes in average physical properties and ultimate analysis in biocrude after the distillation based on all distillation studies.

Capunitan and Capareda [147] separated corn stover pyrolysis biocrude using atmospheric and vacuum fractional distillation and reported the sulphur content changes. The sulphur content reduced significantly for heavy fractions from 0.51 wt. % (for feedstock) to 0.09 wt. % and 0.08 wt. % for atmospheric and vacuum distillation, respectively. In addition, the sulphur content of the lightest fraction also decreased to 0.37 wt. % and 0.23 wt. % for atmospheric and vacuum distillation respectively. There are other studies which have reported a reduction in the sulphur content after distillation, especially for heavy fractions [30, 137, 152, 153] which means the boiling point of the biocrude's sulphur compounds are relatively low, and distillation may be useful for sulphur reduction. On average, a 5-45% decrease in biocrude sulphur content could be obtained using distillation.

Blending high sulphur content biocrude with low sulphur crude oil would be another option for lowering the sulphur content and using the biocrude directly in the conventional refineries in modest proportions. In addition, blending is helpful for reducing the capital costs of construction a new bio-refinery. Ultimately, blending the relatively low sulphur content distillate biocrude with high sulphur content heavy fuel oil (HFO) which is used in marine engines would be also an option. This approach may reduce the HFO sulphur content which

should help meet the new (lower) marine regulations [26, 165]. Sarma and Konwer [166] performed a feasibility study of a conventional refinery distillation with 1:1 biocrude-petrocrude blend and reported that existing refineries could be used successfully for the distillation of blends. In addition, Lavanya, Meenakshisundaram [138] performed fractional distillation for microalgae HTL biocrude-petrocrude blend. The functional groups of distillates and biocrude showed the mixture is comparable with petrocrude. Blending leads to the generation of more naphtha (C5-170 °C fraction) in comparison with pure petrocrude distillation.

## **6. Effect of distillation on the biocrude's higher heating value**

### **6.1. Biocrude HHV before the distillation**

The higher heating value (HHV) quantifies the exact fuel energy content based on energy released in a complete combustion. Similar to HHV, there is another heating capacity evaluation in the form of lower heating value (LHV) which subtracts the latent heat of the water produced during combustion. Oasmaa and Peacocke [163] performed a comprehensive study on physical characteristics of fast pyrolysis biocrude and suggested a correlation which converts between HHV and LHV based on biocrude hydrogen content.

There are different ranges of HHV, however, the mean HHV of HTL biocrude for wood, agricultural wastes, energy crops, other wastes and algae biomass feedstocks are 31.1, 30.2, 30, 34 and 34.7 MJ/kg, respectively which is around 26% less than HHV for diesel (40-46 MJ/kg). More results are available in Table 7.

### **6.2. HHV changes after distillation**

In general, there is an inverse relationship between oxygen content and HHV. Consequently, according to Table 9, simple distillation generally increases the HHV mainly due to the decrease in oxygen content. Simple distillation increased HHV values for two types of microalgae and rice husks biocrude from 35.3, 32.1, 17.42 MJ/kg to 40.4, 40.0 and 34.2 MJ/kg, respectively [30, 31]. In fractional distillation, there is an increase in HHV for most fractions which could be attributed to reducing in the oxygen content due to distillation; however, the percentage increase varies with the difference in feedstock nature, distillation type (atmospheric or vacuum) and temperature range for each fraction. The most obvious changes in HHV using distillation occurs in heavy fractions which increases the HHV value

by 22 % on average. It should be mentioned that, due to the relatively higher oxygen content of the lightest fractions it is more likely to decrease in HHV the lightest fractions [150].

In regards to the difference in the HTL and pyrolysis features and conditions, it could be concluded that distillation may have a different impact on the two biocrudes. There is one study in this area involving duckweed pyrolysis and HTL biocrude upgrading using distillation [82]. However, comparative studies between pyrolysis and HTL are inadequate and only proves that generally, distillation improves HHV and oxygen content for both HTL and pyrolysis. The intensity of increase may be related to several factors including process conditions, catalyst usage and biocrude properties and composition, which affect the separation in distillation and should be further studied to understand the suitability of each biocrude type in upgrading with distillation.

## **7. Effect of distillation on biocrude viscosity, density and water content**

### **7.1. Viscosity, density and water content before distillation**

The viscosity of biocrude is strongly dependent on the chemical composition of the biomass feedstock, conversion method and process conditions as well as catalysts [167, 168]. Kinematic viscosity is calculated based on a capillary-based method (according to ASTM D445) [169] and is more commonly reported than dynamic viscosity in the HTL literature. Decreasing residence time in the HTL process will sometimes increase the viscosity due to incomplete conversion [14, 170, 171]. Increasing water content and the proportion of light hydrocarbon compounds also decreases the viscosity [168, 172]. Adding hydrogen donor solvents to biocrude also decreases the viscosity [37, 173], although it reduces the flashpoint [161]. A more detailed review of the factors affecting the viscosity of the biocrude is an interesting topic, which has not been well studied; however, this topic is outside the scope of this study.

Table 11 shows a brief review of different HTL biocrude and pyrolysis biocrude viscosities, albeit viscosities are reported across different temperatures making the comparison complicated. The table shows that viscosity has not been reported for temperatures out over 50 °C. Due to the polymerisation reactions occurring, it is better to perform viscosity tests for biocrude at temperatures of no more than 80 °C [174], and it is recommended to measure viscosity between 20 °C and 40 °C [175]. The kinematic and dynamic viscosity ranges for the HTL process are 2.3-189 cSt and 64-2100000 cP

respectively, which shows the considerable variance with the type of feedstock. These values for the pyrolysis process are 1.6-264 cSt and 5.0-350 cP. A comparison of HTL and pyrolysis biofuels with marine HFO and gasoline shows that in most cases, an upgrading process such as distillation is needed to decrease the viscosity of biofuel to be comparable with fossil fuel viscosity. However, there is less necessity for reducing biofuel viscosity for marine HFO. Highly viscous biocrude are not suitable for conventional diesel [15]. In addition, highly viscous fuel has poor combustion which reduces the engine efficiency [176, 177].

**Table 11**  
Viscosity and densities of different biocrudes

Feedstock	Density (kg/m <sup>3</sup> )	Biocrude viscosity		Ref.	Feedstock	Density (kg/m <sup>3</sup> )	Biocrude viscosity		Ref.
		Kin. (cSt)	Dyn.(cP)				Kin. (cSt)	Dyn. (cP)	
HTL					Pyrolysis				
Hard wood	970.3 @15.6 °C	11.97 @40°C	-	[49]	Pine wood	1180 @20 °C	55.2 @50 °C	-	[178]
Rubber tree wood	-	-	8.3E+05*	[58]	Switchgrass	-	-	5.0-14.78 @40 °C	[179]
Corn stalk	-	-	1.6E+06*	[58]	Corn stalk	1080-1170 @15 °C	1.6-50.6 @40 °C	-	[180]
Coconut husk	-	-	1.3E+06*	[58]	Straw oil	1186 @15 °C	11 @50 °C	-	[181]
Oil-palm petioles	-	-	2.1E+06*	[58]	Sugarcane bagasse	1050-1130 @20 °C	-	2.3-3.9 @20 °C	[182]
Kenaf	-	-	4.0E+05*	[58]	Rice husk	1140 @30 °C	13.2 @40 °C	-	[183]
Garbage	-	-	5.3E+04*	[91]	Laurus nobilis residues	1133 @15 °C	61 @40 °C	-	[184]
Rice stalk	727.3 @20 °C	5.6 @40 °C	-	[119]	Soybean oil cake	1107 @15 °C	72.4 @50 °C	-	[185]
Blackcurrant pomace	960-990 @15 °C	-	1700 @25 °C	[64]	Grape residue	992 @15 °C	23 @50 °C	-	[186]
Swine manure	-	-	843 @50 °C	[159]	Waste paper oil	1205*	2 @35 °C	-	[187]
oil mill wastewater	915.2 @20 °C	16.6 @40 °C	31.9 @20 °C	[92]	Waste animal fats	886.2 @15 °C	5.2-5.7 @40 °C	-	[188]
Fat meat swine carcasses	1120 @20 °C	189 @40 °C	305 @20 °C	[90]	Sewage sludge	971 @15 °C	7 @40 °C	-	[137]
Spirulina platensis	1250 @40 °C	-	420-940 @40 °C	[121]	Waste fish	886.6 @15 °C	4.8 @40 °C	-	[189]
Dunaliella tertiolecta	1040- 1310 @ 15 °C	-	150-14000 @50 °C	[97, 170]	Pterocarpus indicus	1130-1200 @15 °C	-	70-350 @40 °C	[190]

Scenedesmus sp.	970 @20 °C	70.7-73.8 @40 °C	-	[160]	Streptomyces platensis	1200 @15 °C	-	189.8 @40 °C	[36]
Nannochloropsis	-	-	187.1-214.3 @40 °C	[168]	Chlorella sp.	980 @30 °C	61.2 *	-	[191]
Oedogonium	-	-	2500-30700 @25 °C	[192]	Nannochlorop sis	1180 @25 °C	-	6 @40 °C	[193]
Municipal wastewater algae	-	2.3 @40 °C	-	[194]	Saccharina japonica	1160 @20 °C	264 @50°C	-	[195]
<b>Marine Heavy fuel oil</b>	920-1010 @15 °C	10-700 @50 °C	-	ISO 8217	<b>Diesel</b>	820-850 @15 °C	2-4.5 @40 °C	-	[196]

\* measuring temperature has not reported

In contrast with viscosity, density changes for both HTL and pyrolysis processes are more limited. Table 11 briefly presented the density of different biocrudes. The density ranges for HTL and pyrolysis biocrudes are 720-1250 kg/m<sup>3</sup> and 820-1200 kg/m<sup>3</sup> respectively. Similar to viscosity, comparison of biofuel densities with diesel and marine HFO shows that less change in density is needed for making biofuels comparable with marine HFO. The high density of biocrude could be perhaps due to the high amount of heavy compounds in contrast with diesel [172]. Since the current diesel engines inject fuel in a volume basis, more mass is injected into the engine for biocrude with higher density, although more energy is needed for fuel pumping and the injectors [15, 197, 198].

## 7.2. Viscosity, density and water changes after distillation

There are only a few studies showing the impact of distillation on viscosity and density. In the case of density changes in simple distillation, there is a study which reported an increase in density from 1190 kg/m<sup>3</sup> to 1270 kg/m<sup>3</sup> after simple distillation of rice husks pyrolysis biocrude [31]. In the case of fractional distillation, in the most studies, distillation increased the density of heavy fractions and reduced density of the lightest fractions. For example, there is a study that fractional distillation increased the density of the heaviest fraction of hardwood biocrude from 970.3 kg/m<sup>3</sup> to 995 kg/m<sup>3</sup>. In addition, the density of the lightest fraction decreased to 792 kg/m<sup>3</sup> [49]. However, in contrast with all other studies, there are two studies which reported decreasing density in both heavy and light fractions in fractional distillation [137, 149] which made the conclusion challenging. The irregularity in density change in some studies may be attributed to the lack of standard distillation procedure (and using different operating conditions and specifications in each study) which have previously discussed in section 5.3. Experimental errors may be another reason explaining this issue. However, based

on all reported studies, distillation decreases and increases the light and heavy fractions densities by 15.7% and 1.4%, respectively which shows heavier and denser compounds are rich in heavy fractions. Other results are shown in Table 9.

Distillation normally decreases viscosity. On average, distillation reduced the viscosity of all fractions by 17-84 % which is a positive effect (see Table 10). Decreases in viscosity were much more substantial for light fractions which may be due to presence of heavy fatty acids and long-chain hydrocarbons in the heavy fractions. However, the concentration of phenolic compounds also plays a significant role in the viscosity changes between the distillate fractions due to their considerable difference in viscosity with mean biocrude and diesel [151]. Potential thermal cracking under the severe distillation condition may also decrease the viscosity of distilled biocrude which is a common phenomenon in the conventional refineries industry [199].

In general, water in fuel is undesirable (max 0.05 vol. % for diesel and biodiesel [196]) as it lowers HHV and also causes corrosion [137]. Due to the relatively low boiling point of water, fractional distillation can play a role in separating biocrude water content. It increases the water content in the lightest fraction and decreases the water content of other fractions. Cheng, Wang [150] conducted a destructive lab-scale distillation on swine manure HTL biocrude in the presence of glycerol. The moisture content of all distillate fractions (except the lightest fraction) was less than 1.0 wt. % which showed a significant decrease in comparison with biocrude (5.38 wt. %). The high content of water in the light fraction decreased the HHV to 18.75 MJ/kg in comparison with biocrude (36.41 MJ/kg); however, the HHV of other fractions increased to more than 45 MJ/kg through distillation. The acidity of biocrude, which causes corrosion, also decreased using distillation for heavy fractions. Decreasing the water content may be one of the reasons for the decrease in the density [168, 172] which was previously discussed. Data for water content and corrosivity reduction using distillation was provided in Table 5.

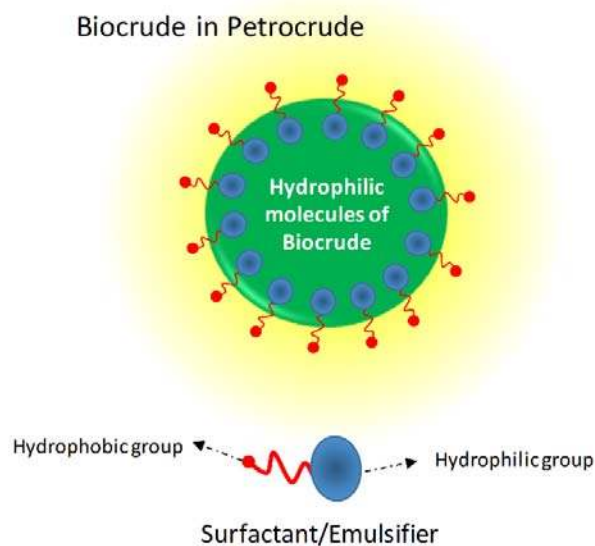
## **8. Distillation impact on biocrude miscibility, storage and stability**

### **8.1. Miscibility with petro-crude and distillation impact on it**

A solution to reduce biocrude acidity and viscosity is blending biocrude with diesel or different types of petrocrude in a conventional refinery for further co-processing. A problem with blending is immiscibility [200]. The high polarity of biocrude due to the highly

oxygenated compounds makes the biocrude almost immiscible in petro-crude fractions. This issue causes incompatibility with both engines and processing units in a refinery [161, 172, 200-202]. However, it has been shown that the miscibility can be improved to some extent by increasing the blending temperature [200].

Emulsification and microemulsification are promising physical methods to improve miscibility [203]. In a simple definition, emulsification is encapsulating of one phase into a layer of another phase using surfactant/co-surfactant. Figure 6 shows a schematic of the emulsification mechanism. For pyrolysis oil, there have been many studies investigating this technique. Researchers have blended biocrude and diesel [204] using an emulsifier [205-207] or with a co-emulsifier (which eases the emulsification) [208]. In addition, there are some studies which have blended biocrude and biodiesel [209]. However, there are fewer papers which have reported HTL biocrude miscibility with petro-crude products [202, 210, 211]. Additionally, stability could be improved using emulsification [211].



**Figure 6.** Schematic biocrude/petrocrude emulsification utilising the surfactant (emulsifier)

In a word, biocrude upgrading using emulsification has some advantages. However, it cannot improve HHV, cetane number and some other fuel properties [212]. In addition, high surfactant consumption and energy usage for fast agitation made it very expensive [14]. Subsequently, it is essential to use the emulsification method as a part of a hybrid method for



biocrude upgrading. Emulsification could be applied as a complementary method for distillation for two possible reasons. Firstly, distillation could increase the fuel HHV, which was the weakness of emulsification. Secondly, distillation may ameliorate blending biocrude with non-polar diesel by reducing the biocrude polarity which leads to lower levels of oxygenated compounds. Subsequently, it might need less surfactant to have a well-mixed blend. However, there is no report so far which looks at the impact of distillation on the HTL biocrude miscibility.

## **8.2. Storage and stability of biocrude and distillation impact on it**

In contrast with petro-crude, biocrude is unstable as the viscosity increases during storage. There have been several studies that have considered pyrolysis biocrude stability [14]. Based on the literature, biocrude is unstable due to polymerisation and condensation reactions [37]. This tendency rises with increasing temperature and leads to an increase in the biocrude viscosity, decrease in the water content and volatile compounds which can cause phase separation [19].

Low molecular weight compounds mostly escalate the polymerisation reactions and most aging reactions occur in the polar aqueous biocrude phase which contains many acids [14, 213]. As a result, separation of low molecular weight compounds or even water-soluble compounds would be an effective method for increasing stability of heavier fractions [214]. Distillation as a conventional method for separation could be an effective method for stability improvement by separation of biocrude into several fraction which are more stable. Similar results are reported for rice husk pyrolysis biocrude in a lab-scale distillation apparatus [31]. The stability of biocrude was studied over 80 days. It was reported that distillation and dividing biocrude into a water-soluble phase, distilled biocrude and residue increased stability significantly. There is another study which reported a 2-4% increase in viscosity for pyrolysis biocrude distillates in comparison with a 27% increase for plain pyrolysis biofuel after three months storage [148].

In the case of HTL biocrude, there are only a few studies investigating stability. Adjaye, Sharma [35] investigated the stability of wood HTL biocrude by storing 30 mL bottles of biocrude in the presence of tetralin as a hydrogen donor solvent which improved the stability. There are also other similar studies available in the literature monitor the viscosity changes by time [36, 201, 215]. However, in contrast with pyrolysis, there is almost no study which investigates the effect of distillation or separation on stability. Nevertheless, there are some

results which proved the stability of distilled HTL biocrude over 48 h [151]. Since there are promising results available for pyrolysis biocrude [31, 148], similar results could be expected for HTL biocrude, although HTL biocrude is more stable than pyrolysis biocrude [36].

## 9. Effect of distillation on engine tests performance and emissions

Despite many studies focusing on testing pyrolysis biocrude or biocrude/diesel or biocrude/biodiesel emulsification in engines [204, 209, 216-227], there are only a few studies which have reported the testing of HTL biocrudes in a diesel engine [151, 228-231]. This section discusses the existing studies and possible roles that distillation could play in diesel engine tests. Nabi, Rahman [228] conducted engine experiments with Licella biofuel that was produced by catalytic hydrothermal liquefaction of monterey pine wood flour. Biofuel was blended 5-20% with diesel to run in a four-cylinder turbocharged diesel engine. An increase in NO<sub>x</sub> emissions was reported, however, particle matter (PM) and particle number (PN) of biofuel were lower than its values for diesel fuel up to 88% and 41%, respectively which may have been due to the higher oxygen content in biocrude [232].

There are a few other studies which have reported the performance of biocrude/diesel blends in engine performance and emission tests [229, 230]. A reduction in the CO, CO<sub>2</sub> and NO<sub>x</sub> emission was reported for sewage sludge HTL biocrude blended with diesel using Span80/Tween80 emulsifier [229]. Similarly, a reduction in PN, PM and CO emissions was reported for a surrogate biocrude/diesel blend [230]. Table 12 gives a brief review of HTL biocrude engine tests.

**Table 12**  
Brief review of HTL biocrude engine test available in the literature.

Fuel used	Engine specification	Engine conditions	Brief results (in comparison with petrodiesel)	Ref
<b>Wood</b>				
Pinus wood flour biocrude blend with diesel.	Four cylinders, 2 litres, 100 kW @ 4000 rpm, multiple fuel injection.	@ 2000 rpm 233.01-243.66 N m At five different loads (0 %, 25 %, 50 %, 75 %, and 100 %).	<ul style="list-style-type: none"> <li>No significant difference in brake power and indicated power.</li> <li>Total unburnt hydrocarbon emissions were higher than for diesel (Max 13 % with R20).</li> </ul>	[228]

			<ul style="list-style-type: none"> <li>• NO emissions were higher for biofuel (Max 11 %).</li> <li>• PM emissions were lower than for diesel (Max 33 % with R20).</li> <li>• PN emissions were lower than for diesel.</li> </ul>
<b>Wastes</b>			
Swine manure and food wastes biocrude blend with diesel.	One cylinder AVL 5402 diesel engine, 0.51 litre 26.1 kW @ 4500 rpm BOSCH common rail CP3.	@ 1200, 1500 and 2000 rpm at three injection load and four different timing.	<ul style="list-style-type: none"> <li>• Using HTL biocrude mixture with diesel in the engine reduced CO emissions due to oxygen reach HTL biocrude. [151]</li> <li>• The lubricity of HTL-diesel mixture was better than simple diesel.</li> <li>• The energy output of using HTL-diesel mixture was comparable with diesel.</li> </ul>
Sewage sludge biocrude and diesel emulsion.	Four strokes diesel engine single cylinder 14.7 kW @ 2200 rpm direct fuel injection.	@ 1200 rpm At brake mean effective pressure from 0.23-0.92 MPa.	<ul style="list-style-type: none"> <li>• Higher BSFC and BTE were reported. [229]</li> <li>• CO emissions were reduced by 21.4 %- 66.7 %.</li> <li>• CO<sub>2</sub> emissions were reduced by 7.1 %- 27.3 %.</li> <li>• NO<sub>x</sub> emissions were reduced by 1.5 %-14.7 %.</li> <li>• Tested at various engine loads.</li> </ul>
<b>Microalgae</b>			
Surrogate microalgae biocrude blended with diesel.	EURO IIIA heavy-duty diesel engine six cylinders, 5.9 litres 162 kW @ 2500 rpm 820 Nm @ 1500 rpm multiple fuel injection.	@ 1500 rpm At for different loads. (25%, 50%, 75%, 100%).	<ul style="list-style-type: none"> <li>• PN, PM, and CO were reduced considerably. [230]</li> <li>• The reduction of PM were 58 % and 88 % at 100 % and 25 % load respectively.</li> <li>• Maximum PN reductions were at lower loads.</li> <li>• NO<sub>x</sub> emission increased.</li> </ul>
Desmodemus sp.	Four Stroke tractor diesel	@ 1000-2600 rpm	<ul style="list-style-type: none"> <li>• Exhaust temperatures of biocrude [231]</li> </ul>

microalgae HTL biocrude.	engine. four cylinders, 3.86 litres 61.78 kW @ 2800 rpm direct fuel injection.	(100 rpm intervals) At full loading.	were always less than diesel No 2. <ul style="list-style-type: none"> <li>• The output power of biocrude was 17 % less than diesel.</li> <li>• At full load and maximum speed:</li> <li>• CO<sub>2</sub> emissions were 5 % higher</li> <li>• PM emissions were 54 % lower</li> <li>• NO<sub>2</sub> emissions were 70 % lower.</li> </ul>
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According to Table 12, using biocrude in diesel engines may improve some emission factors such as PM, PN and CO. However, using neat biocrude in a diesel engine, or a blend with diesel, increases brake specific fuel consumption (BSFC) due to the biocrude's lower HHV and slight water content [229-231]. In addition, using biocrude caused a reduction in brake thermal efficiency (BTE) in some studies [230, 231], and an increase in other studies [228, 229]. Subsequently, it is recommended to improve combustion performance (such as BSFC and BTE) before using biocrude in diesel engines in order to produce a comparable drop-in fuel with diesel.

Distillation could be performed before HTL biocrude combustion as an upgrading method. According to sections 5 and 6, distillation can increase the HHV and decrease the amount of oxygenated compounds. However, there is only one study which used distillation followed by transesterification as an upgrading step before combustion in a diesel engine although the impact of distillation on engine performance was not discussed [151]. In addition, there is a suggestion to perform distillation in above atmospheric pressure in order to remove the biocrude's possible ash and residual materials before doing the engine test [228]. In the case of pyrolysis, Van de Beld, Holle [233], treated the pyrolysis oil using reactive distillation in the presence of a catalyst and alcohol before the engine tests. The distillate lowered the acidity content, moisture and increased HHV.

Distillation has potential for upgrading biofuels beyond pyrolysis and HTL biocrude. Zhang and Wang [234] distilled the tar produced in corncob gasifier and then blended the distillates with diesel prior to performing engine tests. On the other hand, Murugan, Ramaswamy [235] performed vacuum distillation on waste tyre pyrolysis oil before blending and engine testing. They reported that the HHV of oil increased by 7% although the effect of distillation on emissions was not discussed.

## 10. Distillation residue characterisation and properties

In addition to discuss and compare distillate fractions and biocrude feedstock, it is worth to also analyse the remained residue after the distillation. As could be expected, distillation residue is the part of biocrude which cannot be boiled and distilled and so remains at the bottom of the distillation column. The residue which mostly contains substituted aromatic compounds, has higher viscosity and density than distillate fractions. There are very few studies which characterise the biocrude distillation residue and Table 13 shows available data from the literature. In three studies, similar to other distillate fractions, distillation decreased the oxygen content which shows that the most oxygenated compounds are separated to the light fractions. Although, there is one study [49] which reports a slight increase in oxygen content for distillation residue. In addition, it is concluded that increasing viscosity and density as well as decreasing H/C ratio in distillation residue occurs due to the presence of unsaturated high boiling point compounds. Nevertheless, more studies should be conducted to investigate the properties of distillation residue.

**Table 13**  
Reported values for distillation residue in the literature

Feedstock	Distillation type /conditions	Ultimate Analysis (wt. %)					HHV (MJ/kg)	Viscosity (cSt)	Density (kg/m <sup>3</sup> )	Ref.
		C	H	N	S	O				
Hard wood HTL biocrude	Large scale 100-375 °C* 0.013 kPa	83.9	10.4	0.4	-	5.3	40.4	12.0	970.3	[49]
Distillation residue		82.0	8.2	-	-	9.9	38.6	-	-	
Loblolly pine pyrolysis biocrude	Bench scale IBP-400 °C* 20 kPa	70.2	7.2	0.3	-	22.4	-	169.0	1218	[149]
Distillation residue		75.5	5.1	-	-	19.0	-	-	-	
Mesua ferrea L. seed hydroprocessed biocrude	Large scale 35-370 °C* 0.013 kPa	87.7	10.5	0.2	0.03	1.6	40.3	9.6	876.3	[136]
Distillation residue		87.9	11.2	0.1	0.01	0.8	-	-	-	
Sewage sludge pyrolysis biocrude	Large scale 65-374 °C* NRP	57.9	8.3	4.0	0.95	29.0	25.1	7	971	[137]
Distillation residue		80.1	9.4	4.3	0.5	5.7	36.6	-	-	
Saccharina japonica pyrolysis biocrude	Bench scale 108-263 °C* 5.33 kPa	16.2	10.2	<0.3	<0.3	63.9	-	-	-	[153]
Distillation residue		68.6	5.5	4.7	0.6	20.5	28.4	-	-	

\* Atmospheric equivalent temperature (AET)

NRP: not reported pressure

Due to the high boiling point of compounds in the residue, GC-MS analysis is not a viable analytical technique. To solve this problem, Pedersen, Jensen [32] proposed two-dimensional pyrolysis-GCxGC-MS for the distillation residue. The GC-MS analysis showed a significant similarity between pyrolysis of distillation residue and other distillates probably due to re-cracking during combustion. In addition, due to the fact that the sulphur content of biochar is more than for biocrude [35, 236], it is reasonable to conclude that sulphur compounds tend to be attracted to the solid phase [15, 77]. This result suggest performing destructive distillation at high temperatures may be suitable as a physical-thermal upgrading technique for biocrude. However, char production in the residue should also be considered which is unfavourable due to corrosion [161], although char has some applications for industry [11, 12].

## **11. Limitations and outlook for future distillation studies**

Despite HTL's advantages in comparison with other conversion technologies such as pyrolysis, HTL biocrude has not been widely applied in industry and mostly has progressed beyond the laboratory stage due to several issues including unacceptable fuel properties (low HHV, high viscosity, high density, high acidity and undesirably high heteroatom content), immiscibility with petrocruide and instability. In addition, biocrude has not been widely tested in diesel engines so far due to the unacceptable amounts of performance parameters such as BTE and BSFC demonstrating the importance of biocrude upgrading.

Distillation as a physical upgrading technique may contribute to a number of these issues since it reduces the oxygenated compounds, improves HHV and reduces density and viscosity. Distillation may have some positive impact on heteroatom reduction, especially sulphur content, although more targeted research studies are needed. Due to the reduction in the quantity of oxygenated compounds using distillation, the immiscibility of biocrude in petrocruide may improve requiring further study. Additionally, it may be assistive for other methods such as emulsification by ameliorating miscibility. Finally, distillation could be beneficial to reduce aging problems as suggested in several studies [31, 142, 148]. The upgraded biocrude using distillation should also be tested in a diesel engine to analyse biocrude emissions behaviour. Nevertheless, to the best of our knowledge, there are very few studies in total which report the impact of distillation on these issues listed above.

## 12. Conclusion

Nowadays, using the current energy resources have become a major issue due to global warming and pollution. Transportation will rely on liquid fossil fuels for at least the next 10 years which makes alternate liquid biofuels attractive. Subsequently, to make renewable resources such as biomass (plants) into biofuels, they should be easily integrated with the current fossil fuel supply chain to be cost-effective. Biocrude is a biofuel made by thermally degrading plant wastes. Hydrothermal liquefaction (HTL) is one promising method due to the high yield and is suitable for a wide range of feedstocks. However, the main challenge with HTL biocrude is that the low combustion energy and its physical properties (such as viscosity, density and stability) are generally inferior to fossil fuels. Upgrading biocrude using conventional methods used by oil refineries, such as hydroprocessing, is relatively expensive. Distillation units, which already exist at oil refineries, are a highly cost-effective option.. The current review summarises the physical and chemical properties of different biomass feedstocks before and after the HTL process. Moreover, the effect of distillation as a physical upgrading technology on biocrude properties including HHV, viscosity, density, water content, CHO and heteroatom contents, miscibility and stability are also discussed. The results are promising for distillation as an upgrading method in the case of HHV, viscosity, density and elemental content. In addition to reducing oxygen and heteroatoms contents, distillation increases the HHV of heavy fractions by 22% and reduces the viscosity of all fractions around 17-84 %. Distillation has also showed a great potential to improve the biocrude instability and make it comparable with petro-crude during the storage period. Additionally, distillation has a great potential to be used as a part of a hybrid approach for HTL biocrude upgrading. Co-processing petro-crude and biocrude in a single fractionation unit followed by further upgrading (in an oil refinery) may an interesting option.

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