

Comparative study of pyrolysis and hydrothermal liquefaction of microalgal species: Analysis of product yields with reaction temperature

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ABSTRACT

Renewable and sustainable biofuel production from algal biomass has been explored vigorously due to the owing potential of overcoming the limitations of first and second-generation biofuel feedstocks. Thermochemical conversion technologies are considered promising routes for bioenergy production from algal biomass and have been extensively investigated over the last few years. This paper aims to review the various pyrolysis (slow, fast, and microwave -assisted) processes and hydrothermal liquefaction (HTL) techniques. The fast pyrolysis is involving a higher heating rate and shorter residence time compared to slow pyrolysis. Microwave-assisted pyrolysis (MAP) is considered a highly efficient process due to uniform heating. Due to a high moisture feedstock, the HTL process is considered the most energy-efficient processing option for algal biomass. In all these processes, the process temperature is considered the most critical parameter affecting product yield. This paper provides a detailed analysis and discussion on the effect of temperature and heating rates on the product (biochar, bio-oil, and syngas) yields for various microalgal species. The process details, different approaches, and process conditions investigated, challenges and recent advancements achieved in both technologies have been discussed in detail that provides useful insights to design a sustainable process and understand the process feasibility.

1. Introduction

Increased energy demand due to industrialization and rapidly increasing population, limited fuel reserves, and environmental concerns associated with the use of fossil fuels have triggered a search and development of alternative renewable energy sources. Currently, more than 85% of global energy is derived using fossil fuels [1,2]. Over the last few decades, the production of renewable liquid fuels derived from the first-generation feedstocks (starch, sugar, and oil-based crops) has increased significantly. The United States and Brazil produce 15.8 and

8.6 billion gallons of ethanol every year, respectively [3]. Corn is used as the main feedstock in the United States, while Brazil produces ethanol mainly from sugarcane. More than 6.5 billion L biodiesel was produced in the United States in 2019, using soybean and canola oil as major feedstocks. However, this feedstock suffers from several social and technical challenges, including high feedstock prices, intensive agricultural inputs, land, and freshwater use, and food vs. fuel issues. Biofuel production from lignocellulosic feedstock (also known as second-generation biofuel), such as agricultural residues, energy crops, grasses, forestry residues, municipal solid wastes, address some of these

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limitations. Extensive research efforts have been made in recent years for the technologies developed for the commercial-scale production of these cellulosic-based biofuels. Although lignocellulosic biomass is non-food material, the production of these feedstocks still requires land and freshwater use and agricultural inputs. The recalcitrance structure of these feedstocks is the major technical challenge for efficient conversion and economic feasibility of these feedstocks into energy.

Considering these limitations with the first and second-generation biofuels, biofuel produced from aquatic plants such as microalgae (third-generation biofuel) has gained much attention over the last few years. In addition to high carbohydrates and lipid contents, the potential of algae cultivation on non-arable lands and its ability to use various nutrients from the wastewater and carbon dioxide from the air and flue gases for its growth, provide some unique advantages of using algae as bioenergy feedstock and address all major limitations of first and second-generation biofuel feedstock [4,5]. Although the composition of algae is dependent on specific strain and growth conditions (pH, temperature, light, and nutrients), on average, algal biomass contains 9–42% lipids, 17–57% carbohydrates, and 20–50% proteins [4]. Some algae species, especially microalgae, contain as high as 80% lipids [6]. Microalgae, a photoautotrophic organism, can directly and efficiently convert solar energy into chemical energy and have been extensively investigated for biofuel and bioproduct production [2]. The high photosynthetic efficiency (as high as 12% compared to less than 0.5% for the terrestrial plants) and high lipid concentrations (up to 80% accumulation) in microalgae leads to several fold's high lipid productivity per unit land (4.5–7.5 ton/ha) compared to traditional oil crops (0.4 ton/acre for soybean) [7–9]. The energy production capacity per unit of land for microalgae is 30 to 100 times compared to terrestrial plants [4]. Several studies have demonstrated that algae-based biofuels are technically feasible and provide a high net energy ratio (ratio of energy in fuel and fossil energy used to produce fuel) [5,10].

Biomass can be converted to solid, liquid, or gaseous biofuels through biochemical (enzymatic hydrolysis, alcoholic fermentation, anaerobic digestion, etc.) or thermochemical (gasification, hydrothermal liquefaction, pyrolysis, etc.) processing technologies [11]. Microalgae conversion processes can be classified into two broad categories: i) fractionation of algae for extraction of specific compounds (lipids or carbohydrates) and further processing (both biological and chemical methods) to biofuels and bioproducts, ii) processing of entire microorganism (mostly using thermochemical technologies) [5]. Most of the thermochemical technologies require high temperature (>200 °C) and pressure (>5 MPa) and provide advantages of fast conversion rates compared to the biological processes [12]. Pyrolysis (for dry biomass) and HTL (for wet biomass) are the two most commonly investigated thermochemical technologies for algae conversion [5].

The pyrolysis process occurs at high temperatures (300 to 700 °C) in the absence of air, and the biomass decomposes into bio-oil, gases, and char [7]. Many studies have been conducted on the pyrolysis of various algae species and demonstrated high oil and char yields [4,13–15]. The bio-oil produced from algae processing has a calorific value between 31 and 42 MJ/kg and is considered more stable compared to that from the processing of lignocellulosic feedstocks [4]. The pyrolysis studies have been conducted using both direct pyrolysis (using whole algae) and indirect pyrolysis (using defatted microalgae) [5,14]. Although the pyrolysis oil yields are lower in the case of indirect pyrolysis due to the conversion of carbohydrates and protein only, the total oil yields (lipids and pyrolysis oil) are observed higher in the case of indirect pyrolysis [14].

The HTL process involves heating the biomass in a water environment at relatively lower temperatures (200 to 400 °C) under high pressure (5 to 25 MPa) for a time ranging from 10 to 60 min [12,16,17]. HTL provides the advantage of processing wet algae and avoids the need for an energy-intensive drying process. Considering 80–90% moisture in algae biomass, significant energy savings are achieved by processing wet biomass through the HTL process [11]. The high pressure keeps the

water in the liquid phase and the process conditions lead to access ionic reaction conditions [18]. During the process, biomass is converted to biocrude or bio-oil (main product), an aqueous fraction, gases, and biochar (solid by-product). The HTL bio-oil calorific value ranges from 30 to 50 MJ/kg, which is comparable to petroleum oil (41 MJ/kg) [4]. The oxygen content of biocrude is relatively lower than pyrolysis bio-oil, however, an upgradation process is still required to use this as high-quality fuel with conventional diesel. Biochar has some excellent properties as a soil conditioner and is considered a high-value product resulting in improved process economics.

In both HTL and pyrolysis, the reaction temperature plays the most critical role in deciding the process yields [19]. No previous studies reported the effect of reaction temperature on the product yield from pyrolysis for microalga species. In this paper, we reported and analysed the comparison of HTL and pyrolysis of more than 35 algal species. Besides, different processing methods such as slow pyrolysis, fast pyrolysis, catalytic pyrolysis, microwave-assisted pyrolysis, and hydrothermal liquefaction were compared. From an industrial perspective, energy balance and profitability play a pivotal role which was discussed in detail.

2. How microalgae are cultivated and harvested?

Microalgae is a promising feedstock for energy production as it is renewable and efficient. Microalgae can produce compounds such as fatty acids, polysaccharides, sterols, peptides, enzymes, antioxidants, and carotenoids during cell growth. Currently, food and fuel are the key products explored from microalgae. As of now, more than 35,000 species of microalgae have been found including *Spirulina* sp., *Nitzschia* sp., *Chlorella* sp., *Nannochloropsis* sp., *Botryococcus* sp., *Tetraselmis suecia*, and *Dunaliella primolecta*. Microalgae are gaining importance compared to other feedstock due to many advantages that it offers: they can be grown in non-arable land, on water bodies and photo-bioreactors, tolerate a wide range of pH, salinity, and temperature, renewable, yearly harvested, reduces CO₂ emission from industrial and open sources, full utilization of biomass, and also renewable & sustainable [1]. The cultivation of microalgae is challenging in terms of energy use and economics. Presently, the commonly used techniques for industrial-scale cultivation of microalgae include open ponds for high-volume low-value products and photobioreactors for low-volume high-value products. The open pond is the most common cultivation system due to its simple design and inexpensive operation. However, open pond system suffers from several limitations, including, low productivity, large land requirement, and contamination issues. Photobioreactors (PBRs), on the other hand, are cost-intensive, but they provide controlled conditions required for high biomass yields. Various types of PBRs are available, i. e., polyethylene bags, glass fibres cylinder, flat modular PBR, tubular inclined, segmented glass plate, and annular PBR. The growth of microalgae is dependent on external factors such as pH, temperature, nutrients, mixing, and light density. The average pH for the growth of most of the algae is normally 6 to 8 and the pH range required for photosynthesis is from neutral to alkaline. During the cultivation process, pH fluctuation affects microalgae growth in many ways. Photosynthetic CO₂ absorption by the algae during the daytime increases the pH whereas, during the night, the pH decreases due to the respiratory process. A temperature range of 25 to 30 °C is considered optimum for the growth of oil-producing algal species. Variation in temperatures may affect its growth rate or characteristics. Another crucial factor for microalgal cultivation is mixing, it prevents the settling of algae at the bottom of the reactor and rotates the algae between the light exposed and non-exposed areas of the pond/reactor. Electric pumps for air bubbling in reactors are mostly used for mixing in different PBRs. Light cycles are essential for microalgal cultivation since ATP and NADPH are produced by photosynthesis in presence of light, and in absence of light, these energy molecules are used to fix CO₂ into storage molecules. It is recommended that light intensity of 5000 to 10,000 lx is needed for a

higher microalgal yield.

Harvesting microalgae is a challenging task due to their low concentration (0.5 to 5 g/L) in the culture [20]. Harvesting is usually done in two steps: bulk dewatering (concentrating the algae to 2–7% solids) and thickening (final concentration 15–25% solids). Bulk dewatering can be achieved through gravity sedimentation & flocculation, whereas thickening can be obtained using centrifugation & filtration, or a combination of these methods [21]. Most commercial practice centrifugation and filtration methods to harvest microalgal biomass, but it demises large units of electricity or membrane fouling [22,23]. Few researchers investigated vacuum filtration to harvest microalgae cells, but it would be useful for large size algae. The use of any of these technologies is dependent on the end-use of microalgae. For example, producing bio-oil using hydrothermal liquefaction can utilize high moisture biomass, whereas producing the desired metabolite from microalgae might require thickening or drying.

3. Pyrolysis

Pyrolysis is one of the most promising techniques to convert the various types of algal biomass into all the fuel states such as solid, liquid, and gaseous forms. However, the output product distribution is entirely dependent upon the diverse parameters such as heating rate, process end temperature, vapor residence period, and pyrolysis environment [24]. Algal pyrolysis is the thermal decomposition of algal biomasses into a choice of useful products either without the supply of oxidizing agents such as oxygen/air or with a limited supply, yet the reaction conditions are confined and not permitted to the extent of gasification. Under many circumstances of the algal pyrolysis process, the technique involves the heating of algal biomasses without the external gasification agent at a definite heating rate up to pyrolysis temperature without the supply of oxygen/air and holding it at that condition for the desired period.

Till date, numerous studies have been reported on pyrolysis of various microalgae such as *Botryococcus braunii* [25], *Chaetoceros muelleri* [15], *Chlorella protothecoides* [26], *Chlorella sorokiniana* [27], *Chlorella* sp., [28,29], *Chlorella vulgaris* [30–33], *Cladophora* sp., [34], *Dunaliella salina* [32], *Dunaliella tertiolecta* [15], *Lyngbya* sp., [34], *M. aeruginosa* [35], *Microcystis* sp., [35], *Nannochloropsis* sp., [32,36,37], *Scenedesmus* [13,38], *Spirulina platensis* [39], *Spirulina* sp., [30,40], *Synechococcus* [15], *Tetraselmis chui* [15], residues after lipid extraction [15,41], and oleaginous algal species [42].

The pyrolysis studies carried out on microalgae can be categorized into three major purposes; firstly, to explore the applicability of pyrolysis technology for processing a microalgal species. Secondly, to maximize the production of any one of the three desirous products such as algal biochar, algal bio-oil, and gaseous products. Thirdly, to study the influential effect of catalysts and pre-treatment strategies on the extraction of lipids, removal of sugars, or the extraction of any other value-added components [43].

Based on the pyrolysis operating conditions, the process can be categorized as conventional slow pyrolysis, fast pyrolysis, flash pyrolysis, and intermediate pyrolysis. The yield of various pyrolytic products and their composition of the solid, liquid, and gaseous products are varying according to their operating parameters of the pyrolysis type, such as pyrolytic reaction temperature, heating rate, and residence time [44]. There are certain other latest developed pyrolysis processes such as catalytic pyrolysis and MAP, which are explained in section 5.

3.1. Effect of pyrolysis temperature on the product yield from algae

During the pyrolytic reactions, the large complexes of algal biomass hydrocarbon break down into relatively simpler and small molecules of gas, liquid water, or bio-oil, and solid char due to the series of thermochemical reactions. However, the initially formed product comprises condensable gases and solid char, and further, the condensable gases may crack into non-condensable gases (CO, CO₂, H₂, and CH₄), liquid

condensates, and char. The disintegration of the algal feedstocks into small components is affected through both monophasic and multiphase reactions such as gas-phase homogeneous and gas–solid heterogeneous reactions. The non-condensable CO and CO₂ are formed by cracking of condensable vapor during gas-phase reactions. In the case of algal pyrolysis, there might be a substantial release of oxides of nitrogen along with the non-condensable gases that might be possible due to the excessive presence of N-based components in algal feedstocks while compared to conventional lignocellulosic feedstocks.

3.2. Stages of algal pyrolysis:

The algal pyrolysis process is divided into four stages based on the temperature:

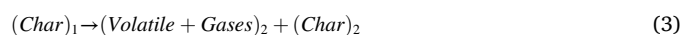
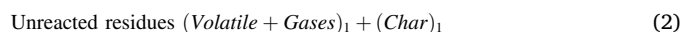
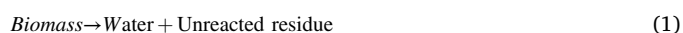
Drying (~100 °C): During this initial stage of heating, the free moisture and some loosely bound waters are released from the algal biomass.

Initial stage (100 – 300 °C): In this reaction phase, exothermic dehydration of the algal biomass takes place. Duly the release of water and low molecular non-condensable gases like CO and CO₂ occurs in this stage.

Intermediate Stage (>200 °C): This zone is the primary pyrolysis that occurs between the temperature range of 200–600 °C. At these stages, large molecules of the algal biomass particles decayed to char, condensable gases, and non-condensable gases.

The final stage (300 – 900 °C): This phase of reaction involves the cracking of volatiles into solid char and non-condensable gases. The long residence time possibly cracks large molecular weight condensable gases and yields secondary char and gases. Higher pyrolysis temperature above 600 °C favours the production of hydrogen and the shift reaction enhances hydrogen yield above 900 °C. At lower temperatures, the generation of carbon dioxide is high. The discharging of hydrocarbon gases is at a peak level around 450 °C and above 500 °C, it starts reducing and escalates the hydrogen production.

Though the reaction mechanisms of the biomass pyrolysis are complex, yet it can be simplified in three main steps as given in Eq. (1) – (3) [45]:



During the algal pyrolysis process, the algal feedstocks are heated from the ambient to pyrolysis temperature at a fixed heating rate and the feed is held there till the completion of the pyrolysis process. However, the quantum and yield of various pyrolytic products obtained from microalgae pyrolysis is depended on various influencing factors such as pyrolysis reaction temperature, heating rate, and residence time in addition to the algal feedstock characteristics such as size shape and type [46]. Temperature is the most significant of these operating parameters and has a tremendous effect on product composition [47,48]. In general, algal pyrolysis is carried out at a temperature range of 400–600 °C and as a result, the liquid phase is mostly produced those accounts for around 60–70 of the wt%. The pyrolysis temperature dictates the amount of algal biochar conversion from algal biomass. The production of algal char was found to be more at low pyrolysis temperatures while compared at high temperature, it favours more algal bio-oil production. The low heating rate gradually removes the volatile matter and favoured the secondary reaction between a char particle and volatiles to produce secondary char. However, further increasing the temperature beyond its optimum will lead to secondary cracking, whereby tar from the primary cracking product will be converted into gas and char. The effect of secondary cracking is a decline in bio-oil products and an increase in gas products [49]. Overall, fast pyrolysis is often preferred because it lessens the secondary cracking process and associated condensation and

polymerization reactions of intermediates during the pyrolysis process [50].

3.3. Conventional pyrolysis

The conventional pyrolysis processes are broadly classified as slow and fast pyrolysis processes based on the heating rate. If the time required for heating the algal feedstocks (t_{heating}) to the end pyrolysis temperature (T_{py}) is much longer than the characteristic pyrolysis reaction time (t_r), then the process is treated as slow pyrolysis. In mathematical terms, slow pyrolysis is referred by $t_{\text{heating}} \gg t_r$ and vice versa ($t_{\text{heating}} \ll t_r$) is considered as fast pyrolysis, whereas the simple linear heating rate is expressed as $T_{\text{py}} / t_{\text{heating}}$ (K/s). The characteristic reaction time (t_r) for a single reaction is taken as the reciprocal of the rate constant (k) evaluated at the pyrolysis temperature. The vapour residence time in the slow pyrolysis process is in order of minutes or longer

whereas in seconds or milliseconds for the case of fast pyrolysis [51]. The slow pyrolysis process is principally used for algal char production through carbonization and conventional methods. The fast pyrolysis method is used to produce algal bio-oil and gas via flash pyrolysis and ultra-rapid techniques. Moreover, the operating norms for the algal pyrolytic process depend on the output product interest and state of the yield. For instance, to maximize the algal char production, a slow heating rate (less than 0.01–2.0 °C /s), a low final temperature, and a long gas residence time are preferred as the optimal pyrolytic conditions. Likely, to maximize the algal bio-oil (liquid) yield, a high heating rate at a moderate final temperature (450–600 °C) and shorter gas residence time is desired, whereas to maximize the gas production, a slow heating rate, a high final temperature (700–900 °C) and a short gas residence time is advocated during the algal pyrolysis process.

Table 1

List of microalgal species and their pyrolytic product yields by slow pyrolysis technique reported in literature.

Sl No	Name of the algae	Pyrolysis Temperature (°C)	Pyrolytic product yield (%)				References
			Biochar	Bio-oil	Liquid water	Syngas	
1	<i>C. like</i>	500	37	41		22	[15]
2	<i>C. muelleri</i>	500	53	33		14	[15]
3	<i>C. protothecoides</i>	500	64.5	17.5		28	[35]
4	<i>C. vulgaris</i>	500	34	41		25	[15]
5	<i>Chlorella</i>	300	48	38		17	[82]
6	<i>Chlorella</i>	350	37	48		12	[82]
7	<i>Chlorella</i>	400	28	48		23	[82]
8	<i>Chlorella</i>	450	29	54		15	[82]
9	<i>Chlorella vulgaris</i>	500	21.6–31.5	49.2	60.7	4.6–25.7	[32]
10	<i>Chrysophyceal</i>	350	35.97	33		22.75	[43]
11	<i>Chrysophyceal</i>	375	30	32		29	[43]
12	<i>Chrysophyceal</i>	400	29	32		30	[43]
13	<i>Chrysophyceal</i>	425	27	35		28	[43]
14	<i>Chrysophyceal</i>	450	27	50		20	[43]
15	<i>Chrysophyceal</i>	475	25	47		25	[43]
16	<i>Chrysophyceal</i>	500	23.37	40		36.81	[43]
17	<i>Cladophora</i> sp.	600	42	20		38	[82]
18	<i>Cladophora</i> sp. dominated algal bloom	600	25	19		38	[34]
19	<i>D. tertiolecta</i>	500	63	24		13	[15]
20	<i>Dunaliella salina</i>	500	28	55.4	64.9	3.9	[32]
21	<i>Lyngbya</i> sp.	600	45	11		44	[82]
22	<i>Lyngbya</i> sp. dominated algal bloom	530	22	5		47	[34]
23	<i>Lyngbya</i> sp. dominated algal bloom	600	17	11		44	[34]
24	<i>Lyngbya</i> sp. dominated algal bloom	650	11	8		51	[34]
25	<i>M. aeruginosa</i>	500	22	23.7		54.3	[43]
26	<i>Microcystis</i>	300	57.09	26.66		16	[60]
27	<i>Microcystis</i>	350	50	28		18	[60]
28	<i>Microcystis</i>	400	35	42.5		20	[60]
29	<i>Microcystis</i>	450	29	48		19	[60]
30	<i>Microcystis</i>	500	23	54.97		20	[60]
31	<i>Microcystis</i>	550	22	51		25	[60]
32	<i>Microcystis</i>	600	21.5	49		27.5	[60]
33	<i>Microcystis</i>	650	20.39	38.9		38	[60]
34	<i>Microcystis</i>	700	20.39	38.28		39	[60]
35	<i>N. gaditana</i>	400	55	14		31	[37]
36	<i>N. gaditana</i>	500	47	31		22	[37]
37	<i>N. gaditana</i>	600	44	38		18	[37]
38	<i>Scenedesmus</i> sp.	300	38	22	22	18	[100]
39	<i>Scenedesmus</i> sp.	450	30	31	27	12	[101]
40	<i>Spirulina</i>	350	34.74	20		43	[43]
41	<i>Spirulina</i>	375	32	30		35	[43]
42	<i>Spirulina</i>	400	26	28		43	[43]
43	<i>Spirulina</i>	425	25	35		41	[43]
44	<i>Spirulina</i>	450	26	22		50	[43]
45	<i>Spirulina</i>	475	27	30		45	[43]
46	<i>Spirulina</i>	500	25.69	35		46.9	[43]
47	<i>Spirulina platensis</i>	350	39.7	23.8	41.1	19.2	[39]
48	<i>Spirulina platensis</i>	500	25.6	28.5	46.4	28	[39]
49	<i>Spirulina biomass</i>	450	24	15	30	15	[101]
50	<i>Spirulina</i> sp.	550	21	21	46	23	[40]
51	<i>Synechococcus</i>	500	44	38		18	[15]
52	<i>T. chui</i>	500	37	43		20	[15]

3.3.1. Slow pyrolysis

Most of the slow pyrolysis studies have been conducted with the microalgal species of *Chlorella protothecoides*, due to their high lipid content during heterotrophic growth. Peng et al. [52] carried out the slow pyrolysis of this microalga at 500 °C and observed a maximum liquid yield of 52–55 wt%, a gas yield of 33–36 wt%, and a solid char yield of 15 wt%. Further, while increasing the pyrolysis temperature from 300 to 650 °C for the same microalgae *Chlorella protothecoides*, the yield of gaseous products was increased from 9.5 to 40.6 wt% [45]. Jena and Das. [39] reported the yield of algal biochar (25.6 to 39.7 wt%) and bio-oil (23.8 to 29.2 wt%) with the slow pyrolysis of *S. platensis* conducted at both 350 °C and 500 °C. The pyrolytic product distribution for the process at low temperature (350 °C) resulted in Solids: Liquids: Gases (non-condensable) [S: L: G] as 39.7: 23.8: 19.2 in percentage, whereas at a higher temperature of 500 °C, the S: L: G ratio was changed to 25.6: 28.5: 28.0 %. The list of microalgal species subjected to slow pyrolysis and the resultant pyrolytic product yields (on a dry weight basis) were tabulated in Table 1.

Demirbas et al. [45] reported that the algal bio-oil yield during the slow pyrolysis of microalgae increased with an increase in temperature until approximately 500 °C and then decline thereafter. Overall, the bio-oil yield from microalgae by slow pyrolysis is normally ranged between 23 and 43 wt%, with a higher heating value (HHV) of 24–34 MJ/kg [15,39]. For instance, the bio-oil (water-free) yields reported for the slow pyrolysis of *Chlorella vulgaris*, *Dunaliella salina*, *Spirulina platensis*, and *Spirulina* sp. at 500–550 °C were 49.2, 55.4, 28.5 and 21 wt% respectively [32,39,40].

Algal biochar has relatively a lower carbon content, surface area, and cation exchange capacity (CEC) when compared to lignocellulosic biochar [53] however, it has a higher pH with rich nutrient contents including minerals such as nitrogen, ash, and other numerous inorganic elements. The maximum liquid yields obtained from the slow pyrolysis of *Chlorella* sp., *Chlorella vulgaris*, *Dunaliella salina*, *Spirulina platensis*, and *Spirulina* sp. were 40 wt% at 425 °C [43], 60.7 wt% at 500 °C [32], 64.9 wt% at 500 °C [32], 46.6 wt% at 500 °C [39], and 46 wt% at 550 °C [40], respectively. However, most of the earlier studies reported the pyrolytic liquid yields without further bifurcating into liquid soluble and bio-oil as the moisture content data were lacking. It is noteworthy to mention that yield of water soluble could be measured by deducting the combined yields of bio-oil, gases, and solids. In general, the liquid stream contains 30 to 50% of pyrolytic water [50].

Due to the virtue of slow pyrolysis processes such as the low heating rate and longer vapor residence time, the larger quantum of biochar and non-condensable gases [CO₂, H₂, CH₄, C₂H₄, and C₂H₆] in the pyrolytic products are generally obtained. However, the HHVs of these gases are in the range of 1.2–4.8 MJ/kg, which limits its application in the bio-energy sector [15]. The resultant pyrolytic products from the slow pyrolysis of microalgae were ranked based on the calorific energy as algal bio-oil >> algal biochar >> non-condensable gases.

3.3.2. Fast pyrolysis

Though microalgae are regarded as the promising alternative to lignocellulosic biomasses for bioenergy production, the third-generation biofuel technology is being limited by the low lipid content of microalgae, incomplete lipid extraction, and pollution issues associated with the extraction reagent recovery, need of a catalyst for further transesterification to biodiesel resulting in meagre economy. Recently, supercritical fluid extraction techniques are employed for the extraction of biodiesel from microalgae apart from direct and solvent extraction. Further, the net energy balance analysis revealed that energy gain is not sufficient to sustain the algal biodiesel technology for microalgae with low lipid contents. Yet, mostly these low lipid microalgae grow much faster than the higher lipid strains [54]. For instance, microalgae containing 30% oil grow 30 times faster than those containing 80% oil [55]. However, these low lipid microalgae possess a greater advantage of faster growth rate and pyrolysis of these algal species could produce

high-quality algal bio-oils as well as avoid the reliance on cost-intensive extraction technologies. Thus, fast pyrolysis of low lipid microalgae gradually becomes an obvious alternative and promising technical route.

In fast pyrolysis, the usual heating rate and vapor residence time ranged from 10 to 600 °C/s and 1–3 s, respectively [26,45]. Thus, the high heating rate and short residence time compared to the slow pyrolysis process led to a higher reaction rate and bio-oil yield. The bio-oil yield and HHV from microalgae fast pyrolysis is between 18 and 72 wt% and 24–41 MJ/kg respectively [26,33,38,45].

Although pyrolysis studies have been extensively carried out for a wide variety of lignocellulosic biomass, there are very limited studies on pyrolysis of algal biomass. Peng et al. [52] subjected *Chlorella protothecoides* with 14.3% lipid content to fast pyrolysis and attained the maximum oil yield of 52.0% at 500 °C for 5 min. Miao and Wu [26] studied the fast pyrolysis on a fluidized-bed reactor with two low-lipid microalgal species such as *Chlorella protothecoides* and *Microcystis aeruginosa* to obtain bio-oil yields of 17.5 and 23.7% with a higher calorific value and a lower oxygen content while compared to lignocellulosic biomass such as wood and straw. Kim et al. [38] evaluated the pyrolytic bio-oil characteristics of microalgae, *Scenedesmus* sp. in a fluidized bed reactor and obtained maximal liquid yields of 51.8% at 440 °C. The list of microalgal species reported in the literature for fast pyrolysis and the resultant pyrolytic product yields (on a dry weight basis) were tabulated in Table 2.

Gong et al. [32] obtained the highest yields of pyrolytic oil in fixed bed reactor as 49.2 and 55.4% (water-free basis) for *Chlorella vulgaris* and *Dunaliella salina* at 500 °C, respectively. The pyrolytic bio-oil of microalgae was found to have substantial levels of alkanes, alkenes, alkynes, esters with rich nitrogenous compounds. The pyrolytic bio-oil from *Dunaliella salina* had a lower water content and lower acid number with greater density and HHV than the oil from *Chlorella vulgaris*. Maliutina et al. [56] executed the fast pyrolysis of *Chlorella vulgaris* in a pressurized reactor to comprehend the impact of pressure on the pyrolytic product yield and composition to observe that higher pyrolysis pressures favoured the formation of nitrogen-containing species in algal bio-oils.

Sotoudehniakarani et al. [57] investigated pyrolysis of commercial and field cultured *Chlorella vulgaris* algae using a custom-built auger reactor with a feed rate of 0.5 kg/h and obtained the highest bio-oil yield (47.7%) from the commercial algae sample pyrolyzed at 550 °C. Though the reported bio-oil yields diverge significantly in literature, the pyrolysis conditions affect the yields considerably and this 47.7% yield is regarded as high compared to many values reported in the literature [26,58]. However, many studies confirmed that the bio-oil yield could be increased further by optimizing the pyrolysis process [26,59] and an increase in temperature enhances the algal bio-oil production [60].

However, the microalgal bio-oil products generated were derived from lipid contents that had superior properties such as lower content of oxygenated compounds and water, a lower total acid number, and a higher heating value when compared to the bio-oils from common lignocellulosic biomasses. Relatively low content of oxygen and water of microalgal pyrolytic bio-oil enhances the stability for storage and thereby overall quality. The microalgal pyrolytic bio-oils had high calorific values thereby fits the desirable purpose of utilizing them as a fuel or heating oil.

Few studies have been done with the pyrolysis of pristine microalgae; rather many studies were carried out with the defatted algal residues to utilize the residues after lipid extraction for an energy recovering option. For instance, Pan et al. [41] performed pyrolysis on the residue of *Nannochloropsis* sp. after lipid extraction in a fixed bed reactor at 400 °C and obtained a liquid yield of 47.6%. The pyrolysis bio-oil had an oxygen content of 30.1% and a calorific value of 24.6 MJ/kg still made it desirable for fuel or heating oil purposes. [59] extracted lipid from *Chlorella vulgaris* by solvent extraction technique and then pyrolyzed the residues in a fluidized bed reactor at 500 °C to obtain the yields of bio-

Table 2

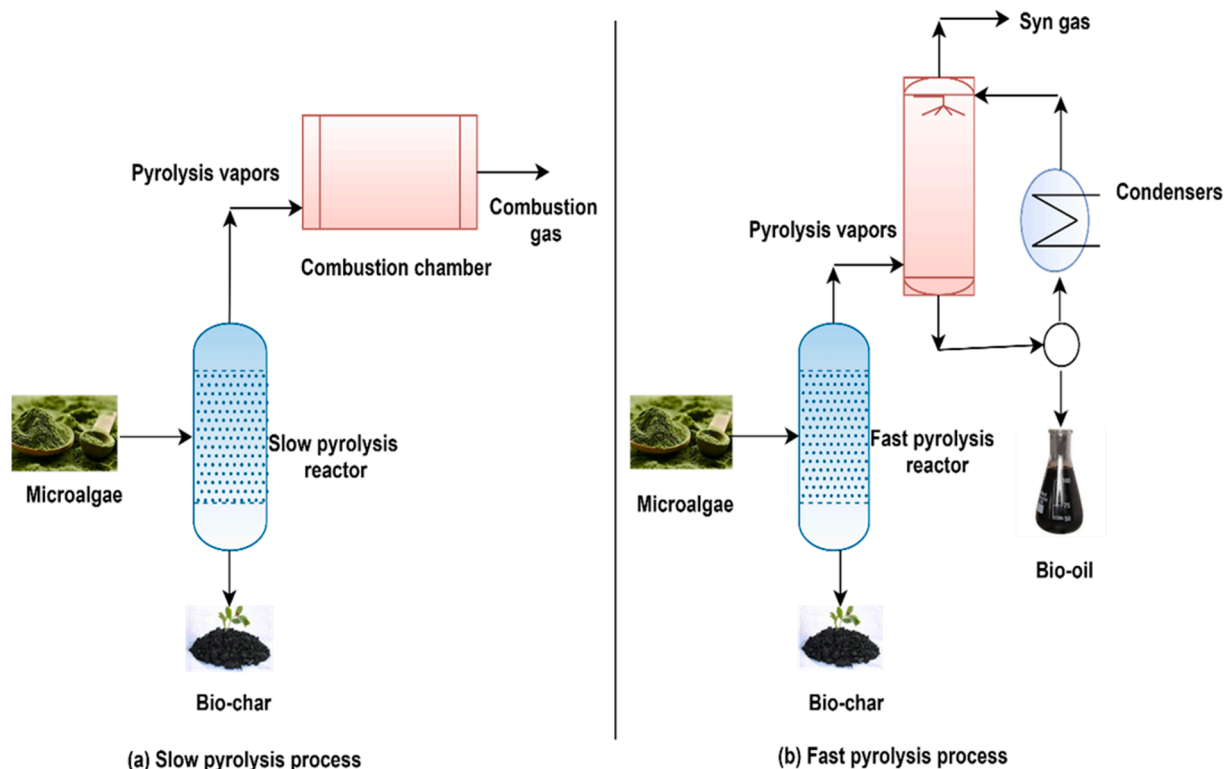
List of microalgal species and their pyrolytic product yields by fast pyrolysis technique reported in literature.

Sl No	Name of the algae	Pyrolysis Temperature (°C)	Pyrolytic product yield (%)				References
			Biochar	Bio-oil	Liquid water	Syngas	
1	BG-11 grown <i>C. vulgaris</i>	400	25	68		5	[33]
2	BG-11 grown <i>C. vulgaris</i>	500	22	65		11	[33]
3	BG-11 grown <i>C. vulgaris</i>	600	20	62		15	[33]
4	BG-11 grown <i>C. vulgaris</i>	700	19	59		22	[33]
5	<i>C. protothecoides</i>	500	54	17.5		28	[26]
6	<i>C. vulgaris</i> remnants	520	32	53		12	[59]
7	<i>Chlorella protothecoides</i>	500	15		52–55	33–36	[45]
8	Heterotrophic <i>C. protothecoides</i>	400	26.8	41.2		32	[26]
9	Heterotrophic <i>C. protothecoides</i>	450	10.7	57.9		34.7	[26]
10	Heterotrophic <i>C. protothecoides</i>	500	10.5	57.3		34	[26]
11	Heterotrophic <i>C. protothecoides</i>	550	11.2	57.2		34	[26]
12	Heterotrophic <i>C. protothecoides</i>	600	11.2	57.2		32	[26]
13	<i>M. aeruginosa</i>	500	20	23.7		56	[26]
14	<i>Microcystis aeruginosa</i>	500	19		23.7	57.3	[26]
15	<i>N</i> starved <i>C. vulgaris</i>	400	21	75		5	[33]
16	<i>N</i> starved <i>C. vulgaris</i>	500	20	70		10	[33]
17	<i>N</i> starved <i>C. vulgaris</i>	600	20	65		14	[33]
18	<i>N</i> starved <i>C. vulgaris</i>	700	19	61		20	[33]
19	<i>Pavlova</i>	450	48.96	14.11		36.93	[85]
20	<i>Pavlova</i>	500	40.9	18.68		40.42	[85]
21	<i>Pavlova</i>	550	38.97	16.57		44.46	[85]
22	Photoautotrophic <i>C. protothecoides</i>	600	53.8	16.6		30	[26]
23	<i>Scenedesmus</i>	440	21.8	41.5	51.8	26.4	[38]
24	<i>Scenedesmus almeriensis</i>	400	44.5	41		14.5	[92]
25	<i>Scenedesmus almeriensis</i>	800	31.1	48.2		20.7	[92]
26	<i>Scenedesmus almeriensis</i> Residues	400	46	34.5		19.5	[92]
27	<i>Scenedesmus almeriensis</i> Residues	800	31.7	33.7		34.7	[92]
28	<i>Scenedesmus</i> sp.	480	14.62	55		[13]	

oil, biochar, and gases as 53, 31, and 10 wt%, respectively. During the pyrolysis of *Spirulina platensis* residue in a fixed bed reactor, Jamilaton et al. [61] observed that bio-oil yields are increasing from 9.22 to 33.99 wt% as the temperature was increased from 300 to 500 °C, and then fallen to 23.34 wt% at 600 °C. Fig. 1 shows the comparison of the slow and fast pyrolysis processes.

3.4. Non-conventional pyrolysis

In the non-conventional pyrolysis process, the process variants include the medium (environment) and the pressure at which the pyrolysis process was carried out, whereas slow and fast pyrolysis is generally carried out in the absence of a medium. For instance, if water

**Fig. 1.** Comparison of the slow and fast pyrolysis process.

or hydrogen is used as a reaction medium during the pyrolysis process, then the process is called hydro pyrolysis or hydrous pyrolysis. However, these methods are generally applied to produce fine chemicals from biomasses.

3.4.1. Intermediate pyrolysis

Conventionally, pyrolysis is conducted in the absence of a medium with slower/ faster heating rates to produce a wide array of products. Though there is a huge difference between the reaction conditions of slow and fast pyrolysis, the intermediate pyrolysis tries to operate between these ranges. Thus the intermediate pyrolysis was operating at a moderate reaction temperature up to 500 °C, residence times of 0.5–25 min, and moderate vapor residence times of 2–4 sec [62]. Therefore, the pyrolytic product distribution due to this intermediate process is typically 40–60% of pyrolysis liquids, 20–30% non-condensable vapours, and 15–25% biochar. In particular, the biochar obtained by intermediate pyrolysis is dry and has a brittle texture as it contains less tar and therefore fewer toxic compounds making it suitable for further applications, such as a solid fuel or as a soil amendment and/or as a fertilizer. Due to the virtue of intermediate pyrolytic operating conditions, the formation of high molecular tars is getting prevented and thus dry and brittle chars suitable for fertilization or combustion could be produced. The benefits of applying intermediate pyrolysis for the treatment of algal biomass generate a range of potentially useful products with wide-ranging specific applications as well as biofuels. The pyrolytic liquid products and vapours are further processed to electricity, heat, and transportation fuels.

Rizzo et al. [63] evaluated the preliminary investigation on pyrolytic bio-oil characteristics of intermediate pyrolysis of microalgal species such as *Chlorella* and attained a liquid yield of 34% w/w and solid char of 29% w/w at 450 °C. Further, this study emphasized that the algae pyrolysis bio-oil through intermediate pyrolysis technique exhibited a few interesting properties of intermediate energy carrier such as low density and oxygen content, a mildly basic pH, high HHV and H/C ratio like diesel when compared to bio-oil derived fast pyrolysis techniques of lignocellulosic biomass.

3.4.2. Flash pyrolysis

Flash pyrolysis is usually performed at higher pyrolysis reaction temperature with much faster heating rates of 1000 °C/sec or even 10,000 °C/sec. Therefore, this process is generally characterized by very short vapor residence time and demands a very fine particle size to get pyrolyzed in a flash time. Many times, flash pyrolysis is referred to as fast pyrolysis as the reaction conditions and product distribution were like that process. However, the discrepancy between flash and fast pyrolysis becomes blurred and it is replaced with a broader definition for fast pyrolysis [64,65]. This process is typically applied to aim for higher bio-oil production from biomass due to the high biomass-to-liquid conversion ratio.

Maliutina et al. [66] compared the flash pyrolysis characteristics of microalgal *Chlorella vulgaris* and lignocellulosic biomass (palm kernel shell) in entrained flow reactor in the temperature range of 600–900 °C. The bio-oil obtained from microalgal *Chlorella vulgaris* was rich in hydrocarbons and nitrogen-containing compounds due to its proteinaceous nature, while phenols, esters, and hydrocarbons were rich in bio-oil derived from palm kernel shells. However, it is noteworthy to mention that the apparatus and reactor configurations in flash pyrolysis are almost the same as those of fast pyrolysis.

Conversely, the bio-oils obtained through flash pyrolysis are acidic, unstable, and viscous. The bio-oils contain solids and a significant quantum of chemically dissolved water in the oil limits its applications as fuel without subjecting to further fining techniques [67]. Therefore, additional upgrading of flash bio-oils through hydrogenation and catalytic cracking to lower oxygen content is usually required for the end product [68,69]. Venderbosch et al. [70] advocated the control of oxygen functionality in bio-oil (–OH, –C=O, –COOH, –C–O–C–, –COOR)

rather than the overall reduction in oxygen content.

4. Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) transforms organic waste into bio-crude oil and antioxidants-rich aqueous phase at elevated temperature and pressure. The reaction extent of HTL can be altered by varying the processing temperature and pressure, yielding different product distribution [71]. Hydrothermal technology is a viable process for the recovery of valuable products from high moisture content organic material since water acts as a solvent, catalyst, and reactant during the liquefaction process [71]. Microalgae is a suitable feedstock for the HTL process since no drying is required for this process, and microalgae are decomposed and converted into bio-oil in hot compressed water [51]. This reduces the cost of harvesting and energy utilized to bring the microalgae to desired solids content [72]. Fig. 2 explains the schematic diagram of HTL of algal biomass.

4.1. Underlying mechanism of temperature in HTL process

HTL is a temperature-specific process that happens at moderate to high temperatures (280–370 °C) and high pressures (10–25 MPa) [51]. HTL provides ideal conditions for the conversion of wet organic mass into bio-oil [73]. Many researchers utilized this technology for a variety of organic wastes [39,74]. HTL process produces a bio-crude oil with low oxygen content and higher heating value than the feedstock at subcritical conditions [75]. It also produces some valuable co-products, in the form of gas, water-soluble substances, and hydro-char. The reaction mechanism of HTL comprises of three major steps (1) depolymerization of biomass, converting long-chain polymers into short-chain hydrocarbons, (2) decomposition of biomass by cleavage, dehydration, decarboxylation and deamination, and (3) recombination, where fragments are repolymerized to form high molecular weight char. With temperatures higher than the activation energy of the bond cessation, the first step of HTL, depolymerization happens to a larger extent, which increases the concentration of free radicals and can lead to rapid repolymerization [16].

4.2. Effect of temperature on yield and composition of bio-oil in HTL

Temperature plays a key role in the outcome characteristics of the

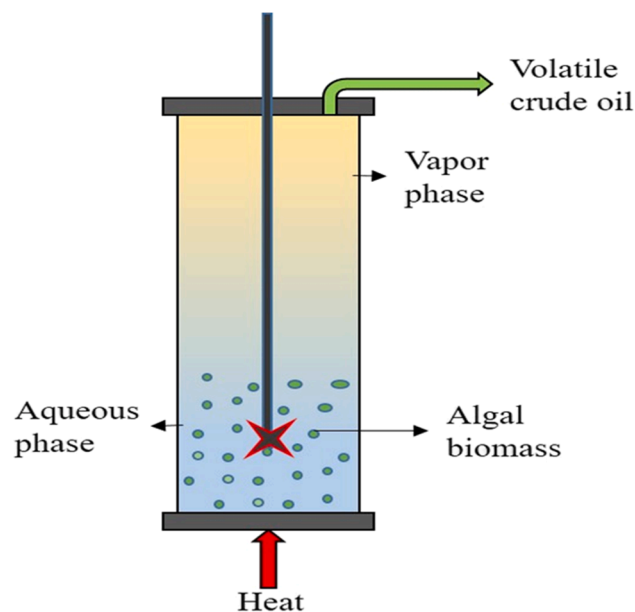


Fig. 2. Schematic diagram of hydrothermal liquefaction of algal biomass.

bio-oil. Hydrocarbons and nitrogenates extraction to bio-oil from feedstock increases with temperature but oxygenates decrease. At temperature and pressure above the critical point, the solvation properties of water resemble more like organic solvents [11]. The effect of pressure and temperature of the HTL process is shown in Fig. 3. The hydrogen bonds present between the water molecules become weaker at subcritical conditions [17]. As a result, oils and fats become soluble in water at sub-critical conditions and become highly miscible with water when conditions reach super-critical [51]. The yield of biocrude from HTL of microalgae sp. improved 33 wt% to 42 wt% and 34 wt% to 58 wt% for *Spirulina* sp. and *Tetraselmis* sp. Respectively, with an increase in the temperature from 300 to 350 °C, [51,76]. Ren et al. [46] studied HTL of microalgae *Botryococcus braunii* under subcritical water conditions without any catalyst, and obtained oil yields up to 68% at 310 °C temperature. The higher heating value of biocrude oil is close to that of petroleum crude oil [46].

5. Advanced pyrolysis

5.1. Catalytic pyrolysis

When the pyrolysis process is performed with the presence of catalysts in *in-situ* or *ex-situ* reactors, this process is referred to as the algal catalytic fast pyrolysis (CFP). The addition of the catalysts to the microalgal biomass might be aimed to either increase the product selectivity or lessen the severity of pyrolytic reaction conditions. In the case of *in-situ* catalytic pyrolysis, the algal feedstocks and the catalyst are pre-mixed mechanically and then fed into the reactor for pyrolysis reactions [77]. However, the same could be attained in the *ex-situ* catalytic pyrolysis process, where the pyrolytic vapours are allowed to cross through the catalyst bed located at the exit of the reactor [78]. The list of microalgal species subjected to catalytic pyrolysis and the resultant pyrolytic product yields (on a dry weight basis) were tabulated in Table 3.

The commonly reported catalysts for microalgae pyrolysis include ZSM-5-based zeolites, for example, Fe-ZSM-5, Ni-ZSM-5, Cu-ZSM-5, and H-ZSM-5 [79,80], zeolite Y-hydrogen (ZYH), zeolite Y-sodium (ZYN), and oxides like MgO, ZrO₂ and TiO₂ [81], Na₂CO₃ [82], CeO₂- (ceria), TiO₂- (titania), and Al₂O₃-supported catalyst [83]. A few of other catalysts that have applied for algal pyrolysis includes Ni supported on zeolite-Y [84], Ce/TiO₂, Ni/TiO₂, Co/TiO₂ [85], MCM-22, ITQ-2 [86], hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O) [87], and CoeMo oxide/ γ -Al₂O₃

[88]. As a result of utilizing catalysts along with algal feedstocks during pyrolysis, the produced algal bio-oil is characterized by better quality features such as higher aromatics and heating value, and lower acidity. However, the biomass to catalyst ratios was maintained in the range of 0.2 and 10 [41,80,81,89] with the pyrolytic reaction temperature of 300–600 °C.

Anand et al. [81] subjected *Schizochytrium limacinum* to fast pyrolysis to comprehend the effects of zeolite Y catalysts, algae: catalyst ratio, and oxides like TiO₂, ZrO₂, and MgO on the production of various pyrolytic products. The study results revealed that the presence of ZYH catalysts enhanced the production of aromatics and organic nitriles and reduced the relative yield (3–4 times) of carboxylic acids compared to non-CFP, while the presence of ZYN catalysts led to the formation of long-chain ketones via ketonization reactions with a concomitant decrease in aliphatic hydrocarbons. Non-CFP of *S. limacinum* revealed that tetradecanoic and hexadecanoic acids were the major pyrolysates in the temperature range of 350–550 °C. Further, this study demonstrated the selective production of valuable chemical intermediates from algal feedstocks via CFP using zeolites and metal oxides.

In the case of microalgal CFP, a higher bio-oil yield of 19 to 40 wt% and lower oxygenic components could be achievable [90] with the HHV of 20–33 MJ/kg [82]. For example, Pan et al. [41] reported 19.5 wt% and 32.7 MJ/kg of bio-oil content and HHV from the catalytic pyrolysis of a microalga (*Nannochloropsis* sp.) residue, while they were 30.1 wt% and 24.6 MJ/kg from the direct pyrolysis of the residue.

Aysu et al. [83] performed nickel ceria-based catalytic pyrolysis of *Tetraselmis* and *Isochrysis* microalgal species in a fixed-bed reactor and reported that higher bio-oil yields with NiCe/Al₂O₃ and NiCe/ZrO₂ catalysts. Further, the oxygen contents in the bio-oils were remarkably lower than those using ZSM-5 as a catalyst. Aysu et al. [85] examined the effects of TiO₂ and Ni-, Ce-, Co-loaded TiO₂ and CeO₂ catalysts on Pavlova microalgae pyrolysis and observed that the bio-oils obtained in the presence of titania catalysts had high HHV of 35–37 MJ/kg [80]. The deoxygenation (9–12 wt%) in the algal bio-oils was accomplished with the catalysts with the hierarchical order of Ni/TiO₂ > Ce/TiO₂ > Co/TiO₂. Babich et al. [82] suggested that catalysts in fast pyrolysis can be recycled, which is an additional advantage to this process. However, CFP results in better deoxygenation of the biomass and enhances the bio-oil quality in terms of higher HHV, lower acidity and O/C ratio [91]. Apart, Babich et al. [82] reported a higher gas yield for Na₂CO₃ based pyrolysis of *Chlorella* than that of non-catalytic pyrolysis at the same temperature.

5.2. Microwave-assisted pyrolysis

The process of subjecting microalgae to pyrolysis with the assistance of microwave (MW) heating is called algal microwave-assisted pyrolysis (MAP). MW is generated in the form of electromagnetic waves in the radio frequency from electrical energy as a sinusoidal perpendicular electric and magnetic field. In algal MAP, the heating of algal biomass occurs through a process called dielectric heating, where the dielectric materials such as water, fat, Fe₃O₄, CuO, etc., were used to heat up by MW irradiation [74]. The polar molecules vibrate and rotate as they attempt to align themselves to the arriving MW radiation frequencies and heat is produced due to friction between oscillating molecules [43].

MAP has numerous advantages such as uniform and rapid heating, ability to produce higher HHV syngas, cleaner production techniques due to the efficient process when compared to conventional pyrolysis techniques [89]. Further, this MAP process does not require very fine particle sizes and saves energy use in the size reduction step. Fig. 4 represents the process flow of the MAP technique. The lack of agitation and fluidization in the process is an added technical advantage when compared to conventional pyrolysis techniques. As a result, the traceable quantum of ashes was presented in the produced bio-oil enhances the overall quality and thereby suits for immense applications [28,29]. Moreover, conventional pyrolysis utilizes the normal heating process

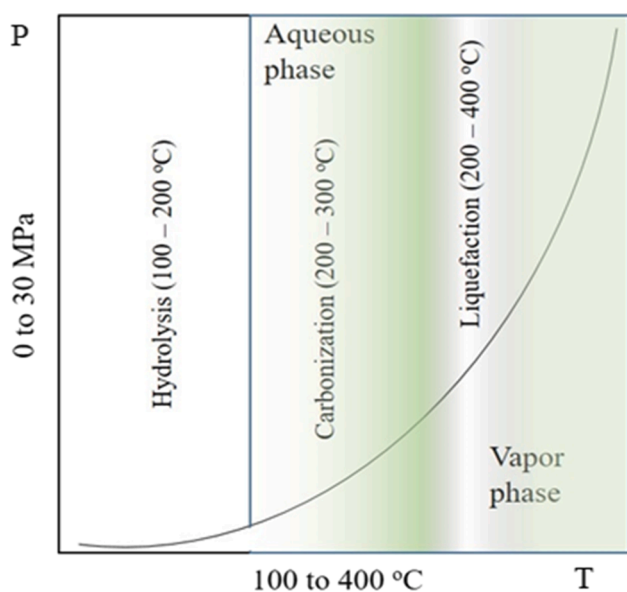


Fig. 3. Effect of temperature and pressure of hydrothermal liquefaction.

Table 3

List of microalgal species and their pyrolytic product yields by catalytic pyrolysis technique reported in literature.

Sl No	Name of the algae	Catalysts	Pyrolysis temperature (°C)	Pyrolytic product yield (%)				References
				Biochar	Bio-oil	Liquid water	Gas	
1	<i>Chlorella</i>	Na ₂ CO ₃	300	55	19		25	[82]
2	<i>Chlorella</i>	Na ₂ CO ₄	350	35	36		28	[82]
3	<i>Chlorella</i>	Na ₂ CO ₅	400	28	38		34	[82]
4	<i>Chlorella</i>	Na ₂ CO ₆	450	29	40		31	[82]
5	<i>Chlorella</i>	HZSM-5	500	27.4	33.1	50.0	22.8	[100]
6	<i>Chlorella</i>	Fe-ZSM-5	500	29.7	30.2	43.1	27.1	[100]
7	<i>Chlorella</i>	Cu-ZSM-5	500	27.9	33.6	46.9	24.6	[100]
8	<i>Chlorella</i>	Ni-ZSM-5	500	30.1	28.9	45.1	25.4	[100]
9	<i>Chlorella</i>	Activated Carbon	350	37.5	47.5		15	[102]
10	<i>Chlorella</i>	Activated Carbon	500	33	47		16	[102]
11	<i>Chlorella</i>	Activated Carbon	650	25	44		28	[102]
12	<i>Chlorella</i>	Fe ₃ O ₄	350	47.5	37.5		15	[102]
13	<i>Chlorella</i>	Fe ₃ O ₅	500	26	52		23	[102]
14	<i>Chlorella</i>	Fe ₃ O ₆	650	17.5	52		26	[102]
15	<i>Chlorella vulgaris</i>	HZSM-5	500	25.7	52.7		21.6	[31]
16	<i>Pavlova</i>	CeO ₂	450	47.96	15.1		36.94	[85]
17	<i>Pavlova</i>	CeO ₃	500	37.86	21.07		41.07	[85]
18	<i>Pavlova</i>	CeO ₄	550	36.26	17.82		45.92	[85]
19	<i>Pavlova</i>	TiO ₂	450	48.18	14.44		37.38	[85]
20	<i>Pavlova</i>	TiO ₃	500	39.49	20.04		40.47	[85]
21	<i>Pavlova</i>	TiO ₄	550	37.76	17.14		45.1	[85]
22	<i>Pavlova</i>	Ce/TiO ₂	450	47.44	15.46		37.1	[85]
23	<i>Pavlova</i>	Ce/TiO ₃	500	37.46	21.67		40.87	[85]
24	<i>Pavlova</i>	Ce/TiO ₄	550	36.36	17.38		46.26	[85]
25	<i>Pavlova</i>	Ni/TiO ₂	450	47.66	15.3		37.04	[85]
26	<i>Pavlova</i>	Ni/TiO ₃	500	37.16	22.55		40.29	[85]
27	<i>Pavlova</i>	Ni/TiO ₄	550	35.9	18.71		45.39	[85]
28	<i>Pavlova</i>	Co/TiO ₂	450	48.28	15.24		36.48	[85]
29	<i>Pavlova</i>	Co/TiO ₃	500	38.85	20.41		40.74	[85]
30	<i>Pavlova</i>	Co/TiO ₄	550	37.98	17.41		44.61	[85]
31	<i>Spirulina</i>	Activated Carbon	350	37.5	31		31	[102]
32	<i>Spirulina</i>	Activated Carbon	500	33	45		22	[102]
33	<i>Spirulina</i>	Activated Carbon	650	23.5	40		34	[102]
34	<i>Spirulina</i>	Fe ₃ O ₄	350	37.5	33		27.5	[102]
35	<i>Spirulina</i>	Fe ₃ O ₅	500	23	47.5		27.5	[102]
36	<i>Spirulina</i>	Fe ₃ O ₆	650	21	45		32	[102]

and produces pyrolysis gas as a by-product while the other pyrolytic products such as bio-oils and non-condensable syngas could be derived after the condensation of MAP products.

Du et al. [28] carried out MAP of *Chlorella* sp. at the microwave output of 500, 750, and 1250 W with a final temperature around 362, 480, and 540 °C. The results revealed the highest yields of 28% char under a 500 W power output, 28.6% bio-oil (water-free) under 750 W power output, and 35% gas yield under a 1250 W power output. The bio-oil of this microalga had an alkaline pH of 9.7, a density of 0.98 kg/L, and an HHV of 30.7 MJ/kg. Further, this study demonstrated that microalgal biochar could be a good microwave absorber to enhance pyrolysis. Hu et al. [30] studied the experimental characteristics of *Chlorella vulgaris* by MAP and obtained the maximum liquid yield of 35.8%. Beneroso et al. [92] compared the MAP with the conventional pyrolysis process for the microalga *Scenedesmus almeriensis* and reported 57% higher gas yields than the conventional process. Borges et al. [29] carried out the MAP of *Nannochloropsis* and obtained the HHV of bio-oil as 42 MJ/kg. The list of microalgal species subjected to MAP and the resultant pyrolytic product yields (on a dry weight basis) were tabulated in Table 4.

It is noteworthy to mention that the pyrolysis reaction temperature of MAP is primarily dictated by the input power of MW generators. However, the pyrolysis reaction temperature is not evenly distributed in the reactor as the feedstocks were not agitated during the process of MAP [43,93]. The power applied in MAP is ranged between 500 and 2250 W and the concurrent reaction temperature is typically 500–800 °C. The bio-oil yield from MAP of microalgae is between 18 and 59 wt% and the corresponding HHV is 30 and 42 MJ/kg, respectively [74]. The schematic diagram of MAP reactor assembly is shown in Fig. 5.

Nevertheless, MAP offers numerous advantages such as low capital

cost, higher energy savings from the non-dependence on size reduction of the feedstocks, appropriate heating methods to yield superior product quality. Since the response to start-up and shutdown was quite faster as well as possible scaling-up due to the mature technology, MAP is preferred in many instances. MAP can be desired in future scale-up production of economical algal pyrolytic products such as algal biochar for soil fertilizer applications, which demands the massive production of end products [53].

Very few studies reported the use of catalysts as MW absorbers to enhance the heating processes of MAP. Usually, the content of MW absorbers ranged from 5 to 30 wt%, which are very well blended with microalgae before subjected to MAP. The few reported MW absorbers include SiC, chars, activated carbon, sulfuric acid, ionic liquids, and metallic oxides [94]. Borges et al. [29] compared the MAP of *Nannochloropsis* with and without the catalyst of HZSM-5 and observed that HHV of bio-oil is reduced to 27.15 from 42 MJ/kg while using the catalyst. However, there is no change in the HHV of bio-oil due to the presence of catalyst HZSM-5 [80] for the MAP of microalgae *Chlorella* sp. Out of the various pyrolytic products generated so far to date, the production of bio-oil is being emerged while biochar production via slow pyrolysis seems to be a mature technology, whereas advanced technologies such as catalytic, and microwave pyrolysis are in nascent stage.

6. Comparison of pyrolysis and HTL

The physical parameters including operating temperature and pressure plays a key role in the type of product and energy efficiency obtained from Pyrolysis and HTL. Pyrolysis decomposes the algal biomass at a higher temperature (300 to 700 °C), while HTL is operated between 200 and 400 °C. In contrast, the pressure needed for HTL processes vary

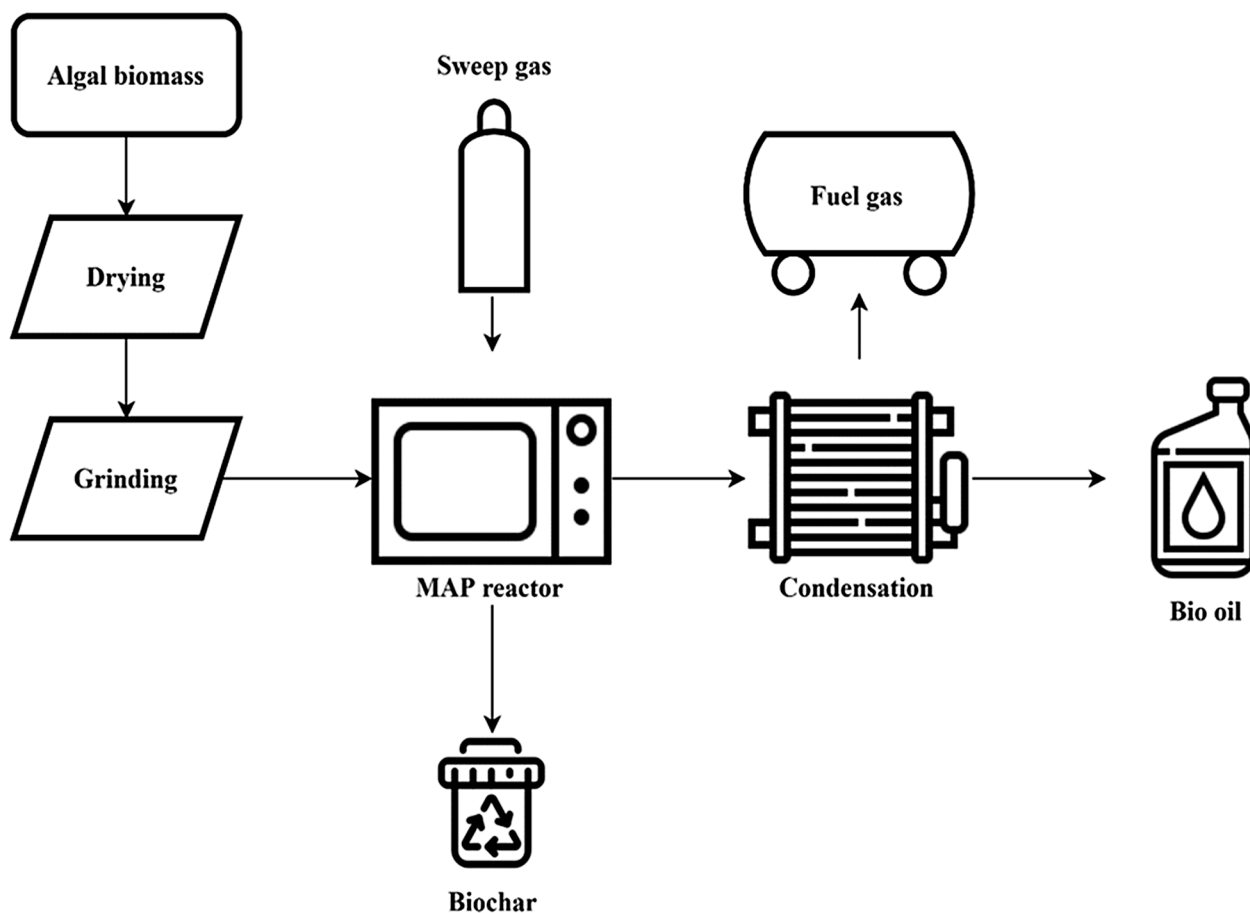


Fig. 4. Process flow diagram of microwave-assisted pyrolysis.

Table 4

List of microalgal species and their pyrolytic product yields by microwave-assisted pyrolysis technique reported in literature.

Sl No	Name of the algae	Power output/Pyrolysis temperature (°C)/	Pyrolytic product yield (%)				References
			Biochar	Bio-oil	Liquid water	Syngas	
1	<i>C. vulgaris</i>	750 W	90	1		9	[30]
2	<i>C. vulgaris</i>	1500 W	30	36		33	[30]
3	<i>C. vulgaris</i>	2250 W	25	22		51	[30]
4	<i>C. vulgaris</i>	390 W	25	20		52	[103]
5	<i>C. vulgaris</i>	540 W	20	30		48	[103]
6	<i>C. vulgaris</i>	700 W	19	32		42	[103]
7	<i>Chlorella</i>	400	7	9		84	[104]
8	<i>Chlorella</i>	550	12	8		80	[104]
9	<i>Chlorella</i>	700	5	16		79	[104]
10	<i>Chlorella</i> sp.	480	24.5	28.6	49	26.5	[28]
11	<i>Chlorella</i> sp.	550	25	28.6	59	16	[29]
12	<i>Nannochloropsis</i> sp.	500	25	36.2	57	18	[29]
13	<i>Nannochloropsis</i> sp.	550	24	28		48	[105]
14	<i>Porphyra</i>	400	13	2		85	[104]
15	<i>Porphyra</i>	550	11	4		85	[104]
16	<i>Porphyra</i>	700	10	3		84	[104]
17	<i>Scenedesmus almeriensis</i>	400	32.4	23.1		44.5	[92]
18	<i>Scenedesmus almeriensis</i>	800	26.9	15.6		57.5	[92]
19	<i>Scenedesmus almeriensis</i> Residues	400	27.8	21.8		50.4	[92]
20	<i>Scenedesmus almeriensis</i> Residues	800	27.4	15.4		57.2	[92]
21	<i>Spirulina</i>	400	9	11		80	[104]
22	<i>Spirulina</i>	550	5	13		82	[104]
23	<i>Spirulina</i>	700	10	6		84	[104]

between 5 and 25 MPa, while that of pyrolysis is operated at atmospheric conditions. Typically, pyrolysis yields 30–45% as liquids, however, in HTL the liquid product yield varies between 60 and 75%. When comparing slow and fast pyrolysis, the former has a higher gas yields

(30–45%) than the latter (13–20%) [51].

Pyrolysis is a thermochemical process, where dried biomass is used, whereas in HTL processes liquid or bio-crude is obtained as a product, which means it is operated at a higher moisture content. To remove

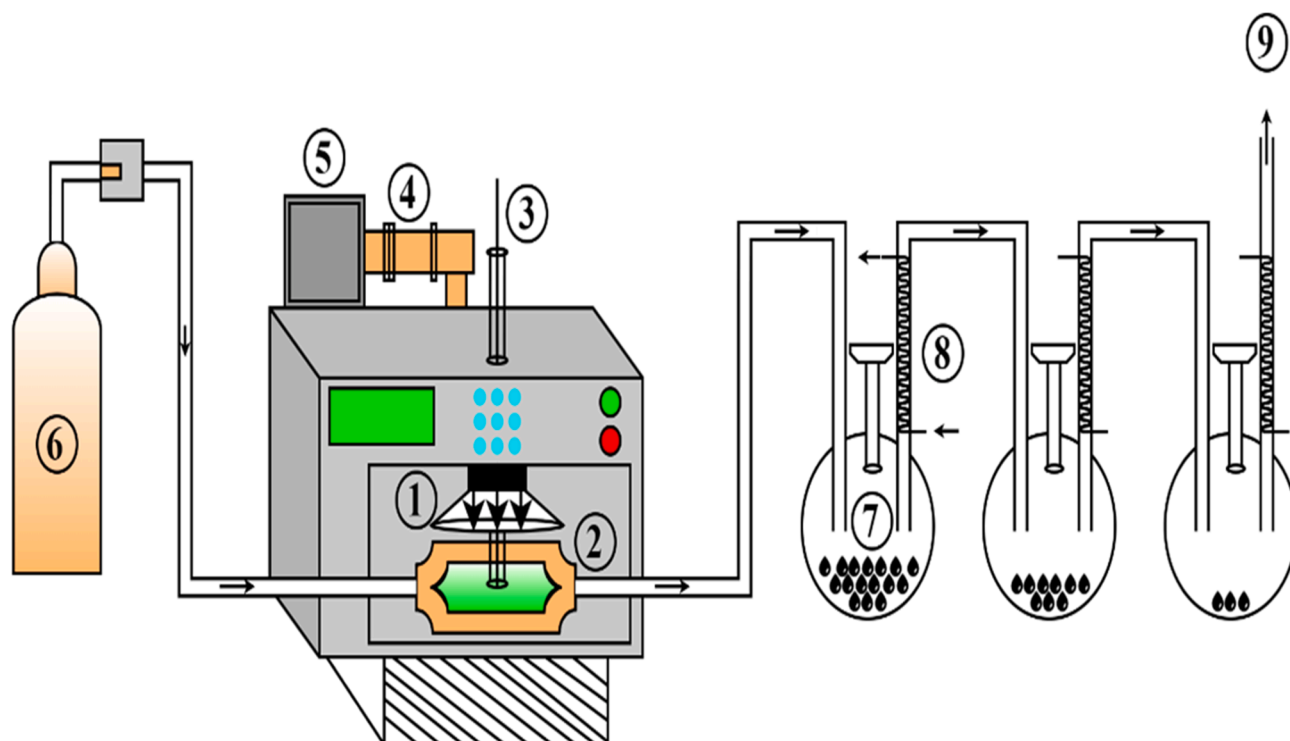


Fig. 5. Schematic representation of microwave-assisted pyrolysis (MAP) reactor assembly; 1) microwave cavity; 2) quartz reactor; 3) Infrared temperature sensor; 4) waveguide; 5) magnetron; 6) N₂ gas; 7) condensable bio-oil; 8) condensers; 9) fuel gas.

excess moisture, drying or centrifugation is necessary. This dewatering process consumes additional energy. Fig. 6 highlights the various products obtained from pyrolysis and HTL processes. A comparison of pyrolysis vs. HTL on the energy requirement was performed. A 1-Ton algal biomass with a 20% TS needs 1.6 times higher energy for pyrolysis than HTL. Most of this additional energy consumption is used for the drying biomass in the pyrolysis, as it is a dry process (~50%) [95]. Energy Recovery Ratio (ERR) is defined as the amount of useful energy that is recovered from the energy source, which is microalgae. ERR for a MAP was the lowest at 57.2%, while for the fast pyrolysis it was 78.7% and that of HTL is 89.8%. To reduce such high energy consumption in pyrolysis, a solar dryer could be attached, which in turn reduces the energy requirements. The pyrolysis and HTL process were compared with various factors and its tabulated in Table 5.

7. Challenges and perspectives

Although algae are a high potential feedstock for energy production and avoid the need for arable land, freshwater, and agricultural inputs like other conventional crops, several technical challenges, and high process costs limit the commercial-scale application and success of the process. One of the major challenges is related to scalability and associated costs of algae harvesting. Hydrothermal liquefaction can process dilute algae slurries without the need for expensive and energy-intensive dewatering and can address this limitation to some extent. The capital cost of the HTL process is higher compared to other thermochemical technologies because of the high-pressure requirement. Although extensive studies have been conducted on the HTL of algae, a limited understanding of the chemistry of conversion is still a critical hurdle in the efficient process design [99]. Conversion kinetics of individual components of biomass are available. However, the interaction of these components in different biomass still needs understanding and investigation. Due to the composition difference (high lipids, protein, high organics) between algae and lignocellulosic feedstocks, the pyrolysis reactor design for algae processing should be specific to algae

(optimizing feeding system and heating methods) to achieve high process efficiency [67]. During the HTL process, inorganics need to be removed from the liquid stream (aqueous phase) to allow its reuse.

The process intensification approaches by integrating processes, such as the use of wastewater for algae growth, recycling of the HTL aqueous phase for microalgae growth, and the use of low-temperature heat streams for algae drying, can address some of the challenges and improve the overall process economics. Biomass fractionation before conversion, such as extracting lipids and pyrolysis of defatted algae, can improve the overall process yields. The careful selection and optimization of process parameters by integrating experiments, reaction kinetics, and process models would lead to the development of a sustainable process.

8. Conclusions

Algae can be processed to biofuels using both biochemical and thermochemical processing technologies, however, thermochemical technologies are considered more feasible for microalgae due to faster reaction rates, high oil yields, and high resource use efficiencies. Pyrolysis and hydrothermal liquefaction are promising thermochemical technologies that can process whole algal biomass and eliminates the expensive oil extraction step and accomplish high bio-oil production and energy efficiency. Processing of biomass in the water environment eliminates the need for drying and provides high process efficiency and economics in the case of the HTL process. The product yields are dependent on the process conditions, the temperature being the most critical parameter. Bio-oil obtained from HTL of algae is characterized by relatively low oxygen content compared to the pyrolysis oil but still requires upgradation before its use as a high-quality fuel. Although pyrolysis is a relatively mature technology, the HTL process is a more promising pathway for algae conversion in terms of energy yields and product quality.

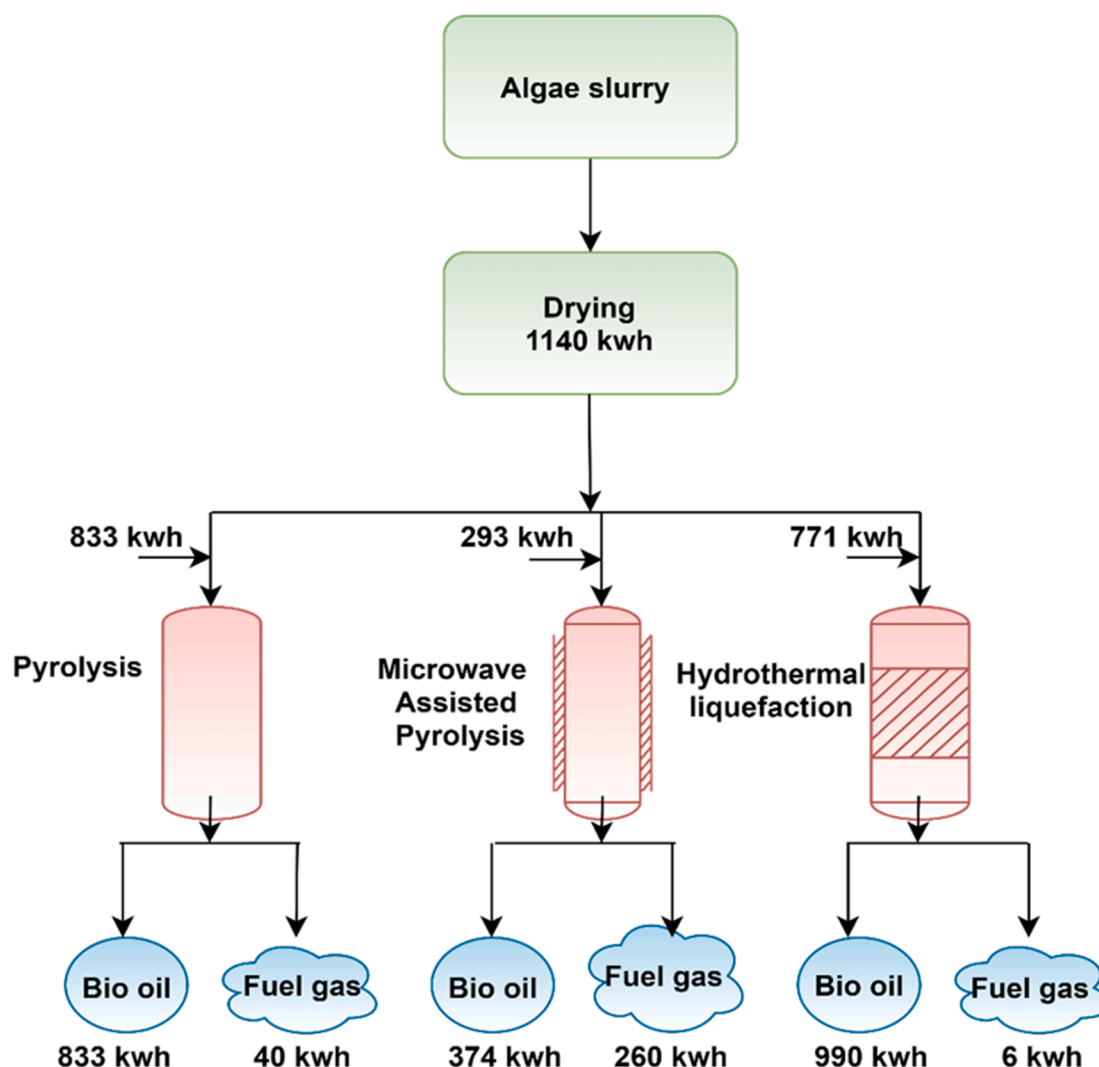


Fig. 6. Comparison of various process in terms of energy content.

Table 5
Comparison of Pyrolysis and HTL.

Factors	Pyrolysis	HTL
Type of biomass	Dry biomass	Wet biomass
Temperature	300 to 700 °C	200 to 400 °C
Pressure	Atmospheric pressure	5 to 25 MPa
Drying needed	Yes	No
Main products	bio-oil, fuel gases	Bio-crude or bio-oil
Co-products	Biochar	Mixture of gas
Heating value of bio-oil	30–42 MJ/kg	30–50 MJ/kg
Energy input	504 MJ	2776 MJ
Energy recovery ratio (ERR)	78.7%	89.8%
Energy cost *	High energy cost (80% of the energy used for drying, gas compression and size reduction)	Less energy cost (not needed drying process but includes catalyst)
Capital cost (M \$)	358.0	244.3
Fixed operating cost (M\$/a)	21.9	22.1

* Assumption – 30 MJ/kg HHV of bio-oil.

CRediT authorship contribution statement

Changlei Xia: Conceptualization, Methodology, Writing – original draft. **Abhijeet Pathy:** Investigation, Writing – original draft. **Balasu-bramanian Paramasivan:** Writing – review & editing. **Prabakaran Ganeshan:** Writing – review & editing. **Kondusamy Dhamodharan:** Writing – review & editing. **Ankita Juneja:** Writing – review & editing. **Deepak Kumar:** Writing – review & editing. **Kathirvel Brandadevi:** Supervision, Project administration. **Sang-Hyoun Kim:** Supervision, Project administration. **Karthik Rajendran:** Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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