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REVIEW

Hydrothermal liquefaction of Malaysia's algal biomass for high-quality bio-oil production

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Currently, fossil materials form the majority of our energy and chemical source. Many global concerns force us to rethink about our current dependence on the fossil energy. Limiting the use of these energy sources is a key priority for most countries that pledge to reduce greenhouse gas emissions. The application of biomass, as substitute fossil resources for producing biofuels, plastics and chemicals, is a widely accepted strategy for sustainable development. Aquatic plants including algae possess competitive advantages as biomass resources compared to the terrestrial plants in this current global situation. Bio-oil production from algal biomass is technically and economically viable, cost competitive, requires no capacious lands and minimal water use and reduces atmospheric carbon dioxide. The aim of this paper is to review the potential of converting algal biomass, as an aquatic plant, into high-quality crude bio-oil through applicable processes in Malaysia. In particular, bio-based materials and fuels from algal biomass are considered as one of the reliable alternatives for clean energy. Currently, pyrolysis and hydrothermal liquefaction (HTL) are two foremost processes for bio-oil production from biomass. HTL can directly convert high-moisture algal biomass into bio-oil, whereas pyrolysis requires feedstock drying to reduce the energy consumption during the process. Microwave-assisted HTL, which can be conducted in aqueous environment, is suitable for aquatic plants and wet biomass such as algae.

KEYWORDS

algal biomass, crude bio-oil, environmental impact, microwave assisted, renewable resources

1 | INTRODUCTION

One of the main challenges in the 21st century is the development of technologies that enable to sustain an ever-increasing demand of energy, chemicals and materials without significantly affecting the environment. The increase in worldwide energy consumption together with new guidelines and ongoing concerns about global climate change have led researchers to seek renewable materials and develop more sustainable processes to produce energy and chemicals. Current technologies are heavily based on fossil materials, which not only represent a limited resource and are increasingly difficult to extract, but are also heavily contributing to anthropogenic carbon dioxide (CO_2) emissions. Climate change is one of the major problems due to huge amount of CO_2 in the atmosphere. This carbon overload is mainly caused by the burning of fossil fuels including coal, oil and gas, and the unrestricted deforestation. There are other heat-trapping gases (from methane to water vapour), but CO_2 puts us at the substantial risk of irreversible changes if it is continuously accumulated in the atmosphere [1,2]. CO_2 remains in the atmosphere longer than the other major heat-trapping gases emitted from human activities. It is estimated that 40% of CO_2 from the emission will remain in the atmosphere for 100 years and 20% will reside for 1000 years, while the final 10% will take 10,000 years to turn over [3]. An

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Abbreviations: CO_2, carbon dioxide; GHGs, greenhouse gases; HTL, hydrothermal liquefaction; LCA, life-cycle analysis; PHA, polyhydroxyalkanoates; PLA, polylactic acid established statistics illustrate that CO_2 forms around 72% of total greenhouse gases (GHGs) emission and it has steadily increased 1.6 times in recent decades [4]. Hence, the necessity of GHGs reduction alternatives has been globally highlighted. Renewables offer cost-effective and readily available solutions to address the pressing environmental issues facing humanity and the planet at both global and local levels [5].

The climate change and the depletion of fossil fuel are spurring towards a transition from conventional fossil-based economy to a bio-based economy. The concept of a bio-based economy, in which biomass resources are used for the production of energy and materials instead of fossil fuels, is gaining a lot of attention. Over the past decades, the global demand for materials has grown roughly in line with the world's human population and economy [6]. Plastics have become indispensable for many applications throughout society. Both fossil fuel depletion and climate change are linked to the energy-intensive nature of plastics. Plastics production uses energy carriers not just to supply process energy (e.g. heat, steam, electricity required to run a process) but also as feedstock. In 2015, over 99% of plastics produced globally were based on fossil fuel. As the fossil fuel reserves are non-renewable, hence it is not sustainable [7]. Plastic wastes are now found throughout the natural environment, including the 'plastic soup' in oceans. Plastic pollution can damage wildlife through entanglement and ingestion, and enter food chains after breaking down into microplastics [8]. Some of the additives used in plastics have raised health concerns, for example related to toxicity and endocrine disruption [9–11].

Furthermore, a water-quality study disclosed that roughly 83% of testing sites across five continents and dozens of samples are contaminated with plastic fibre. That number is even higher in the United States with 94% of the samples testing positive [12]. Hence, the development of bio-based material is suggested to solve the water pollution caused by the excessive amount of plastics. Bio-based material refers to a product's main constituent consisting of a substance, or substances, originally derived from living organisms. These substances may be natural or synthesised organic compounds that naturally exist. Many of the modern innovations use bio-based materials to produce biodegradable products. Bioplastics are plastics made from plants, including corn, sugar cane and algae. Conventional petroleum-based plastic takes a long time to break down. When it does break down, it just disintegrates into smaller and smaller pieces that are eventually absorbed into the environment – mostly becoming more hazardous than its first form ever was.

In Malaysia, National Biomass Strategy 2020 was launched in November 2011. It aims to access how Malaysia can gain more revenue through the utilisation of biomass not only from palm oil industry, but also from forestry sector and the dedicated crops on marginal land [13]. Moreover, Biomass Technical Advisory Committee has developed a vision for Bioenergy and Bio-based Products in the United States, established a long-term goals that 20% of transportation fuels and 25% of chemicals and materials would be produced from biomass by 2030 [14]. The global biopolymers market is predicted to amass benefits from the use of bio-based raw materials. The dependence on petroleum-based plastics is gradually reducing with the development of bioplastics in numerous applications such as packaging and domestic goods. Although new bio-based products development is preferred to reduce GHG emissions, the related production processes must be cost-effective. The raw materials used in the production of biopolymers are originally renewable and are available in abundance across the world, compared to petroleum and fossil-based raw materials. Thus, the global outlook for bio-based raw materials for polymers is significantly more potential than conventional petroleum-based raw materials. The increasing focus on sustainable production is one of the key trends in the bioplastics and biopolymers market. The growth of biodegradable polymers market is projected to be high as a result of the growing focus on sustainability and the advent of favourable government regulations for green procurement. In fact, a recent report predicts that the biodegradable plastics market will grow from $2 billion in 2015 to $3.4 billion by 2020. It is believed that Western Europe is the main contributor this growth due to strict regulations on single-use petroleum products comprising almost half of the global market [12].

In particular, most studies in the renewable energy and sustainability sectors focus on the electricity generation from the alternatives of conventional fossil fuel. It cannot be denied that the potential of nuclear, wind, solar, and hydrotechnologies in the electricity generation sector is high. However, their potential is limited, as the energy derived is not in the liquid form and hence, it cannot directly replace the liquid fuels derived from fossil fuels. As most of the transportation and industrial engine require liquid fuel to operate, the biofuel obtained from biomass offers a superior advantage over the others. Besides, the biofuel derived can also be further processed to produce bio-based material. In short, biomass can be converted into different forms of energy, chemicals and materials that are conventionally derived from fossil resources.

PRACTICAL APPLICATION

Algal biomass can potentially be used to produce crude bio-oil that can replace existing conventional bio-oil, either for producing polymer or upgrading into fuel. The thermochemical conversion using microwave might also become a high potential implementation to enhance the productivity of oil in more economical way.

Biomass is the only renewable source of carbon that can be transformed into gas, liquid and solid products. Furthermore, biomass has the potential to reduce the CO_2 level in the atmosphere through photosynthesis during their growing process. Although CO_2 is released during the burning of biofuel, however, no new carbon is emitted as it is part of the carbon cycle and so, it is a renewable process. Hence, the biomass technology might have more potential on emerging sustainable products development.

2 | BIOMASS RESOURCES

Biomass is a carbon-neutral energy source. The resources are abundant and broadly available on the earth [15]. The utilisation of biomass to produce bio-oil is well accepted both as an energy source and a feedstock for chemical production. The usage of biomass as renewable resource provides significant environmental advantages as it absorbs atmospheric CO_2 during its growing. This eventually offsets the increase in atmospheric CO_2 that results from fuel combustion. The CO_2 emitted will then again be utilised to generate more biomass feedstocks [16]. Moreover, based on the fact that there are abundant crop residue and limited forestry resource, significant efforts should be taken to utilise these residues to fulfil large-scale industrial production of bioenergy.

Biomass is usually a heterogeneous mixture of organic substances with a small amount of inorganic substances, which is typically 30–40% oxygen, 30–60% carbon and 5–6% hydrogen on a dry basis, depending on the ash content. Other inorganic elements include nitrogen, chlorine and sulphur, which together make up less than 1% of the biomass. Generally, biomass is composed of cellulose, hemicellulose, lignin and extractives including proteins, ash and pectin [17]. In practical, biomass sources are abundance which include a wide range of terrestrial plants, aquatic plants, agricultural crops and animal wastes. Most of them are considered as potential sources of fuels and chemical feedstock [18]. The diversity of biomass sources has gained attention, and continuous research has been conducted to investigate the potential of biomass in replacing the conventional fossil fuel.

Looking into the current biomass scope that is actively being studied, the terrestrial plants may seem to gain more attentions. Terrestrial plants get their nutrients from two main sources which are soil and air. The roots absorb the water and minerals from the soil, as well as strongly hold the plant in place. Those essential nutrients are transported to cells in leaves by a system of tubes called vascular tissue. The leaves of terrestrial plant absorb the CO_2 gas from atmosphere for photosynthesis process, where the second set of vascular tissue carries the food made by the leaves to the rest of the plant once the photosynthesis is done. Land plants are also equipped with woody stems and branches that hold them upright so that the plants are able to receive plenty of sunlight for photosynthesis.

Apart from the plant living on the land, plants living in water might also be biomass resources. Oceans cover most of the earth's surface. Almost 99% of organisms, approximately five million species (most of them unclassified), live in oceans [19]. As a result, oceans are significant to the well-being of life and economies. Aquatic plants or macrophytes are commonly multicellular and some of them consist of certain features, such as roots, leaves and stems. These plants are generally characterised by the place they live, and thus, they can be divided into three categories: floating, submerged and emergent. Algae are similar to aquatic plants; however they do not have roots, leaves or stems. Both algae and aquatic plants produce their own energy through photosynthesis, which means they have the ability to fix CO_2 from the atmosphere in the presence of sunlight. At the same time of making organic carbon, they also release oxygen in the process. Algae are a food source for a number of species. They can be classified as primary producers in the ecosystem, and thus, they are located at the bottom of the food chain [20].

Generally, aquatic plants obtain their nutrients, water and dissolved gases from seawater. Since the entire marine plant is surrounded with water, these dissolved nutrients simply absorbed by each cell. Hence, marine plants do not have vascular tissue for photosynthesis process or to transport the products to each cell. In addition, marine plants do not require support structures because they are held up by the buoyant force of the water. The bodies of marine plants are flexible since water in the ocean is always moving, permitting them flexibly follow that movement. Some marine plants secrete mucus to make their surfaces slick, further reducing their drag or resistance to water movement [21].

Previously, it is often claimed that the aquatic habitat is less beneficial for growth of higher plants than the terrestrial plant, especially the availability of inorganic carbon is assumed to be a limiting factor for the photosynthesis and growth. Hence, these plants have evolved a number of strategies to cope with this situation. However, a research found that there are no significant differences in the growth rates [22]. Hence, the potential of accumulating the aquatic plant as biomass resources should not be ignored. Besides, the comparison between the terrestrial plants and aquatic plants can be found in Table 1.

One of the promising biomass feedstock from aquatic resources is algae. Algae have a fast growth rate compared to other terrestrial plants and higher photosynthetic efficiency. Furthermore, algae able to grow in various liquid media, giving advantage to it since less competition for arable land. Hence, due to the prolific growth rate and lipid productivity, utilisation of waste CO_2, and production of fuel precursors and high-value biochemical, algal biomass gained increased attention as a feedstock for renewable fuels and chemicals production [28–30]. There is a wide range of biomass conversion

TABLE 1 Aquatic plant and terrestrial plant comparison

Plant type	Aquatic plants and algae	Terrestrial plants	Reference
Characteristic	Usually without lignin No stem visible Shape broader than tall	Usually plant with lignin Stem and roots Taller than broad	[23]
Waxy layer	Lack a waxy coating because carbon dioxide is easier to absorb without this layer	Have waxy cuticles covering the tops of their leaves to resist evaporation.	[24]
Photosynthesis	Conducting photosynthesis under water	Conducting photosynthesis in the air	[25]
Sunlight absorption	Difficult to absorb sunlight underwater, chloroplasts in these plants are often situated on the leaf surface to maximise exposure to sunlight absorption. Some plant species have anatomical, cellular or biochemical adaptations that allow photosynthesis successfully in deep or murky water although the availability of sunlight becomes lower	May have direct sunlight absorption if less competition with surrounding plants. The competition of absorbing sunlight might happen for high crop population area.	[25]
Carbon dioxide absorption	Absorb carbon dioxide (CO_2) diffused in the water. CO_2 diffuse slower in water than in air.	Absorb CO_2 from the air. CO_2 diffuse faster in air than in water.	[25]
Nutrient and water absorption	Plants absorbs nutrient directly from the water surrounding	Plants absorb nutrients and water from the ground through their extensive root system	[26]
Plant growth competition	Less competitive to grow May have excessive growth in response to human activity, such as the addition of too many nutrients in the waterbody	High competitive to arable land	[27]
Available space for crop development	Lots of space available for growth or cultivation development	Limited space for crop and development	[27]

processes at varying stages of technical maturity. However, it is reported that the algal-based oil production platform is technologically immature [28]. Considering the conversion technologies of algal biomass specifically into phenolic bio-oil, thermochemical conversion process might drive towards the solution. Although the previous research found that algal bio-oil might has a lower density than lignocellulosic bio-oil, and a viscosity in the typical range of wood bio-oil, the potential of algae in producing high quality of phenolic bio-oil compound is undeniable [31]. Thus, the main purpose of this paper specifically is to focus on thermochemical conversion process of the algal biomass into the phenolic compound of bio-oil.

3 | ALGAE AS A POTENTIAL BIOMASS

The term algae originally refers to aquatic plants and it is now broadly used to include a number of different groups of unrelated organisms. Algae can be either single-cell or large-cell, multicellular organisms. They can be found in freshwater or salt water (most seaweeds are algae) or on the moist surfaces of soil or rocks. The multicellular algae generally lack of true stems, leaves or roots, although some of them consist of tissues that may be organised into structures to serve particular functions. The cell walls of algae are generally made of cellulose and can also contain pectin, which gives algae its slimy feel.

Algal biomass, as one of the potential biomass for biofuel production, is currently gaining much attention. It is considered as the third-generation biofuel feedstock. Unlike the first-generation biofuel feedstock (edible crop), such as soybean, palm tree, coconut and rapeseed, algal biomass does not create conflict with the food interest [32]. Besides, the utilisation of algal biomass as biofuel feedstock will also reduce the conflict arose by the second-generation biofuel feedstock (non-edible crop), as some of the non-edible crops are used for commercial application [32]. Apart from biofuel production, algae also play an important role in serving as the biomass feedstock for application, such as waste treatment, CO_2 mitigation, cosmetic production, synthesis of drug and pigments, and act as the biofertiliser, nutrition and food additives.

One of the significant advantages of using algae as the biomass source is that it can be grown very easily, and potentially achieve higher production rates of biomass compared to land-based crops in term of the land surface area used. Algae are fast growing eukaryotic microorganisms that convert sunlight, water and CO_2 into biomass by photosynthesis, and can be cultivated with inexpensive water and nutrients, such as municipal and agricultural wastewaters [33]. Wastewater which normally hinders the growth of plants instead is very effective for growing algae. Algae are typically found growing in ponds, waterways or other wetlands which receive sunlight and CO_2. They can grow in any kind of the water-based area, while utilising photosynthesis for biomass production [34,35].

Growth of algae varies on many factors, including temperature, sunlight utilisation, pH control, fluid mechanics and others [36]. Man-made production of algae tends to replicate the natural environments to achieve ideal growth conditions [35]. For algal cultivation purpose, several factors that influence the growth rate are listed as below [37].

1. Temperature: The culture temperature varies with algae species. The temperatures higher than 35°C can be lethal for a number of algal species, while temperatures lower than 16°C may slow down the algal growth.
2. Light: Algae need about one-tenth of direct sunlight for the growth in most cultivation. Bulk algal biomass may block light from reaching into deeper water, thus light only penetrates the top 7–10 cm of water in most water systems.
3. Mixing: Agitation or circulation is needed to mix the algal cultures.
4. Nutrients: Autotrophic growth needs carbon, hydrogen, oxygen, nitrogen, phosphorous, sulphur, iron and trace elements.
5. pH value: Algae prefer a pH from neutral to alkaline growth medium for efficient growth.

The number of products that can be produced from algae is virtually unlimited, due to the large assortment of species where the composition can be influenced by varying the conditions of cultivation. With only a few commercial algae-based products available, this resource is largely untapped. The market of potential microalgae products is wide, including food, protein powder and edible oils [38]. However, the main factors limiting the development of algae markets is the production and processing costs of algal biomass, mostly affected by the complexity of the cultivation phase and the downstream processes required to extract the high-value products in a biorefinery concept. Despite these critical issues, and the photosynthetic efficiency, algae can (i) be produced on marginal or degraded lands, avoiding competition with other food crops; (ii) garner a significant amounts of lipids (for biodiesel, green diesel and other processes) or carbohydrates (for bioethanol); (iii) grow effectively without pesticides; (iv) grow in saline waters, hence can avoid effecting fresh water resources; (v) fix CO_2 from flue gases and (iv) be cultivated on wastewaters consisting nutrients that are needed for algal growth [39,40].

The technology of cultivation of algae and its contribution in reducing CO_2 in atmosphere is actually well established. Algae can efficiently convert CO_2 into biomass by their photosynthesis process [34]. Some species of algae are able to produce up to 60% of dry weight in liquid form (oil) based on previous analytical studies. The cells grow in aqueous suspension, where they can effectively acquire water, CO and nutrients and capable to produce huge amount of biomass and usable oil in either with the help of photo bioreactors or high rate algal ponds [35].

3.1 | Diversity of algae species

There are numerous types of algae, which are normally differentiated by their species and also size ranges [35]. Two major classifications of algae are microalgae and macroalgae. Macroalgae and microalgae can either be heterotropic or autotropic. Autotropic algae need inorganic compounds, such as CO_2 and a light energy sources for growth. Heterotrophic algae are non-photosynthetic and require an external nutrient for growth. Some of photosynthetic algae are mixontropic that acquire exogenous organic nutrients and perform photosynthesis as well [34,41].

Macroalgae, or widely known as seaweeds, are multicellular organisms and belong to the category called 'lower plants', consisting of a leaf-like thallus instead of leaves, stems and roots [27,42,43]. Seaweed is an established term embracing macroscopic, multicellular, benthic marine algae which includes some major classification which are red, brown and green algae. They are photosynthetic, like plants, and 'simple' because they lack many distinct organs found in terrestrial plants [44]. Typically, macroalgae consist of (i) thallus: the body; (ii) lamina/blade: a leaf-like flattened structure; (iii) sorus: a spore cluster; (iv) fucus/air bladder: a hollow structure that is filled with gas, which can be found on the blade to help the macroalgae to float; (v) floats: organs that help the macroalgae float, and is located between blade and stipe; (vi) stipe: a stem-like structure, might be absence; (vii) holdfast: a specialised structure that holds the macroalgae in place; (viii) haptera: finger-like extensions of holdfast to allow the macroalgae anchor to benthic substrate. The basic structure of macroalgae is shown in Figure 1.

Microalgae comprise a vast group of photosynthetic, heterotrophic organisms which have an extraordinary potential for cultivation as energy crops. Microalgae are microscopic organisms that can rapidly grow in both salt and fresh water environments [45]. In fact, it can also be grown in the extreme environments, such as ice or hot springs. From the previous research, microalgae are thought to be one of the most primitive life forms on the earth with a very fast growing rate [27, 46]. Microalgae can survive in diverse ecological habitats. In other words, they are able to grow in flexible conditions, even at high temperatures and growth medium with high pH value.

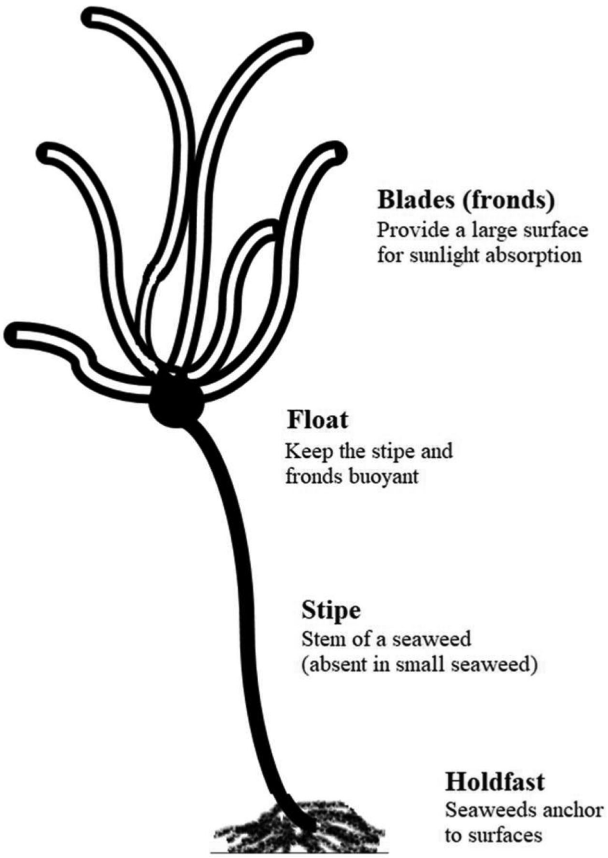


FIGURE 1 Basic structure of macroalgae

Furthermore, microalgae are able to divide their cells within 3–4 h, but mostly divide every 1 and 2 days under favourable growing conditions [47]. These abilities make microalgae the most abundant living organisms on earth. For cultivation purpose, they can also be cultivated under difficult agro-climatic conditions and are able to produce a wide range of commercially interesting by-products [44].

Microalgae can be unicellular and multicellular microorganisms, including prokaryotic microalgae that are cyanobacteria (chloroxybacteria) and eukaryotic microalgae for example, green algae (chlorophyta) and diatoms (bacillariophuta) [35]. The production of biofuel from microalgae is widely for several reasons: (i) they have higher biomass production of oil crops per unit surface area which is up to 30 times; (ii) less competition with traditional agricultural resources as they can be cultivated on non-arable land or on wastewater [31,48]; (iii) rich oil content, around 20–50% dry weight of biomass in most of the species [49].

Although microalgae relatively gain much more attention compared to macroalgae for research purpose, macroalgae also have undeniable potential to be developed and improved for bio-based substance production. The differences between macroalgae and microalgae are presented in Table 2.

3.2 | Algae potential in Malaysia

Algae species have a flexible grow and can survive over a wide range of temperatures. However, the maximum algae productivity can be obtained for some particular algae strain at specific range of temperature. The area with average ambient temperature below 15°C, which is shown outside the purple rectangle map in Figure 2, was assumed to be unpropitious for achieving high algae productivity. The regions within the blue rectangle map, however, are considered to have suitable condition and have a huge potential to maximise the algae productivity, and Malaysia is located within this area [53].

Malaysia is located in a geographic area covering the waters adjacent to six countries (i.e. Indonesia, Malaysia, Papua New Guinea, the Philippines, the Solomon Islands and Timor-Leste) in Southeast Asia and the Pacific, or generally known as the Coral Triangle. Malaysia is situated at the coordinate of 4.2105°N, 101.9758°E which is located near the equator line and the climate is categorised as equatorial, being hot and humid throughout the year, 250 cm (98 in.) average rainfall a year and 27°C (80.6°F) average temperature. The tropical conditions in the coastal waters of Malaysia provide a favourable environment for the growth and production of diverse types of algae species [54]. Geographically, the South China Sea borders Peninsular Malaysia in the east and both Sarawak and Sabah in the north that has natural advantages for algae culture. Malaysia has various salt lakes that offer researchers advanced algae-based technology. Hence, Malaysia region is surrounded by sea and has an extensive coastline fringed by numerous islands, providing various habitats for the proliferation of tropical algae.

Until recently, more than 100,000 algae species have been identified. According to the general estimates, around 400,000 species of algae exist worldwide [55]. Malaysia also has the vast algae resources. Several studies have been carried out in Malaysia, and the reports show that 375 specific and intraspecific taxa have been identified in Malaysia with reference to the regular collections and documentations of algae strains up to 2016 [27,56,57]. The number of known species of marine algae in Malaysia and the world are presented in Table 3 [58].

The use of algae as a potential biomass feedstock is still in infancy in Malaysia and has been receiving a lot of interest in recent years. Microalgae and macroalgae typically have their own development strategy, and the current cultivation development of both algae is typically exiled. A review data state that 31 countries and territories are recorded with algae farming production, and 99.6% of global cultivated microalgae production comes only from eight countries, as shown in Figures 3 and 4. Malaysia plays a role in global algal production. As one of the major microalgae-producing country, Malaysia has contributed about 1% of annual microalgae production, which is approximately 207,900 tons compared

TABLE 2 Algae species major classification [27,34,45,50–52]

Algae classification	Macroalgae (known as seaweed)	Microalgae
Growth	Fast growing Size up to 60 metres in length	Fast growing Very small size
Plant type	Multicellular plants Macroscopic Benthic marine algae	Unicellular plant Simple multicellular microorganisms Microscopic thallophytic plants (Plants with out of leaves, stems and roots)
Main classes	Brown seaweed (*Phaeophyceae*) Red seaweed (*Rhodoophyceae*) Green seaweed (*Chlorophyceae*)	Diatoms (Bacillariophyceae) Green algae (Chlorophyceae) Golden algae (Chrysophyceae) Blue-green algae (Cyanophyceae)
Main commercial use	Food production Hydrocolloids extraction	Biofuel and biodiesel production
Example of commercially used algae species	Gracilaria Sargassum Sea lettuce *Ulva lacuta*	Arthrospira (Spirulina), Chaetoceros Isochrysis Dunaliella Chlorella *Pleurochrysis carterae* *Botryococcus braunii*
Contents	Mostly carbohydrate and some protein	High heating value and lipid content Contain carbohydrate, lipid and protein Lower ash and salt content
Advantages	Many different species and less pests and invasive species Simpler to cultivate and easy to harvest No land required No added water required	Easy to cultivated in laboratory Easier growth control Easier to genetically manipulate

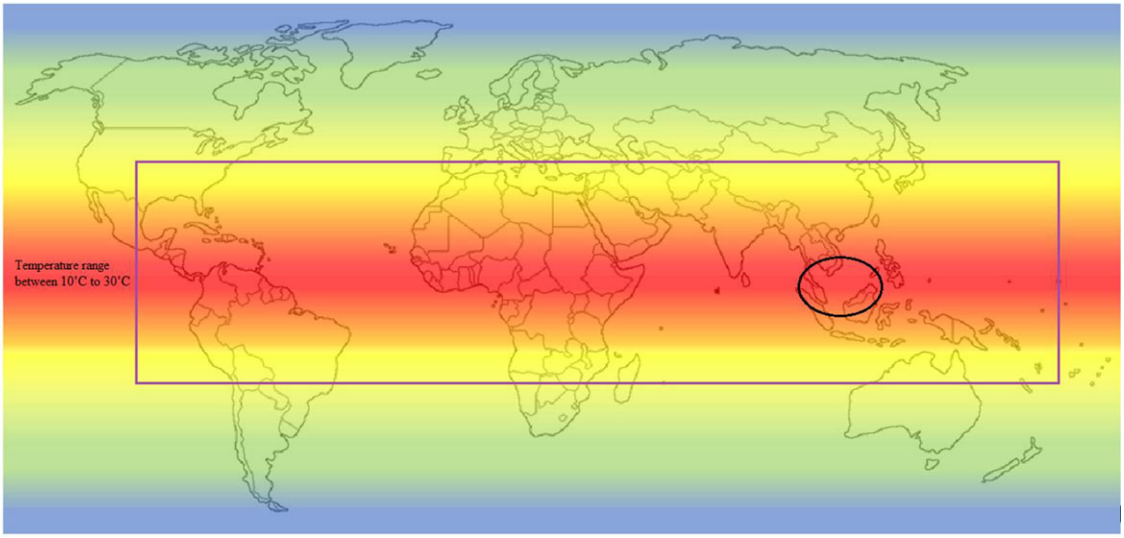


FIGURE 2 Temperature zone projected to be suitable for algal biomass production

TABLE 3 Estimates number of known species of marine algae as reported by Mazlan et al

Major categories	Groups	Estimate numbers in Malaysia	Estimate numbers in the world
Seaweed and other algae	Chlorophyceae	78	800
	Rhodophyceae	69	4000
	Phaeophyceae	49	1500
	Cynophyceae	13	1500
Microalgae	Diatoms	70	4200
	Dinoflagellates	30	1200

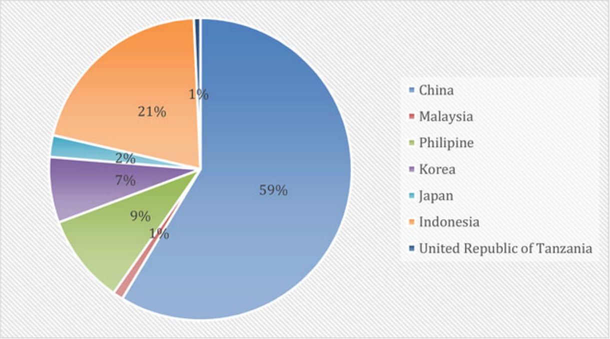


FIGURE 3 Malaysia annual microalgae production in comparison to major algae-producing countries

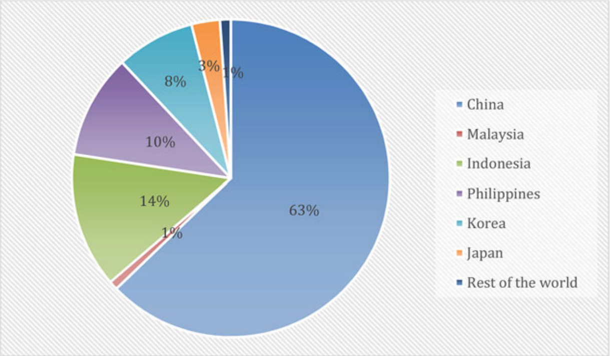


FIGURE 4 Global seaweed production up to 2018 [50]

to those other major microalgae-producing countries [27,59]. Meanwhile, about 1% of global macroalgae seaweed production is also attributed by Malaysia.

The fundamental studies in algal research have shown in many publications that recorded the microalgae diversity in Malaysia [27]. Besides microalgae, macroalgae also gained attention on some research area in Malaysia, such as research and commercial applications [60,61]. A study on red algae or scientifically known as *Rhodophycaea* has been reported by a group of researchers from Malaysia [62]. The research found that besides being a sustainable source of energy, red algae has exciting prospects in several product markets. The primary algae project at the university lab, in fact, is creating paper from red algae. From that particular research, red algae are preferable to wood as a source material for paper products. This shows that the composition in algae has the potential to be used as a source of diverse type of application. Table 6 shows the list of several established algal species with their respective biochemical composition on dry matter basis.

Besides, studies have been conducted to identify the suitable algal species to be a source of alternative fuel and chemical feedstock. Numerous efforts have been also undertaken mainly in Sabah and Sarawak area in order to produce algal biomass. Algae are a promising source for crude bio-oil production as it will not undermine to the other products derived from crop plants [63]. Although palm oil is one of the major raw materials for biomass in Malaysia and has been widely investigated, the production of palm oil is insufficient to meet the current demand, and also there is conflict with the food interest [27]. Biochemical composition of algae expressed on a dry matter basis (%dry weight) is shown in Table 4 and some of the potential products or application of algal biomass is shown in Figure 5.

The majority of the seaweed production in Malaysia comes from Semporna, which is located at the East coast of Sabah [68,69]. Hence, Sabah is the main seaweed producer in Malaysia. However, Malaysia still has huge potential in becoming the top leader player in global seaweed production as Malaysia consists of a lot of potential areas for seaweed cultivation. Table 5 records some of the macroalgae (seaweed) species and their respective location in Malaysia.

Sabah is geographically situated below the monsoon and typhoon belt, and, therefore, it is known as the land below the wind. Sabah is located on the Island of Borneo and well known as the only part of Malaysia where seaweed is cultivated commercially [54]. The eastern coast of Sabah has a suitable environment for growing good value seaweed that includes several species from red seaweed and the green seaweed [57]. Figure 6 highlights the potential locations in Sabah for seaweed growing.

Other than as a sustainable nutrient-dense food source, seaweed is acknowledged to have wide application potentials similar or even better than other established biomass resources, such as palm oil and cocoa. Seaweed-based industries, including seaweed cultivation or farming had started and are gradually developing. Besides, apart from the government agencies focussing on socio-economy development for rural peoples, there are also private local companies

TABLE 4 Biochemical composition of algae expressed on a dry matter basis (%dry weight) [27,64–66]

Algae	Protein	Carbohydrates	Lipid
Macroalgae			
Acanthophora spicifera	12.0–13.2	11.6–13.2	10.0–12.0
Boergesenia forbesii	7.43	21.38	11.42
Caulerpa fergusonii	7.76	23.63	7.15
Caulerpa peltata	6.41	45.00	11.42
Caulerpa racemosa	11.8–12.5	16.0	9.0–10.5
Chaetomorpha aerea	10.13	31.50	8.50
Chaetomorpha antennina	10.13	27.00	11.45
Codium tomentosum	5.06	29.25	7.15
Dictyosphaeria cavernosa	6.00	42.75	10.51
Enteromorpha compressa	7.26	24.75	11.45
Halimeda macroloba	5.40	32.63	9.89
Laurencia papillosa	11.8–12.9	12.0–13.3	8.9–10.8
Ulva lactuca	11.4–12.6	11.6–13.2	9.6–11.4
Ulva reticulata	12.83	16.88	8.50
Valoniopsis pachynema	8.78	31.50	9.09
Microalgae			
Anabaena cylindrical	43–56	25–30	4–7
Botryococus braunii	8–17	8–20	21
Chlamydomonas rheinhardii	48	17	21
Chlorella vulgaris	51–58	12–17	14–22
Dunaliella bioculata	49	4	8
Euglena gracilis	39-61	14-18	14-20
Isochrysis sp.	31–51	11–14	20–22
Neochloris oleoabundans	20–60	20–60	35–54
Porphyridium cruentum	28–39	40–57	9–14
Scenedesmus obliquus	50–56	10–17	12–14
Tetraselmis maculate	52	15	3

venturing in seaweed processing and cultivation for a larger scale in Semporna.

Cultivation of seaweed or macroalgae in Sabah can be traced back to 40 years. The development of seaweed production has been improved progressively from time to time since the early stage of development, and eventually seaweed has become an economically important natural resource for Malaysia. Table 6 shows the seaweed evolution since the early stage of development [54] and Figure 7 shows the increasing production of seaweed in metric tonnes based on its dry weight.

Currently, there are plenty of companies, government entities, scientists and researchers actively working around the world to develop the potential products from algae. In the United States alone, there are more than 50 research institutions and over a 100 companies working on algae technologies across the value chain. These companies and institutions are working in all aspects of the algae product lifecycle including identifying and optimising specific strains of algae, developing growth and cultivation systems, enhancing refining technologies, farming large quantities of algae and oil production. In Malaysia, there are several established company that focussing on algae development such as Algaetech International Sdn Bhd (Algaetech Malaysia) [75] and Algae

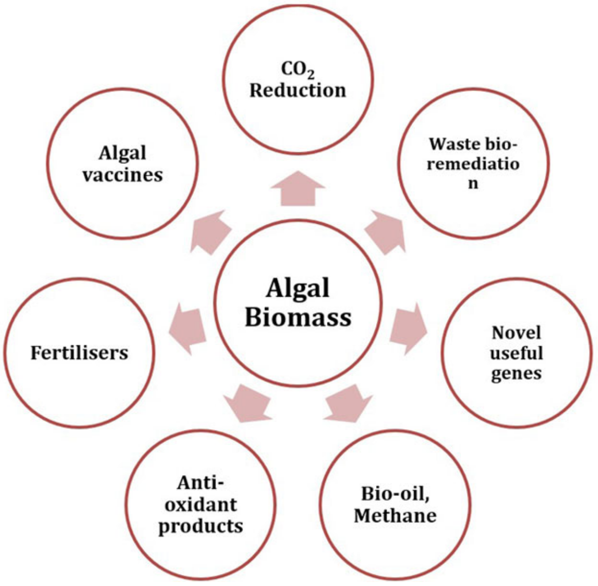


FIGURE 5 The potential products and application of algal biomass [67]

TABLE 5 Location and habitat of various kinds of seaweed in Malaysia [57]

Macroalgae (Seaweed) species	Location in Malaysia[a]	Habitat[b]
Acanthophora spicifera	W, E, P	C, D, R, S
Boergesenia forbesii	E	C, E, R
Caulerpa fergusonii	W	R
Caulerpa peltata	W, E	C, R, S
Caulerpa racemosa	W, E, Sb	C, M, S
Chaetomorpha aerea	E	-
Chaetomorpha antennina	W	R
Codium tomentosum	E, P	C, R
Dictyosphaeria cavernosa	W, E	C, R
Enteromorpha compressa	W	-
Halimeda macroloba	W, E	C, S
Laurencia papillosa	W, E, Sb, Sk	C, R, S
Ulva lactuca	W	D
Ulva reticulata	P, W	D
Valoniopsis pachynema	W	R

[a] *Distribution*: E, East Coast Peninsular Malaysia; P, Peninsular Malaysia; Sb, Sabah Malaysia; Sk, Sarawak Malaysia; W, West Coast Peninsular Malaysia.
[b] *Habitat*: C, coral; D, driftweed; E, epiphyte; M, mud; R, rock, bedrock and stones; S, sand.

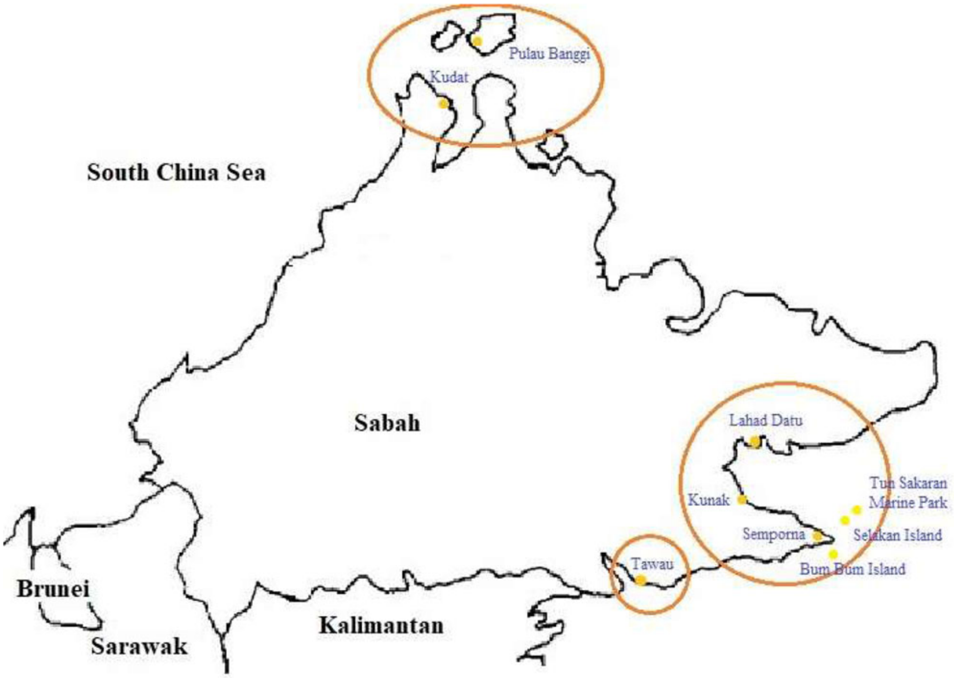


FIGURE 6 Location of seaweed growing areas in Sabah; Banggi, Kudat, Lahad Datu, Kunak, Semporna, Selakan Island, Bum Island and Tawau (extracted information from [54])

International Berhad (AIB) [38]. Those companies have made algae competitive with fossil fuels at current prices. This is a major inflection point for the energy industry. In short, Malaysia has the potential to be a major seaweed player in the region including infrastructure, manpower, product quality, transfer of technology, industrial support and marketing. Malaysia has reliable resources for both microalgae and macroalgae, which can be optimally utilised. It is believed that if more efforts are put into improving the seaweed industry, the seaweed production volume and value will further increase.

3.3 | Conversion strategies of algae biomass

Biomass conversion from its natural solid form to liquid fuels is not an unsolicited process. The conventional liquid fossil fuels that have been harnessed on a large scale took thousands of years of geochemical processing to convert biomass into crude oil and gas. Since then, several conversion technologies of biomass have been developed to obtain liquid products for fuels and chemicals usage. The technologies of conversion are broadly classified into two categories, namely biochemical and thermochemical conversion [18]. In order to obtain liquid products from different sources, the main difference between both is that thermochemical conversions are processed at several higher degrees of temperature compared to biochemical conversions in the presence of appropriate catalysts. However, thermochemical conversions are generally much rapid and commonly carried out in much shorter time than the biochemical conversions. Thermochemical conversion implied to upgrade biomass by heating under pressurised and oxygen deprived enclosure [18]. Moreover, one of the main advantages is that the thermochemical conversion has the potential to be integrated into the existing petroleum-processing infrastructure [31].

Algae biomass is a type of biomass that has high moisture content. The aqueous phase of algal feedstocks has biogenic carbon, phosphorous, nitrogen and micronutrients that can be recycled for algal cultivation purposes. In addition, by extraction and catalytic processes, high-value chemicals such as ethanol, acetone and acetic acid can be obtained [17]. Hence, the conversion process involving drying requires a large amount of thermal energy due to the high latent heat of vaporisation of water [76]. From Figure 8, the thermochemical algae biomass can be processed with three conversion method categories which are transesterification, biochemical conversion and thermochemical conversion, while each category consists of several specific conversion methods. Each conversion method of algae will produce a different end product which is listed in Table 7.

In short, the selection of conversion methods depends on the desired form of the end product and techno-economic considerations. A large number of scientific works pointed out that the biofuel production from algae is technically feasible [39,77], even if not yet optimised where the positive economical and energy balance achievement is still under demonstration [39,78–80].

TABLE 6 Development, Strategies and Policy of Seaweed industry in Malaysia

1973	Cultivation of seaweed *Eucheuma cottonii* (Webervan Bosse 1913) has been introduced to the Semporna district of eastern Sabah by The State government of Sabah [70,71]
1980	A seaweed project has been initiated in Sabah by the Federal government. It was initially failed due to lack of support from local people, and the techniques and knowledge for cultivation were not yet properly implemented [54]
1988–2001	Seaweed production started to rise and grow
2002	Seaweed production declined to its lowest level
2004	Seaweed production gradually improved [72]
2008	Malaysia was ranked ninth among the top 10 seaweed-producing countries (0.4% contribution of the world seaweed production [71]; 111,298 ton of total growing seaweed [71] which is from
	Semporna (95%) Lahad Datu (4.4%) Banggi (0.3%) Kunak (0.3%)
2010–2015 (10th Malaysia Plan)	The promotion and development of the seaweed industry also procured importance in that plan [54]
2011–2020 (Malaysian National Agro-Food Policy)	Sea weed was considered a high-value commodity [72]
	By 2020, through the seaweed industrial zone development, the Ministry of Agriculture and Agro-Based Industries aims to
	1. Provide a safe cultivation environment of 20,500 ha **2.** Capitalise on Malaysia's competitive advantage [72] **3.** Increase dry seaweed production to 900,000 ton, which would be worth approximately RM 1.4 billion (approximately USD 344.76 million)
2013	Malaysia was ranked eighth, produce about 269,431 ton of seaweed (1% of the total worldwide seaweed production) [73]
2014–now	Seaweed industry gradually improved
2015–2020 (11th Malaysia Plan)	The plan did not directly refer to the seaweed industry, the industry was included in various key areas related to coastal development, conservation of natural resources, and improvement of the livelihood of coastal area populations [54]

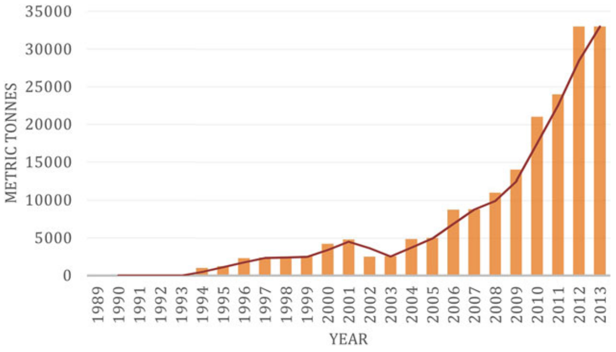


FIGURE 7 Total production of Seaweed in Sabah, Malaysia (1989–2013) based on the dry weight)
Source: Sabah Annual Fisheries Statistic [74].

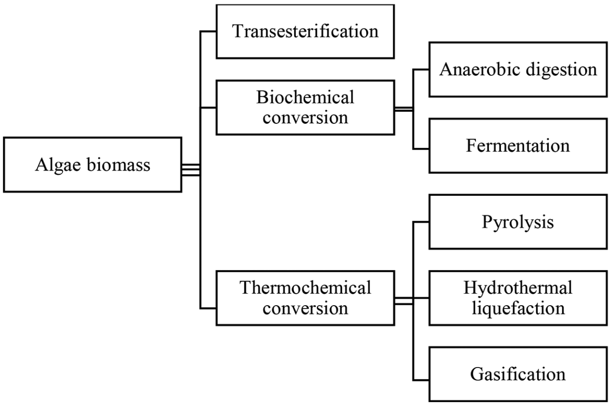


FIGURE 8 Current strategies of biofuel production from algal biomass

4 | THERMOCHEMICAL CONVERSION PROCESS OF ALGAL BIOMASS TO PRODUCE BIO-OIL

Algae cultivation, algae harvesting, algal biomass to bio-oil conversion and utilisation of co-products from extracted algal oils are the important steps in algal bio-oil production. Those several steps make bio-oil production process and energy more intensive. The conversion process of algal biomass has significant techno-economic challenges in algal bio-oil commercialisation. The major challenges include (i)

TABLE 7 Conversion methods of biomass and the end product [31,50]

Conversion method	Method description	Advantages	Disadvantages	Products
Transesterification	Converting biomass into biodiesel by the reaction of biomass feedstock catalytically with a short-chain aliphatic alcohols [81]	No dewatering	Poor yield	Biodiesel
Anaerobic digestion	Biological processes in which microorganisms break down biodegradable material in the absence of oxygen	Do not require drying Matured technology	High nitrogen and sodium inhibition	Methane, hydrogen
Fermentation	The chemical process by which molecules such as glucose are decomposed anaerobically. It can involve complete decomposition of the glucose to carbon dioxide and water (with energy) or can be adapted to produce ethanol (ethyl alcohol and energy) [82]	High carbohydrates contents	Low efficiency, mixed sugars	Ethanol
Pyrolysis	Biomass feedstock is subjected to high temperatures at low oxygen levels and it may be carried out under pressure	No caustic chemicals required Fast rate of process	High temperature and energy consumption	Bio-oil, biochar, syngas
Hydrothermal liquefaction	Converting into liquid form at low temperature with high pressure thermochemical conversion process carried out in the liquid phase	Drying not required	–	Bio-oil, biochar, syngas
Gasification	Converting a solid or liquid form of biomass into a gaseous fuel without leaving any solid carbonaceous residue [81]	–	–	Syngas

less efficiency of harvesting method; (ii) require high energy for drying algae; (iii) consumption of large amounts of hazardous chemicals in lipid extraction; (iv) extensive process of lipid separation and purification; (v) high cost of the conversion processes. Therefore, it is necessary to initiate a simple and eco-friendly conversion that diminishes the chemical and energy consumption, and duration of overall process in bio-oil production [83].

Thermochemical processing technologies have been employed since 18th century to convert biomass into crude bio-oil. They are gaining prevalent interest as an alternative to accommodate the energy demands while tackling the arise concerns on environment related to increasing global warming issue and limited fossil fuel reserves [17,76]. Thermochemical conversion is the thermal decomposition of organic matter in biomass for oil production. Moreover, thermochemical conversion has the potential to be integrated into the existing petroleum-processing infrastructure [31].

Bio-oil production from algae is a straightforward process that consisted of growing the algae by providing necessary inputs for photosynthesis, harvesting, dewatering and oil extraction. Algae cells absorb energy in the form of photons, which convert inorganic compounds of CO and water into sugars and oxygen. The sugars are eventually converted into complex carbohydrates, starches, proteins and lipids within the algae cells. In order to extract the valuable lipids, a series of steps must be undertaken to isolate the algae cells and oil [35]. However, avoiding the drying step is a significant advantage by wet extraction. In wet pathways, cell disruption can be based on mechanical approaches such as microwave, ultra-sonication, high-pressure stresses, sudden changes of pressure and others. Meanwhile, the biological approaches include the use of enzyme for cell disruption or osmotic stresses, or else thermochemical processing such as hydrothermal liquefaction (HTL) [39].

Pyrolysis and HTL are both technologies to maximise liquid products from biomass. These liquids produced are, however, not one-to-one replacements for all petroleum products. The liquids can directly replace petroleum products for heating and electricity purposes and some chemical compounds. The replacement of some other chemicals and transportation fuels requires an additional upgrading step, in which the quality of the bio-oil/biocrude is elevated to the higher requirements of those products [84–86]. The bio-oil produced by these technologies can be used to replace petroleum in other markets as well. The scope of the research will include all those markets, as they all contribute to the technological development of Fast Pyrolysis (FP) and HTL [84]. Figure 9

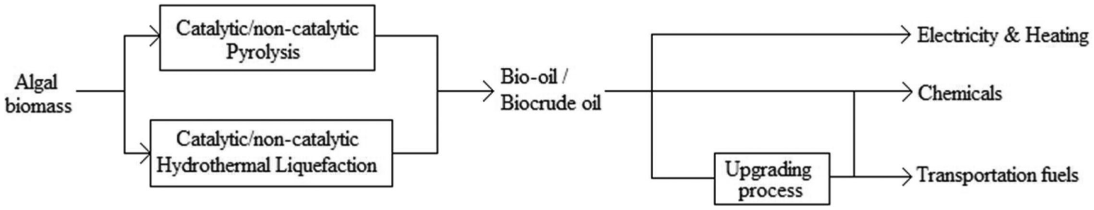


FIGURE 9 Overview of algal bio-oil process and application

shows the process overview of algal bio-oil and the application.

In thermochemical conversion process, these biomass pyrolysis and HTL are two comparable technologies, as they both can produce bio-based intermediate products which is referred as crude bio-oil. However, the complex associated reaction pathways of these technologies are not yet clear, and many researchers are at present focussing on understanding these pathways [[76]]. The present work examines the possible routes for thermochemical conversion of algae into liquid biofuels, distinguishing between dry processes, namely pyrolysis and wet processes (near-critical water) using HTL [39].

In the recent years, the phenolic-rich bio-oil production has garnered some attentiveness to be the desirable compounds for the fuel properties of bio-oil because their low oxygen contents notably enhance the heating value of bio-oil. Phenolic compounds also cover a wide application range for the production of energies and fine chemicals [87]. Although algal bio-oil might has a slightly lower density than lignocellulosic bio-oil, and a viscosity in the typical range of wood bio-oil [31], the potential of algae in producing high quality of phenolic bio-oil compound is undeniable.

4.1 | Pyrolysis of algal biomass

Pyrolysis is one of the eco-friendly and cost-effective conversion technologies to extract bioenergy from biomass [88]. It is the thermal disintegration process of biomass operating in the absence of oxygen. Pyrolysis is the conversion of biomass into bio-oil, biochar and syngas (CO_2, carbon monoxide, hydrogen and methane). This particular thermochemical process is commonly carried out at atmospheric pressure and high temperature range, from 300°C to 700°C and above. The yield and properties of the pyrolysis products depend on the pyrolysis temperature, heating rate, residence time and catalyst [31,39,89]. Pyrolysis is classified into stages which are shown in Table 8.

Broadly, there are two main classes of pyrolysis: slow pyrolysis and fast pyrolysis [90]. The difference between both is the heating rate that is used during the process. Slow pyrolysis is characterised by lower heating rates, and with the purpose of maximising the char yield. On the other hand, fast pyrolysis is heated at rapid rates and thereby maximises the liquid yields [84,91]. Usually, fast pyrolysis involves high operating temperatures, very short contact times (residence time) and fine particles [92]. Moreover, pyrolysis can be catalytic, as well as non-catalytic [84,93]. Pyrolysis processes is applicable for a broad range of biomass feedstocks. The pyrolysis process is very dependent on the moisture content of the feedstock, which should be around 10%. At higher moisture contents, high levels of water are produced and at lower levels there is a risk that the process only produces dust instead of oil. Generally, high-moisture waste streams require drying before subjecting to pyrolysis [89].

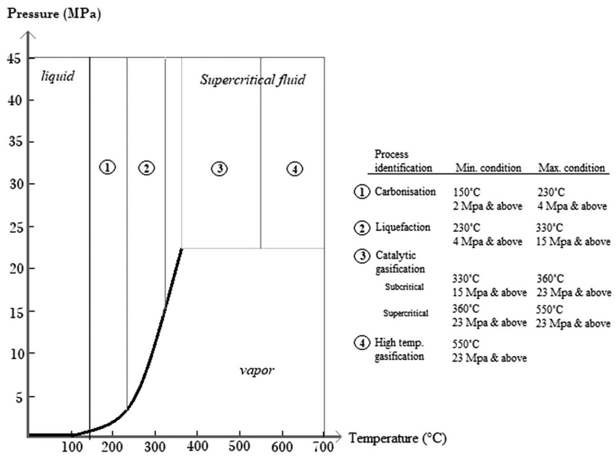
Besides those main classes, some variations have been put forward. There is a reaction that is slightly quicker than slow pyrolysis, known as intermediate pyrolysis [94]. The heating rate of intermediate pyrolysis is significantly lower than in fast pyrolysis, and residence time of intermediate pyrolysis is much longer. The derived products are more evenly distributed between liquid, char and gas compared to fast pyrolysis. In addition, a very fast pyrolysis is also introduced as flash pyrolysis, in which requires even higher temperatures and shorter residence times compared to fast pyrolysis. The products derived by flash pyrolysis contain a higher oil yield, however, there are still a lot of technological limitations. Therefore, fast pyrolysis has gained popularity in producing liquid yields [95].

4.2 | Hydrothermal liquefaction of algal biomass

HTL is another propitious route of biomass conversion that recently drawn attention. HTL is actually similar to hydrous

TABLE 8 Classification of Pyrolysis

Pyrolysis	Temperature	Heating rate	Main yield
Slow pyrolysis	Low temperature (less than 450°C)	Slow heating rates	Biochar
Fast pyrolysis	High temperature (higher than 800°C)	Rapid heating rates	Gases
Intermediate pyrolysis	Intermediate temperature	Under relatively high heating rates	Bio-oil



Process identification	Min. condition	Max. condition
① Carbonisation	150°C 2 Mpa & above	230°C 4 Mpa & above
② Liquefaction	230°C 4 Mpa & above	330°C 15 Mpa & above
③ Catalytic gasification		
Subcritical	330°C 15 Mpa & above	360°C 23 Mpa & above
Supercritical	360°C 23 Mpa & above	550°C 23 Mpa & above
④ High temp. gasification	550°C 23 Mpa & above	

FIGURE 10 Graphical overview of hydrothermal processing variations [84,97,101]

pyrolysis but is operated at lower temperatures and heating rates compared to pyrolysis [18]. HTL also involves the thermochemical conversion of diverse type of biomass in the presence of hot compressed water at subcritical water conditions to produce bio-oil [17]. The HTL process convert biomass into a crude bio-oil containing monomeric to oligomeric compounds, which mimics the natural geological process of fossil fuels production [33]. The HTL of algal biomass involves liquefaction process in the presence of water, a hydrogen donor solvent at temperature below 400°C and pressure between 4 and 20 MPa for 5–30 min, where subcritical water conditions (temperature range of 250–350°C) are typically reached [84,96,97]. Hydrothermal processing that involves thermal decomposition of biomass in hot compressed water, wherein a series of complex reactions causes changes in the physical properties of the water including density, solubility and dielectric constant [17,98]. Following HTL, energy rich bio-oil and biochar can be obtained and easily separated.

It obviously shows that hydrothermal processing technologies have notable potential for high moisture content biomass processing. Conventional technologies is generally not an economical option for the biomass with high moisture content such as algae, as a quite large amount of energy required for drying process and incur high costs for drying and dewatering [35], even the energy required for drying may exceeds the energy used for hydrothermal processing at supercritical conditions for the moisture content higher than 30%. Thus, the use of aqueous phase organics is an option where the operating costs of the hydrothermal technology can be reduced, as using organics helps reduce wastewater treatment costs [17,99]. Therefore, HTL is suitable to accommodate the production of crude bio-oil from various biomass resources with varying moisture content including wood, waste, and algae-based biomass [76]. HTL can directly convert wet biomass into liquid bio-oil either with or without a catalyst [39,100]. HTL mainly produces the product in liquid form. At even higher temperatures, gasification reactions dominate, which results in the production of gas [101]. The latter happens above the critical point of water [102]. An overview of the main classes is given in Figure 10.

This study focusses on HTL to mainly produce liquids. Compared with gasification, there are more publications and reports on HTL of algae which could directly produce liquid oil. Previous research reported the yield of bio-oil, which is estimated to be in the range of 10–50% with a heating value of 35–40 MJ kg^{-1}, slightly lower than petroleum crude oil of 43 MJ kg^{-1} heating value [103–105]. However, some other research found that the typical HTL oil yield reported in several studies is equal to approximately 50–60% depending also on the use of homogeneous or heterogeneous catalysts [104]. The bio-oil from HTL contains approximately 10–20% of oxygen and nitrogen, with energy density in the range of 30–37 MJ kg^{-1} [39,106]. Meanwhile, [107] operated a continuous-flow HTL reactor to decompose several different algae feedstocks at 350°C and obtained a crude bio-oil yield around 38–64% [33].

The efficiency, yield and quality of algal bio-oil by HTL conversion are influenced by several parameters such as feedstock composition, reaction temperature and residence time, retention time, biomass loading and presence of catalysts. Different from the algae-to-biodiesel pathway, which essentially only depends on the algae strain and lipid contents, HTL and pyrolysis can be used to convert not only the lipid fraction of microalgae but also the other organic components including proteins and carbohydrates [39,104].

4.3 | Comparison between pyrolysis and hydrothermal liquefaction

Pyrolytic bio-oil consists of compounds with lower mean molecular weights and contains more low boiling compounds than bio-oil produced by HTL [31].

In data, it is found that the value of the HTL bio-oil was increasing with the temperature while it was constant for pyrolysis (Table 9). According to previous experimental research, the HTL led to bio-oil yield decreasing from 67% mass fraction at 220°C to 59% mass fraction at 310°C, whereas the bio-oil yield increased from 53% mass fraction at 400°C to 60% mass fraction at 550°C for pyrolysis. Energy ratios (energy produced in the form of bio-oil divided by the energy content of the initial algae) between 66% at 220°C and 90% at 310°C in HTL were obtained, whereas it was in the range 73–83% at 400–550°C for pyrolysis. Algae cultivation in aqueous phase produced by HTL was also investigated and showed promising results [108]. Furthermore, Hu et al. concluded that HTL produced higher yield of bio-oil and lower yield of biochar for the same raw samples compared with pyrolysis process [109]. The comparison between

TABLE 9 Pyrolysis and hydrothermal liquefaction comparison [18,31,108,109]

Process	Pyrolysis	Hydrothermal liquefaction
Operating temperature	300–700°C	250–350°C
Operating pressure	Lower pressure Atmospheric pressure	Higher pressure 4–20 MPa
Feedstock	Suitable for dry feedstock	High-moisture biomass
Process condition	In hot compressed water Subcritical water condition Presence of water as medium	Absence of oxygen
Drying feedstock	Drying process needed	No drying process
Energy density	Produce a bio-oil that contains approximately twice the energy density of pyrolysis oil	30–37 MJ kg
Oil yield relative to operating temperature	Constant	Increasing with the temperature 50–60%
Water content (moisture of biomass)	Less than 40%	80–85%
Feedstock	Low moisture content	High moisture content
Oil quality	Low	High

TABLE 10 Comparison between pyrolysis and hydrothermal liquefaction using different algal biomass

Methods	Algal biomass	Temperature (°C)	Bio-oil yield (%)	Remarks	Reference
Pyrolysis	*Chlorella vulgaris*	400	19.7	Non-catalytic, fixed bed reactor	[110]
	Enteromorpha clathrata	500	41.2	50 L h^{-1} carrier gas flow	[111]
		550	29.56	Fixed bed reactor	[112]
	Saccharina japonica	350	44.99 wt	Fluidised bed reactor	[113]
	Sargassum natans	500	33.7	50 L h^{-1} carrier gas flow	[114]
Hydrothermal liquefaction	*Alaria esculenta*	350	17.8	Batch-type reactor	[115]
	Enteromorpha clathrata	550	32.52	Autoclave reactor, co-solvent	[112]
	Laminaria saccharina	350	35.97	16.5 bar, muffle furnace	[116]
		350	13	Batch-type reactor	[115]
	Laminaria digitata	350	17.6	Batch -type reactor	[115]
	Laminaria hyperbore	350	9.8	Batch-type reactor	[115]
	Nannochloropsis Oceanica	260	54	Batch reactor, co-solvent	[117]
	Oedogonium macroalgae	300	25 wt	Co-solvent, batch reactor	[118]

the pyrolysis and HTL process using different algal biomass is presented in Table 10.

4.4 | Advancement in liquefaction process of algae using microwave to produce bio-oil

The microwave-assisted technology in organic chemistry emerges in the mid-1980s, and there has been a significant increase in the number of publications on microwave-assisted organic reactions since the 1990s [119,120] because of increased valuable application associated with the process. The encouragement of microwave-assisted reactions in organic chemistry has improved the speed, reduced energy and cost spent, brings it to become a sustainable process [121, 122] and are continuously encouraged until today's applications to reduce the non-renewable resources as well as polluting solvent, and to minimise secondary toxic products generation and reduce harmful gases emission [123–125]. Microwave-assisted reactions in organic chemistry attain the same by faster reactions under bulk conditions and reducing the reaction time [119,124]. Scientists investigate the microwave dielectric heating mechanism and identify the advantages of the chemical synthesis [126]. Table 10 shows the advantage and disadvantage of microwave reaction.

Microwave energy engages as a part of electromagnetic spectrum, characterised by being situated in the wavelength interval between 1 mm and 1 m, and frequency interval, and consists of electromagnetic radiation which operates at the high-frequency waves, ranging between 0.3 (300 MHz) and 300 GHz [127,128] (Table 11). Electromagnetic waves with a higher frequency are associated with higher energy and shorter wavelengths [32]. In the electromagnetic spectrum, the microwave radiation region is located between infrared radiation and radiowaves. Microwaves are a form of

TABLE 11 Advantages and disadvantages of microwave reaction [32,119,126]

Advantages	Rapid in reaction
	Produce products with high purity
	Minimum unnecessary side-products
	High product yields
	Synthetic procedure is simplified and improved
	Flexible usable operating temperature
	Energy-efficient
	Cost-saving
	Environmentally friendly
	Sophisticated measurement and safety technology
	Modular systems enable changing scale adjustment
Disadvantages	Difficult control of heat force
	Dangerous closed container – risk to burst
	Water evaporation

electromagnetic energy which is a non-ionising radiation that causes molecular motion by migration of ions and rotation of dipoles but does not cause change in molecular structure.

Generally, microwave-assisted process commonly operates at a frequency of about 2.45 GHz (12 cm), causing dielectric heating primarily by absorption of energy in water and other polar compounds available in wet biomass or in a given sample [129,130]. In order to prevent the interference with telecommunications devices, the frequency range between 2 and 8 GHz is generally used for domestic and synthetic purposes [119,131]. This may be the reason that all commercially available microwave reactors for chemical use operate at the same frequency [126] which is at 2.45 GHz. The energy of the quantum involved can be calculated by Planck's law $E = h\nu$ and is found to be 0.3 cal mol^{-1} [126].

Compared with conduction/convection heating, which is based on interfacial heat transfer, microwave uses the ability of direct heating of the target object due to applied electromagnetic field. Precisely, polar substances, such as water, are the main ingredients that allow a substance to be heated by microwaves during microwave heating process. The higher the water content of the substance, the faster the heating rate. Water in molecular level behaves exactly like a magnet. Water has two oppositely charged ends due to the presence of positively charged two hydrogen atoms and a negatively charged oxygen molecule. In other words, due to two different poles in water, water molecules rotate when microwaves oscillate. This happens because the positive end of water is attracted to the negatively charged end of microwave, while the negatively charged end of water is attracted to the positively charged end of microwave. The microwaves rotate at severely high speed of 2450 times per second which means that the water molecule also rotates 2450 times for every second a microwave rotates. This extremely high rotation rate causes molecules of water to collide with each other at very fast rate, and then creates friction between them. This friction generates heat which can flow through the substance by conduction, convection or radiation [127].

With this heating mechanism, the most renowned characteristic of microwave heating is volumetric heating, which is quite different from conventional heating and eventually becomes an advantage of microwave processing technology [127]. Table 12 shows the comparison between conventional and microwave heating, and Figure 11 shows the illustration comparison between conventional heating and microwave heating mechanism.

Due to the advantages and potential of microwave energy, there have been a lot of research and application using microwave – even the bio-oil conversion from biomass. Numerous studies have been conducted on the implementation of microwave technology into the liquefaction of various biomass feedstocks, such as algae, wood and corn stover [134–136]. The microwave-assisted liquefaction process generally gives higher efficiency compared to conventional liquefaction process. Hence, it has been reported that microwave-assisted reactor should be one of the best way to convert algal biomass into high quality of bio-oil. Table 13

TABLE 12 Comparison between microwave heating and conventional heating [132]

Microwave heating	Conventional heating
Microwave effect	Thermal effect
Conversion of energy within the system	Transferring energy into the reacting system
In-core volumetric and uniform heating at molecular level	Superficial heating via conduction, convection and radiation
Rapid heating	Slow heating
Volumetric heating of materials – extensive heating inside the material	Heating from outer layers of the material
Higher conversion efficiency	Lower conversion efficiency
Lower thermal inertia	Higher thermal inertia
Microwaves couple directly with the molecules of the entire reaction mixture, cause rapid rise in the temperature	Heat is transferred gradually from outer surface to inner surface

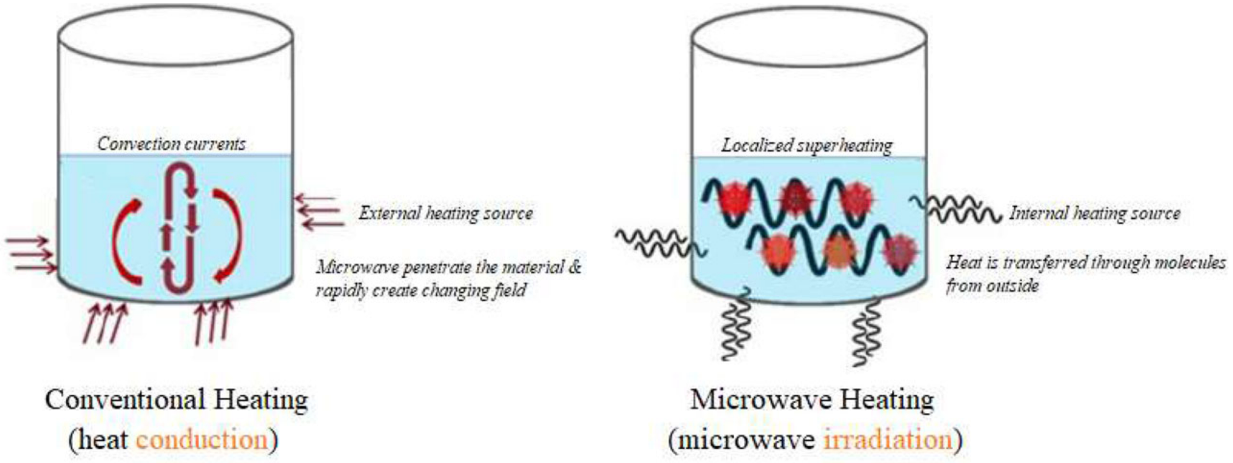


FIGURE 11 Different heating mechanisms for microwave and conventional heating (modified information from [133])

shows several previous studies associated with microwave-assisted liquefaction. Based on the results from each study, it is proven that the microwave-assisted liquefaction is better than conventional liquefaction process in implementation.

To further increase the depth of study of microwave-assisted conversion of algal biomass, the energy efficiency can be described by the following equation:

$$Q_{\mathrm{mv}} = P_{\mathrm{mw}} t. \tag{1}$$

This equation shows the heat energy supplied by the microwave system in terms of power dissipation and exposure time [83]. Thermal effects caused by the microwave radiation system in the sample volume, however, can be quantified by the following equation:

$$Q_{\mathrm{th}} = mc_{\mathrm{p}}\Delta t = \left(m_{\mathrm{a}}cp_{\mathrm{a}} + m_{\mathrm{m}}cp_{\mathrm{m}} + m_{\mathrm{c}}cp_{\mathrm{c}}\right)\Delta t. \tag{2}$$

Hence, the microwave energy efficiency is calculated by the ratio of both values:

$$\text{Energy Efficiency, } \eta = \frac{Q_{\mathrm{th}}}{Q_{\mathrm{mv}}}. \tag{3}$$

5 | UTILISATION OF ALGAL BIO-OIL FOR BIOPLASTIC PRODUCTION

Nowadays, the applications of plastic and plastic-based material are almost infinity. Plastic are flexibly used as a chemical material, including packaging purpose, automobile production, construction materials, furniture manufacture, as well as in the electronics industry and in the manufacturing of domestic equipment. According to the global statistics, the plastic consumption in 1976 is 50 million tonnes worldwide and continues to increase, which is expected to rise 330 million tonnes in 2015 [141]. Plastics are organic polymers, which can be processed in assorted ways. Their technical properties, such as formability, hardness, elasticity, rigidity, heat resistance and chemical resistance, can be varied across a diverse range by stipulating the correct raw materials, manufacturing process and additives.

For the current status, vast amounts of traditional plastic materials are produced from petroleum since the predominant availability of petroleum at the early of the 20th century [142]. This is another significant effect to the environment by dumping the use of fossil fuel based on materials production. Petroleum-based plastic is a non-renewable fossil material that causes huge carbon emissions. The widespread consumption of petroleum-based plastics has proven to be a significant source of the carbon footprints in atmosphere that leads to global climate change. The other challenges with respect to plastic are from health perspective. The elements of plastics, such as pthalates and bisphenol A, which are added to resin to reduce brittleness and promote plasticity, are two commonly cited examples of chemicals that have shown to cause a negative impact on human health. These products may remain in surrounding environment for centuries and live on in human bodies. Chemical- and petroleum-derived plastics often contain allegedly harmful chemicals, such as bisphenol A and phthalates, linked to hormone disruption and developmental disorders.

The emerging market demand for green products creates problems for plastics manufacturers and suppliers to find the substitutes for petroleum-based plastics. The abundant and reliable biomass source needs to be secured to sustain the bioplastics business model. While bioplastics have the potential to become green solutions for many environmentally harmful conventional plastics problems, being a bio-based material does not instinctively guarantee that it is biodegradable or even environmentally friendly. Plastics have not always been produced from fossil materials, such as petroleum, which is generally known as the contributor towards the

TABLE 13 Microwave-assisted liquefaction application from previous study

Feedstock	Reaction condition	Catalyst	Results	References
Lignin	Optimal condition: 150°C 5-min microwave heating time	No catalyst	- Yield: 93% - Hydroxyl number of 670 mg KOH g^{-1} - The reaction time is significantly shortens by microwave heating, which finally reduce the costs of the final product	[137]
Baggase Lignin (sugar cane)	200°C 30 min under microwave irradiation	Oxalic acid	- Yield: 78.69% - The liquefaction product was mainly composed of single or double-displacement phenolic compounds and a few acid-soluble lignins with low molecular weight	[138]
Cork	160°C 150–300 W power 5–20 min	2-Ethyl hexanol/DEG and p-toluene sulphuric acid	- Yield: 96% - Efficiency of liquefaction is increased by microwave heating: ■ with higher yield ■ with higher microwave power shorter reaction time	[139]
Corn stover	–	Sulphuric acid	- Microwave dramatically increased the liquefaction extent and rate compared to conventional heating - Molecular weight of products with microwave-assisted liquefaction is lower than those with conventional heating - Optimal reaction time for microwave-assisted liquefaction is 20 min, with the minimal residue content of 4.85%	[136]
Rape straw	Moderate : 140°C/15 min Severe : 180°C/15 min	Acid	Kunak (0.3%)	[140]
Ulva prolifera (Algae species)	8% moisture content 600 W power 30 min 180°C 16:1 solvent-to-feedstock ratio	Sulphuric acid	The bio-oil obtained under the optimum conditions had a high liquefaction yield (84.81 ± 0.13%) and heating value (15.05 MJ kg^{-1}) by microwave reaction. However, it contained large quantities of O, S and N, which would have to be removed before being used as a fuel	[134]
Wood	–	Sulphuric acid and phosphoric acid	- The viscosities of the product using H_3PO_4 as the catalyst in the liquefaction were higher than those using H_2SO_4 - The wood residue content with H_2SO_4 catalyst dropped to zero within 5 min with microwave heating - The advantage of microwave heating over conventional heating by substantially shortening reaction time during liquefaction	[135]

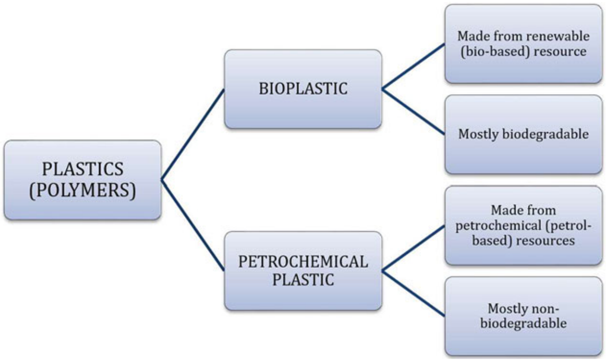


FIGURE 12 Plastics (polymer) resources and degradability

environmental negative impact. Bioplastics consist in a large part, or even completely, of renewable resources. Thus, bioplastics are bio-based plastics. Biodegradable, but petroleum-based plastics, are not considered as bioplastics, as shown in Figure 12. Hence, selecting the raw material to produce bio-based should be emphasised in order to produce safe products with high quality [143].

The worldwide production capacity for bioplastics is expected to rise from around 1.6 million tons in 2013 to approximately 6.7 million tons by 2018; there is a predicted increase of 83% for Europe's bioplastic production, totalling 511,480 ton [144]. The strongest growth in the bioplastic industry is the bio-based and non-biodegradable group such as bio-based versions of bulk plastics, polyethylene and polyethylene terephtalate, which entirely differ from their conventional counterparts in terms of their renewable raw material base, and are building up in large capacities. Meanwhile, biodegradable plastics also denote impressive growth rates, which is expected to increase their production capacity by two-thirds by 2016. Polylactic acid (PLA) and polyhydroxyalkanoates (PHA) are the leading contributors in bioplastic growth. PLA was the most produced biodegradable biopolymer in Europe in 2013. PLA accounts for 298,000 tons (+60%), while PHA accounts for 142,000 tons (+700%) [144]. It is a sustainable alternative to petroleum-based plastics and is compostable and biodegradable. In observation, a disturbing trend of geographic distribution of production capacities should also be looked through, which is generally simplified in Table 14.

TABLE 14 Geographic distribution trend for Bioplastic development

Location	Bioplastic development
Europe and North America	Research and development Sales markets
South America and Asia	Establishment of new production capacities

TABLE 15 Energy required from non-renewable sources and CO_2 emissions for different types of plastics currently on the market

Type of plastic	Energy requirement (MJ kg^{-1})	Global warming (kg CO_2 eq kg^{-1})
From non-renewable sources		
HDPE	80.0	4.84
LDPE	80.6	5.04
Nylon-6	120.0	7.64
PET	77.0	4.93
PS	87.0	5.98
PVOH	102.0	2.70
PCL	83.0	3.10
From renewable sources		
TPS	25.4	1.14
TPS + 15% PVOH	24.9	1.73
TPS + 60% PCL	52.3	3.60
PLA	57.0	3.84
PHA	57.0	Not Available

PET, polyethylene terephtalate; PS, polystyrene; TPS, thermoplastic starch.

There are several factors for the growth in bioplastics, including consumer demand for environmentally sustainable products, the development of bio-based feed stocks for commodity plastic resins and increasing restrictions on the use of non-degradable plastic products, particularly plastic bags. Certainly, a key aspect in assessing the applicability of bioplastics is the impact on the environment resulting from their use during the entire life cycle – from production to final disposal. The life-cycle analysis (LCA) is based on finding some factors considered crucial in assessing the impact that a particular product can have on the environment.

Table 15 shows a collection of LCA literature data [148, 149] in which each LCA characterises and compares the environmental impact of various bioplastics (thermoplastic starch, PLA and PHA and traditional plastics [high and low density] polyethylene, Nylon 6, polyethylene terephtalate, polystyrene, polyvinyl alcohol [PVA] and polycaprolactone) with an approach cradle to grave.

Overall, the data reported in Table 15 show how the production and use of bioplastics is more advantageous compared to conventional plastics from the energy demand and emissions of GHG point of view. Previous studies identified that phenolic bio-oil, generated from renewable resources, contains chemical-active compounds, effectuate it to successfully prepare the interior and thermal-curing adhesives or composites [145]. Bio-based plastics can be produced from a wide range of plant-based raw materials including algae. Thus, the production of bio-oil from algal biomass might be one of the promising ways to be one of the alternatives to replace petroleum-based plastic. Algae are one of the potential raw materials that can be utilised for bio-based plastic production.

Emphasising the advantage of utilising algae for this purpose, there is an established project funded by EU, which has initiated and developed a process of using seaweed as a novel base for bioplastics. Seaweed-based plastic does not compete for land use, besides it will also save water and perhaps achieve higher productivity, biodegradable bioplastics, contributing to innovation in the bioplastic sector and the transition from petrochemistry to green chemistry. Utilising seaweed for bioplastic production gives various environmental benefit and financial advantages. Thus, the project will help to minimise the harmful environmental effects of fossil fuel based plastics, thereby helping to achieve the EU 2020 target of 10% of market plastics being bioplastics [146].

6 | CONCLUDING REMARKS

Fossil fuel and fossil materials utilisation for industrial development had the negative impact to the environment. The truth is that the vast range of plastic materials used in every industry is produced from petroleum: a non-renewable fossil fuel with a huge carbon footprint. The widespread consumption of petroleum-based plastics has proven to be a significant source of the carbon emissions that cause global climate change. Biomass-derived fuels with zero net CO_2 emission are promising substitutes for fossil fuels. In fact, a significant reduction of non-renewable energy consumption and CO_2 emission can be accomplished. The development and exploitation of renewable and sustainable energy sources can give a significant contribution to the solutions to these problems. Since biomass is one of the potential renewable energy, the enhancements of bio-oil production quality have been continuously researched from time to time according to the technological development while considering the economical aspect. In order to reduce the CO_2 gas that can be harmful to the environment, the renewable energy and sustainable product alternatives need to be given more attention.

Algae have an abundance resource, and this type of biomass with proper quality enhancement might have high potential to replace conventional fossil fuel in future. By utilising the resources, it will relatively reduce the pollution and secure more sustainable future especially in sustainable product. There are many companies specialising in algae cultivation and development, and AIB is an established company in Malaysia. This shows that algae resources are reliable and less likely for shortage of resources in future. Algae species are broadly classified into microalgae and macroalgae. The previous studies mostly reported on the microalgae, as it is fast growing and easy to cultivate. However, the macroalgae species potential as biomass is also undeniable as it can contribute to biomass feedstock. In this particular review, two major potential thermochemical conversions are identified to produce crude bio-oil from algae, which are HTL and pyrolysis. In fact, both conversion methods are relatively similar but different in application. HTL seems to be more suitable and effective in processing algae into crude bio-oil because of high moisture content of the feedstock. HTL operates at lower temperature compared to pyrolysis process. Microwave-assisted reactor for HTL shows an interactive way for crude bio-oil production and widely established technology.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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