

Algae biofuel: current status and future applications

Oladapo Martins Adeniyi, Ulugbek Azimov, Alexey Burluka

Department of Mechanical and Construction Engineering, Northumbria University,
Newcastle upon Tyne, NE1 8ST, United Kingdom.

Abstract

An algal feedstock or biomass may contain a very high oil fraction, and thus could be used for the production of advanced biofuels via different conversion processes. Its major advantage apart from its large oil fraction is the ability to convert almost all the energy from the feedstock into different varieties of useful products. In the research to displace fossil fuels, algae feedstock has emerged as a suitable candidate not only because of its renewable and sustainable features but also for its economic credibility based on the potential to match up with the global demand for transportation fuels. Cultivating this feedstock is very easy and could be developed with little or even no supervision, with the aid of wastewater not suitable for human consumption while absorbing CO₂ from the atmosphere. The overall potential for algae applications generally shows that this feedstock is still an untapped resource, and it could be of huge commercial benefits to the global economy at large because algae exist in millions compared to terrestrial plants. Algae applications are evident for everyday consumption via foods products, non-foods products, fuel, and energy. Biofuels derived from algae have no impact on the environment and the food supply unlike biofuels produced from crops. However, any cultivation method employed could control the operating cost and the technicalities involved, which will also influence the production rate and strain. The scope of this paper is to review the current status of algae as a potential feedstock with diverse benefit for the resolution of the global energy demand, and environmental pollution control of GHG.

Keywords: Algae biofuel, Renewable fuel, IC engine combustion, Biofuel blends, Exhaust gas emissions, Greenhouse gas emissions.

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1. Introduction

Algae biofuels are advanced renewable fuels derived from algal feedstock via different conversion processes, this is due to the oil-rich composition of this feedstock that can be associated with its ability to abundantly photosynthesize [1]. Algae are aquatic species with over 3000 different breeds and they have the fastest ability to reproduce, therefore more diverse than land plants [2]. They suck up CO₂ from the atmosphere and convert it to oxygen [3], and have great oil yield which is extracted by breaking down their cell structure [4]. The major advantage apart from their oil mass is the ability to convert almost all the feedstock's energy into different varieties of useful biofuels [2]. Other application includes wastewater treatment, production of energy co-generation (electricity or heat) even after the extraction of oil, CO₂ removal from industrial chimney gases (algae bio-fixation), bio-fertilizer, animal feeds, healthcare and food products. Algae exist in any imaginable environment and can

withstand extreme temperature, irradiation, drought, and salinity. However, the environmental condition of a country will definitely influence their cultivation method. For example, marine and freshwater algae such as Cyanophyceae (blue-green algae), Chlorophyceae (green algae) and in some cases Pyrrophyceae (fire algae) could be cultivated naturally in the UK. While Phaeophyceae (brown algae) could be genetically modified along with artificial cultivation methods of photobioreactors (PBRs). Though lipidic algae such as Cyanophyceae, Chlorophyceae and Pyrrophyceae were recommended for the production of fatty acid methyl ester (FAME) [6-12], the Phaeophyceae, on the other hand, tends to be the most suitable algae feedstock for ethanol production due to its high sugar content [13, 14].

In the research to displace fossil fuels, algae have emerged as a suitable candidate due to its renewable and sustainable features coupled with economic credibility to match up with the global demand for transportation fuels [2]. Though, algae biofuel conversion methods such as transesterification, fermentation, and hydrotreatment are more complex and economically expensive, when compared to fossil-derived fuels and even biofuels from other feedstocks. There is potential ground for optimism based on the sustainability of this feedstock [15] and greater likelihood of new applications and products due to its diversity. Therefore, from all the above positive algae features, it can be inferred that this feedstock is one of the world most valuable, sustainable, and renewable fuel resource which could also play a fundamental role in controlling environmental pollution [2].

CO₂ emissions from different fossil fuel sources have been a major threat to the environment. Though the global economy has in the past benefitted from fossil fuel, yet it contributes greatly to the CO₂ level in the atmosphere, which has led to global warming. In 2012, CO₂ emissions generated from the consumption of liquid fuels alone was 36% of global emissions and this has been a major concern to both fuel producers and engine manufacturers [20, 21]. This has led to overall CO₂ emission projection to be doubled by the year 2035 [20] and might as well get up to 45000 mega tonnes by the year 2040 [6] as indicated in Fig. 1. For this reason, the European Union Renewable Energy Directive (RED) recommends that 15% of energy delivered to the UK consumers by 2020 should be obtained from renewable resources [21]. This would mean 6% reduction of emissions from transport sector, 12% reduction from heating energy generation sector and 30% reduction from electrical energy generation sector. The European Renewable Energy Policy objectives were to drastically reduce greenhouse gas emission to 20% by the year 2050, with an initial reduction plan to the 60% mark due to major emissions from the power sector as illustrated in Fig. 2 [22]. Which led to the short-term targeted agreement for the reduction of GHG emissions for the year 2020 and 2030 [22] as indicated in Table 1.

Technology improvements in the exploration of crude oil have successfully reduced the production cost of fossil fuel over the years, though affecting biofuel growth [21]. However, the global concern for crude oil's sustainability and emission effects cannot be overruled. Another global challenge with fossil fuel is its biased and uneven allocation, which has resulted in some countries been threatened to run out of petroleum reserves while others became wealthy and control the foreign exchange market because of their crude oil reserves [2]. The only viable solution to all these aforementioned challenges for both the global economy as well as the GHG emissions is a fuel produced from plant material.

Though other sources of renewable energy such as solar, wind and geothermal might not be as economically feasible as biofuels, these green energy sources still play a significant role in solving the problem of global warming. From the statistics in Fig. 3, constant growth in the global production of other renewable energy sources was reported but biofuel production was even behind its 2014 expectation [23]. These biofuels are products of different biodegradable and sustainable feedstock that can be converted liquid, gaseous and solid fuels by biological and thermochemical process [16]. And these feedstocks are capable of creating opportunities for agricultural development due to direct involvement with agricultural plants [2].

Major oil producing countries have shown great interest in biofuel and renewable energy by setting specific future goals and targets about the production as well as the applications. Countries like UAE have planned to run 10% of its transportation on biofuel by 2020 and USA has proposed to substitute 20% of its road transport fuel for biofuel by 2022 [24]. The role of legislation policies devised by the government to reduce or eliminate CO₂ emissions from fossil fuel has buttressed the need for renewable fuel. The renewable transport fuel obligation statistics from the UK department of transport, recommends that every transport fuel supplier must make sure proportions of renewable source (biofuel) are present their products [25]. In line to ensure that there is consistency in the renewable fuel proportional quality, a certificate called Renewable Transport Fuel Certificates (RTFC) will be awarded to the supplier that fulfills this requirements [25]. Global demand for this renewable fuel was also supported politically due to the global imbalance in the exploration of crude oil and uneven allocation, which affects energy security, rural development and climate change [26].

From 2021 car manufacturers will have to comply with the 95g CO₂/km threshold, set by the EU in order to reduce CO₂ emissions from their fleet of new sold passenger cars, this means that biofuels will be one of their viable solutions [27]. With this in mind, the UK Sustainable Biodiesel Alliance (UKSBA) has recommended the implementation of a minimum price of 15p per litre for RTFCs in order to facilitate more market for biofuel producers [28]. The

Renewable Energy Directive (RED) has also drafted a legislation to boost the production of advance biofuels like algae by 2020 [29]. Since the European Parliament have capped all food crop-based biofuel in order to support the production of biofuels from algae and other non-edible biomass [29].

Land availability with respect to the increase in biofuel demand has also contributed to GHG emissions, due to the current land mass carbon generation [30]. For this reason, biofuel from aquatic cultivated feedstock such as algae could be the solution [2], because they can be produced using non-arable land, brackish or non-potable water [4].

The major reason for biofuel is to displace fossil fuel in order to sustain the energy sector with natural fuels that will preserve our environment [31]. Biofuels produced from both the first and second generation feedstock are currently the principal substitutes for the replacement of fossil fuel [24], but their sustainability has been questioned by their competition with food products as well as land consumption [32]. Therefore, it is very necessary to find another suitable biofuel source that will not compete with food products and algae seems to be the valuable option [2].

2. Algae classification

Algae is the collective name given to a group of eight divisions of distantly related organisms based on human convenience, rather than the reflection of their biological ordered evolutionary relationships [33]. They can be unicellular (microalgae) or multicellular (macroalgae), the former can be referred to as microphytes and the latter seaweeds [2]. Microphyte has no roots, stem, and leaves, yet it can grow up few hundreds of micrometers and can be found in marine or freshwater bodies [12]. Macroalgae, on the other hand, possess a body like structure and can be found around sea beds growing up to hundreds of meters [2]. Their structures are majorly for storing and converting energy without any development beyond their cells, and the simplicity of their growth and development has made them more sustainable than any other renewable sources [16].

Due to the low temperature and the level of sunlight in areas such as the UK, it is highly recommended that extensive research and development on the discovery of algal strain that can be cultivated in such environment must be done [34]. Positive results from such research will facilitate the reduction of the recorded 80% biofuel products imported into the country [28]. Recent biofuel research on the green algae family by Johnson and Wen [7] indicated that *Schizochytrium limacium*, heterotopic microalgae, could be used for the production of biodiesel from different preparation methods. This specific microalgae feedstock is best suitable for biodiesel production by direct transesterification, because of its ability to produce

high levels of total fatty acid biomass. *Chlorella* a common algae from the green algae family was also suggested by Mata, et al. [6] as a good option for biodiesel production due to its high lipids productivity. Considering its efficiency and productivity for development under normal environmental conditions, *Chlorella* lipids production was better than other species under the same environmental conditions [35]. The impact of the growing conditions of *Chlorella* on the properties of biodiesel was investigated by Al-lwayzy, et al. [8], whereby the lipid content was increased by adding iron to the media as a stressor treatment. Iron addition to the culture medium influenced lipid production positively by providing different fatty acid methyl ester (FAME) component, which eventually improved the overall properties of the fuel. This valuable feedstock was commended by Mishra, et al. [36] for its versatility in biofuel production and heavy metal remediation while providing a better sustainable approach to wastewater treatment.

Brennan and Owende [16] highlighted that the high protein content and nutrient value of *Chlorella* was the reason for its large-scale commercial production in 2003, which summed up to 2000 tonnes that year. It was used as medicine and food additives, for the treatment of renal failure as well as to promote intestinal lactobacillus growth.

Other species of algae such as the brown algae was considered by Lee and Lee [13] as renewable biomass for the production of bioethanol via metabolic engineering. The high sugar level of this algal biomass was analyzed by saccharification. Their conclusion was that the conversion of those sugars to bioethanol in the absence of lignin could play a very important role in the commercialization of bioethanol production from these distinctive algae. Islam, et al. [10] assessed the effects of dinoflagellate *Cryptocodinium cohnii* (fire algae) biodiesel blends with waste cooking oil, on the engine performance. It was established that at different engine loads this species of algae possessed the capability to meet all the fuel property standards and engine performance. The emission characteristics of this diesel blend were improved of up to 50% blend ratio for regular use in diesel engines. The fuel performance of algae biodiesel produced from the diatoms family, *Chaetoceros gracilis*, was compared with other biodiesels by Wahlen, et al. [11]. Using a two-cylinder diesel engine to actively pursue a better renewable replacement for petroleum diesel, this microalgae displays the lowest NO_x emission compared to petroleum diesel. This was due to the substantial amount of palmitoleic and myristic methyl ester present in this specific microalga. This improves the oxidative stability without forfeiting the cold flow performance. The different types of algae are summarized in Table 2.

3. Cultivation of algae biomass

Cultivating algae feedstock is very easy and can be developed with little or even no supervision, using waste water which is not suitable for human consumption while absorbing CO₂ from the atmosphere [37]. Algae use sunlight for photosynthesis, which is a very important biochemical process for plant growth and reproduction, to convert sunlight into chemical energy [19]. The formed CO₂ is transformed into different forms of chemical energy such as carbohydrates, lipids and protein via photosynthesis [18]. Therefore for algae to grow and multiply, it only needs the support of basic nutrients such as sunlight, CO₂, and water for the conventional plant photosynthesis to convert solar energy into chemical energy through CO₂ fixation [4]. The cultivation method employed plays a huge role in the harvesting process as the preceding step depends very much on the commercial value of the biofuel or bioenergy produced [38]. Table 3 highlights the generalized condition for the cultivation of algae, which include parameters like temperature, salinity, light intensity, photoperiod and pH.

3.1 Natural cultivation

Natural cultivation methods include pond, lakes, and lagoon, which are classified based on natural water bodies e.g. shallow ponds, circular ponds and raceway ponds. These ponds are constructed in excavated pits or raised above the ground level [2], and they are incorporated with paddlewheels, water jets or air pumps [39] as illustrated in Fig. 4 (A). This is to enable flow and circulation of algae, water, and nutrients due to the limited depth penetration of the sunlight, as well as to suspend algae in water close to the surface for CO₂ absorption [18]. The use of arable land cannot be avoided due to the requirement of large area of land mass [40], especially when operation around these ponds are continuous. This continuous operation is required in order to enhance CO₂ and nutrients circulation while harvesting the biomass at the collecting end [17]. These ponds are easy to construct and operate due to their simplicity, which made this method relatively cheaper to run compared to the artificial methods [41]. However, failure to maintain the laboratory organisms in the ponds have always been a major setback [42], while other limitations and challenges affecting the cost effectiveness of this cultivation method are poor cell light utilisation, unregulated temperature, predator contamination, evaporation loss, and CO₂ diffusion into the atmosphere [12].

Natural cultivation systems are normally cheaper to construct and operate, but the ponds make use of more energy to homogenize the nutrients [6]. According to Sawant, et al. [43], modifying a convectional raceway pond could generate higher convective current to

homogenize nutrients at high depths. However, this cultivation system is more susceptible to environmental conditions such as variability in water temperature, lighting, and evaporation. Production of large quantities of microalgae is a possibility, but the issue of occupying more extensive land mass is a challenging factor that in most cases results in contaminations from bacteria or even other microalgae [2].

Brennan and Owende [16] suggested that high production rate of algae biomass can still be achievable from natural cultivation methods, but it will require a selective environment with an extremely cultured maintenance system. This is because of the inherent threats of contamination, predator, and environmental pollution from bacteria. A very good example of this scenario is the toxic effect of algae bloom on nature and environment around Salton Sea in California in 1992 [44]. Where three smaller rivers from nearby agricultural irrigation systems discharged over 10000 tonnes of nitrogen and phosphate fertilizers every year, resulting in massive algal bloom that could have mitigated hundreds of thousand tonnes of CO₂ had it been properly managed [45].

3.2 Artificial cultivation

Artificial cultivation methods are majorly photobioreactors which come in different shapes such as flat plate, tubular, and column [12] as illustrated in Fig. 4 (B), (C) and (D) respectively. This is a closed cultivation method of algae in a controlled environment that improves productivity via a complete control process [16]. Algae, water, CO₂ and all the nutrients required for algae growth and development are fed into the photobioreactor where light and pH level are cultured with temperature and density in a controlled process [39]. All the limitations and challenges affecting the natural cultivation methods have been eliminated in photobioreactors, but the major bone of contention on these methods is the capital cost [19].

The technology behind this cultivation method was to overcome some of the major problems associated with the natural systems such as contamination and pollution risk, which disqualified natural cultivation methods from producing high valued health and food products [16]. The performance of this cultivation method can be optimized by the physiological and biological characteristics of the species of algae to be cultivated [6]. Which could enable the cultivation of some special algae species that cannot be cultivated naturally. This cultivation method permits the prolonged duration of cultured single-species of microalgae with no contamination risk. The comparison between natural and artificial cultivation methods is shown in Table 4. Huang, et al. [18] suggested that high value of long chain fatty acid can be achieved through artificial cultivation method, from some readily contaminated microalgae

due to the better environmental control of photobioreactors. However, the effect of operating cost and the technicalities involved can be the influential factor for such achievement. Though photobioreactors possess the capability to produce and control algae biomass with greater production rates than ponds, but their practice are currently limited to research laboratories and pilot scale plants [40]. Xu, et al. [46] recommended that understanding the energy consumption of these photobioreactors could be the key to their commercial success. Therefore, a significant reduction in the energy consumed by photobioreactors will save valuable time and money while improving productivity. Darzins, et al. [30] suggested that the anticipated success of the commercial venture of algae plants could be accelerated beyond 2020, and the commissioning of the first algae large scale plant should be by next decade. Therefore, an estimated 170,100ML facilities must be commissioned to achieve the 50% contribution from algae biofuels towards the 2030 total biofuels supply. The advantages of the artificial cultivation are:

- Better controls over growth parameters and culture conditions such as temperature, pH, mixing, CO₂ and O₂
- Prevented evaporation
- Reduced CO₂ losses
- Allowed cell concentrations
- Higher volumetric productivity
- Safe and protected environment against predators
- Minimized invasion of competing microorganisms
- Prevented contamination

and the challenges are:

- Overheating
- Bio-fouling
- Oxygen accumulation
- Scaling up difficulties
- Cell damage by shear stress and overtime deterioration of material used for the photo-stage
- Operating cost

3.3 Genetically engineered algae

Maximizing both aforementioned cultivation methods depends on the ability of genetically engineered algae cultivation, where all the standardized characteristics of algae could be modified to produce high yields of both the primary products and by-products [47]. This cultivation method is the deliberate modification of algae to produce an improved feedstock from synthetic biology [48]. Most algae strains make use of cell structures called antennae for capturing sunlight, and these light-harvesting complexes are responsible for yield production. Modifying the DNA responsible for this antennae would enable visibly lighter genes for further light penetration through the cells. Transformation methods such as artificial transposons, electroporation, particle bombardment, viruses, agitation of a cell suspension in the presence of DNA and glass beads, grobacterium infection, silicon carbide whiskers and recent agrobacterium-mediated transformation have been employed for transferring DNA into algae cells. Both electroporation and particle bombardment methods have yielded the highest transformation rate for the process [49]. Algae genetic engineering has become progressively more efficient and cheap for advanced methods of algae DNA restructuring. This because DNA restructuring such as sequencing, hybridization, metagenomics and enhanced evolution could create possibility for tolerance in harsh conditions [50]. Modifying the genomic DNA of algae to achieve the required metabolism of a specific site could also improve performance in harsh condition. New qualities could also be obtained from the nontransgenic methods which may require proper evaluation for performance improvement to develop the best algae strains that could survive under a wide range of natural biotic and abiotic conditions [48, 51]. However, it is likely that this metabolic changes may favour one application than the other, for example, a better production yield for fuel and energy production may results in harmful algae strains for food and non-food applications [52]. This is because the majority of these genetic improvements were initially focused on the production of useful by-products from algae such as cosmetics and medical products, in order to compensate for the production cost [49].

Genetically engineered algae technology was recommended by Snow and Smith [48] to complement both natural and artificial cultivation because most algae strains can be screened, restructured and hybridized for faster growth even in extreme conditions with the aid of dominant molecular techniques. But this can only be materialized with the support from government and private investors. Such support could significantly reduce the high cost of operating a commercialized PBR, which has been the major technical challenge of the PBR [53]. Tabatabaei, et al. [49] highlighted lower growth rate and gene quality as the major

challenges of genetic engineering which could affect the global commercialization of algae. Companies such as Sapphire Energy and Monsanto are working on the development of new genes that would enhance rapid growth and other useful qualities. Rismani-Yazdi, et al. [50] acknowledged some pathways and genes that could influence biofuel production in *Dunaleilla tertiolecta* a marine flagellate, emphasizing that the DNA reconstruction could enhance faster growth rates as well as the nitrogen-use efficiency. However, there is need for suicide genes to control dangerous algae strains from surviving an open environment in case of an accidental escape [48, 54]. This is because these so called dangerous algae strains possess high risk of environmental hazard [55].

4. Applications

The overall potential for algae applications generally shows that this feedstock is still an untapped resource, and it can be of huge commercial benefits to the global economy at large because algae exist in millions compared to terrestrial plants [2]. Algae application as illustrated in Fig. 5 is evident for everyday consumption via food, non-food products, fuel, and energy.

4.1 Food and non-food products

Generally, algae are the regular source of food for most aquaculture species such as fish and shrimps due to their beneficial properties [2], which includes improved fertility, improved immune response, healthier skin, better weight control and lustrous coat. However, it could be detrimental if overconsumed in a high concentration of persistence feeding [16]. The high protein content of algae has made it an important recombinant extract, such as C-phycocyanin, astaxanthin, and β -carotene which is a source of vitamin A and can be used as a food coloring agent as well as cosmetic additives [6].

Algae were first produced commercially as food additives in Japan in the early 60s, with the large-scale cultured production of *Chlorella* which later expanded into USA, India, Israel and Australia [16]. The post-harvest processing of algae biomass that preserves algae intrusive character tends to give some delicious food products such as Nori (a species of red algae porphyria which is a primary constituent of Sushi), Kombu and Wakame [2]. Though strict food safety regulations restricted the human consumption of algae biomass to very few species such as *Chlorella*, *Spirulina*, and *Dunaliella*, which are generally marketed as health and food products that come in either tablet or powdered forms [56].

Biofertilizer from algae biomass which is a product of pyrolysis could be used for agricultural application as well as processed fuel in the bioenergy conversion of carbon sequestration [6].

This carbon negative fuel tends to reduce CO₂ emission up to 84%, due to its ability for a long-term sink in the carbon sequestration process [16]. Food and non-food algae derived products are shown in Table 5.

Wastewater treatment from algae production's heterotrophic cultivation systems tends to be a promising idea for environmental cleaning, this unique and distinct operation will serve both purposes simultaneously and constructively [16]. This will result in the removal of chemical and organic contaminants from the water bodies while producing biomass for several biofuel productions of as well as other products. This is a feasible method to offset the treatment cost of recycling harmful contaminants into nutrients for algae biomass, which will in return release oxygen-rich effluent into water bodies [57, 58]. Organic compounds such as phosphorus and nitrogen from some manufacturer's waste in water bodies can also be used as nutrients for algae biomass [6]. Shuba and Kifle [59] described this multipurpose operation of wastewater treatment as an effective method of fertilizing algae ponds for biofuel production and provision for nutrient uptake, heavy metal remediation as well as oxygen for bacterial growth. Brennan and Owende [16] recommended algae biomass production for water treatment process as a very reasonable idea, because there will be a great deal of savings on the chemical remediation of fresh water. This will result in minimal dependency on chemicals for fresh water production in conjunction with affordable and sustainable energy production [60].

A very good example of this operation is illustrated in Fig. 6, whereby wastewater from sewage pipes was treated with CO₂ emissions and converted into floating photobioreactors [61]. Therefore, this will result in a possible reduction of fresh water for algae biomass production and minimal chemical dependency for fresh water production [60].

4.2 Fuel and energy

Algae are generally more efficient converters of solar energy, this is because their cells grow in aqueous suspensions, and they have efficient access to CO₂, water, and other nutrients [62]. The oil content of algae in relation to their dry weight made them the ideal renewable fuel and energy source through different conversion processes such as transesterification, anaerobic digestion, hydrotreatment, fermentation, pyrolysis and direct combustion [2, 7, 12, 13, 17, 39, 41, 63-65]. However, some of these conversion methods are complex and economically expensive, yet they can be commercially viable if all the by-products are optimally utilized.

4.2.1 Transesterification

Biodiesel production from algae involves the chemical conversion of algal biomass through transesterification [16]. This chemical conversion process involves the reaction of triglyceride (lipid) with alcohol in the presence of a suitable catalyst such as acidic, alkaline or enzyme based to produce FAME with glycerol [2, 6, 12, 16, 39, 41, 63, 66]. This process is necessary because the viscosity of algal oils is higher than that of petroleum diesel, thereby reducing the original viscosity of the algal oil to increase fluidity [18]. Then creating glycerol, a by-product that could be used for pharmaceutical and cosmetic purposes [2]. This process is described by the chemical equation in Fig. 7, and it depends on reaction conditions such as alcohol type, catalysts type, molar ratio, etc. in order to convert raw algae lipid to FAME of lower molecular weight [17].

With the original viscosity of algae oils reduced and the fluidity increased, then FAME can be blended with petroleum diesel and applied to diesel engines directly without any engine modifications [8]. Milano, et al. [12] stated the possibility of a great yield up to 90% FAME conversion from algae such as *spirogyras* and *oedogonium* when an alkaline catalyst is used. Extremely high lipid content could be achieved through special conditions which may result in strain isolation [4]. Chisti [67] described this production process as an equilibrium reaction, whereby a large amount of alcohol drives the whole reaction toward FAME production. This equilibrium reaction is not complete without a suitable catalyst such as acids, alkalis or lipase enzymes. Bharathiraja, et al. [39] highlighted how the poor solubility of short chain alcoholic solvents can affect the inhibition of the active catalyst used in transesterification. This is because some novel solvent tends to eliminate complex glycerol separation, while other novel acyl solvents will eliminate both glycerol production and microemulsion formation during transesterification process. Transesterification of freshwater microalgae *Chlorella Vulgaris* was conducted by Al-lwayzy, et al. [8], where the lipids were heated to temperature of 48⁰C before reacting with methanol in the presence of NaOH catalyst. The resulting mixture of FAME and glycerol was 20 times greater than the initial lipid weight. There are two types of transesterification process in biodiesel production, which are: direct transesterification and conventional transesterification.

Direct transesterification: also known as in-situ or the single stage method, is a chemical process that involves the simultaneous extraction of lipid content [12, 68]. The wet unwashed algae biomass is directly fed into the reaction system for direct transesterification [69]. This method eliminates any form of pre-treatments such as degumming and extraction while tolerating some water level due to the surplus methanol used in the reaction system as

illustrated in Fig. 8. This method yields more biodiesel compared to the conventional method [7] and is very important for the development of a competitive biodiesel production process [70].

Conventional Transesterification: This method is the two-stage method that extracts lipids by mechanical process before transesterification [7, 12]. Pre-treatment operation such as degumming and extraction using a cheap, unreactive non-polar solvent like hexane as described in Fig. 9 is extensively required for this method [70]. This conversion method could yield a refined fuel product ideal for the conventional high speed diesel engine [71]. The water content in the algae feedstock can be controlled along with catalyst used by pre-treating the biomass, but this will affect 88% of the total production cost [72]. Apart from the high production cost due to the pre-treatment operations involved, this method is energy-intensive and time-consuming [69].

Johnson and Wen [7] compared both direct and conventional (extraction) transesterification, in the production of biodiesel from green algae *Schizochytrium limacinum*. It was observed that direct transesterification gives a much lower biodiesel yields compared to the conventional transesterification, which is due to the wet biomass used as the feedstock. However, after extracting the oil from the feedstock, 98% biodiesel yields was achieved due to the nature of the solvent used for treating the biomass. Johnson and Wen [7] further recommended that biomass pre-treatment with either chloroform or hexane would give a biodiesel yields of 100%. The biggest challenge in this process is the high pre-treatment cost of drying the biomass, which accounts for almost 80% of the raw material preparation [68]. [73] recommended combining both microwave and ultrasound irradiation techniques as the best method to eliminate the energy-intensive drying process of pre-treatment. This practice tends to yield over 90% FAME content with energy input to output ratio of less than one, and this could alternatively reduce the overall production cost. In order to make transesterification cost-effective and economically feasible, the in-situ method was critically analyzed and reviewed by Jazzar, et al. [70] using wet unwashed *Chlorella* sp. It was recommended that high lipid conversions to biodiesel with standard close to UNE-EN14214 can be achieved by the in-situ supercritical methanol transesterification method. Skorupskaite, et al. [68] further proposed that in-situ transesterification process could be cost effective if high oil content is obtained for fast growing algae strains. Salam, et al. [72] suggested that using microalgal residue for biogas (methane) production could provide the required energy for the pre-treatment of biomass prior to in-situ transesterification, hence reducing the production cost. However, some key process variables such as the stirring rate, reaction time, alcohol to oil

molar ratio, moisture content, temperature, microalgae cell wall and the type of catalyst employed should be considered. Ehimen, et al. [69] stated that biodiesel yields from in-situ transesterification could be improved significantly with the stirring process, this is because the reactors can be stirred intermittently without reducing the yield, thus saving some stirring energy. In addition, biomass drying plays a significant role in this application because the FAME equilibrium conversion depends on the moisture content of the biomass.

4.2.2 Anaerobic digestion

This is a conversion process that promotes energy recovery from sunlight through photosynthesis, and it integrates efficiency into the production of biofuels from algae [17]. Algae anaerobic digestion is technically more viable than other conversion method, due to its ability to generate other sources of energy and co-products [41]. This prospective conversion process for algae biomass is an environmental feasible option that will create a renewable energy source for domestic and industrial use [74]. This process is capable of fixing great amount of carbon because it efficiently extracts most of the nutrients from the harvested biomass and let them back into the cultivation system [4]. Organic waste from algae biomass can be converted into biogas, by breaking down the organic matter to produce majorly CH₄ and CO₂ which can be used for domestic cooking as well as generating power by gas engines [12]. This process is accountable for the huge quantity of fixed carbon recycled annually, and most natural gas deposit from methane [60]. With the capability of converting biomass of high moisture content, this conversion process is capable of obtaining a methane worth of energy from the extracted lipids of carbon and nitrogen content of delipidized algal biomass, via the following consecutive stages taking place in the digestion tank [39]: 1) hydrolysis, 2) fermentation, 3) acetogenesis, 4) methanogenesis.

Hydrolysis: this first stage could be employed in form of wastewater management process, whereby algae cell walls would be broken down by the bacteria actions in the digestion tank [74]. This is the breaking down of particulate organic substrate of algae into soluble sugars and amino acid [39].

Fermentation: this second stage is a pathway that demonstrates the anaerobic digestion after the degradable algae cell walls prior to the main conversion [74]. The conversion of soluble sugars and amino acid from the first stage into hydrogen, carbon dioxide and ammonia takes place by the acidogenic bacteria [39].

Acetogenesis: this third stage demonstrates the oxidation of fermented products into acetate substrates that are suitable for methanogenesis [74]. These substrates aided by the partial pressure of hydrogen in order to oxidize all the acids from the fermentation process [39].

Methanogenesis: this final stage of the digestion involves the conversion of hydrogen, carbon dioxide, and ammonia into methane and carbon dioxide [39]. This conversion process of algal biomass into a renewable gas could obtain enough energy from the lipid cell extraction, and there will be enough rich nutrients left, that can be recycled into a fresh medium for algae growth and reproduction [74]. Fig. 10 illustrates anaerobic digestion conversion process, highlighting all the pathways involved.

Suganya, et al. [2] suggested that the addition of a co-digester that possesses high carbon to nitrogen mass ratio such as waste paper, could resolve the issue of low carbon to nitrogen mass of algae. Which is a common challenge with the aerobic digester due to high percentage of protein in the system that tends to reduce the system performance. A similar problem was addressed by Brennan and Owende [16], on the effects of algae's high protein content on anaerobic micro-organisms. Where it was suggested that using salt-adapted micro-organism for this biochemical conversion process could be a feasible solution. This ubiquitous conversion process was recommended by Hallenbeck, et al. [4] for the conversion of leftover algal residues, that have already been used by methane and even more useful biofuels such as biodiesel and bioethanol. Even residues from other conversion processes can be maximized for the production of a methane-rich biogas. Ward, et al. [74] commended this conversion method as an efficient integration of the production of algae biofuel with the wastewater treatment.

The influence of pre-treatment on methane yields in anaerobic digestion of algae was highlighted by Ehimen, et al. [75], where the enzymatic methods yield greater methane than the mechanical methods. Rodriguez, et al. [76] identified thermal pre-treatment as the ideal method to achieve the highest methane yield during anaerobic digestion with lower energy requirements, but mechanical pre-treatments favours some algae species over others. However, the high energy requirement for these pre-treatment processes is a major challenge to algae anaerobic digestion, therefore this method needs more extensive research. Rodriguez, et al. [76] further suggested that there is the possibility of different techniques for high methane yield with a positive energy balance if the pre-treatment parameters could be specified using multi-objective optimization technique. Marsolek, et al. [77] also recommended thermal pre-treatment as favourable, because of the excess heat from other algae biofuel. The heat generated from other algae conversion processes, which is feasible in

many systems could compensate for the energy required for pre-heating the digester feedstock.

4.2.3 Hydrotreatment/Gasification

This is the conversion process of algae oil into jet fuel by hydrotreatment (hydrotreated fatty acid and esters, HEFA) [17]. This is a promising route for the production of synthetic paraffinic kerosene (SPK), a bio-jet fuel with improved energy efficiency from algae lipid production, as a means of reducing carbon emissions from the aviation sector [78]. In this process, the oil impurities are removed by hydrogen treatment in a synchronized order. The oxygen molecules will be removed and converted to oil with shorter chain diesel-range paraffin, prior to cracking and isomerizing into diesel-range paraffin with jet fuel carbon number distribution between 8 and 16 [64]. Fisher-Tropsch gasification process is a characteristic conversion method of algae oil into jet fuel by hydrocracking SPK, where FAME technically synthesize to produce liquid hydrocarbon fuel [2].

Yang, et al. [79] described this process using different conversion pathways which includes Fisher-Tropsch gasification where carbon atoms of algae lipids were distributed between C_7 and C_{18} as a result of hydrotreatment reaction such as hydrodeoxygenation, hydrocarbonnylation and decarboxylation. The carbon distribution of hydrothermal liquefaction-hydrotreatment is similar to the pyrolytic-hydrotreatment, which gives a better SPK product with a distribution between C_8 to C_{16} due to the high pyrolytic temperature. While the hydrothermal liquefaction-hydrotreatment has less heteroatom composition, the nitrogen content is significantly higher in algae oil [80]. This nitrogen content is a major setback that needs resolving in order to develop hydrothermal liquefaction technology for the conversion of algae biomass to aviation fuel. The need for hydrotreatment for the conversion of algae to aviation fuel was strengthened by Chuck, et al. [81] due to the poor energy balances involved in the entire conversion process. This conversion process is energy intensive and required a huge amount of biomass for successive operation even if it is via gasification. Trivedi, et al. [17] highlighted that blending microalgae biofuels with the conventional petroleum-derived jet fuel is capable of reducing flight related greenhouse gas emissions in the aviation sector by 60-80%. This is due to the high level of unburned or partially combusted hydrocarbons in the atmosphere coupled with other trace compounds that jointly affect the global atmospheric composition. This has been a major challenge to the aviation industries for years, and the global aviation industries could use algae biofuel composition as a tool to address this problem [82]. A good example was the algae derived jet fuel used for the test flight on 7th January 2009 which was commended by Ullah, et al. [83] for its low flash point. During this test on the twin-engine commercial jet that included mid-

flight shut down, this biofuel proved that there was no need for engine modification as it made the aircraft 10% more efficient, and fuel consumption was reduced by 1.5 litres per hour compared to conventional Jet-A1 fuel.

4.2.4 Fermentation

This is a biochemical process of converting the cellulose sugar or starch stored in algae biomass into bioethanol [12], this metabolic reaction involves the activities of enzymes to change an organic substrate into alcohol [2]. Sugar compositions in algae such as alginate, mannitol, and laminarin are converted into ethanol with the activities of yeast [13]. This biochemical process can also produce acetone and butanol through acidogenesis and solventogenesis [39]. Algae's high carbohydrate contents have made it suitable for the production of bioethanol even after hydrolysis [41]. The high content of mannitol in the resultant hydrolysates can stand as a cost-effective organic substrate for algae bioethanol production [63]. Algae bioethanol productivity is two times higher than ethanol's production from sugarcane [65] and five times higher than that of corn. A good source of ethanol from microalgae is *Chlorella Vulgaris*, due to its high starch content where the ethanol conversion efficiency was recorded up to 65%. Pre-treatments such as milling, liquefaction, and saccharification or alginate extraction as illustrated in Fig. 11, are required for efficient fermentation of algae biomass [13].

The feasibility of ethanol production from algae biomass via fermentation was supported by Brennan and Owende [16] based on the technical potential of the lipid production context, which can be treated as a conversion route even for algae biomass residue of oil extraction. Fermentation residue could offset the feedstock cost and make up for the whole cost price of the product. Sirajunnisa and Surendhiran [65] suggested that bioethanol from algae could have massive impact and significance in the global renewable and sustainable development without affecting food production and supply. Moreover, with the current research and development aimed at the production of valuable secondary by-products, the economic sustainability of bioethanol could be maximized [84]. Pre-treating the biomass could improve bioethanol yields during fermentation, though this process is not economically justified due to the capital cost of pre-treatment reactors. Chen, et al. [85] reported that bioethanol yield during fermentation depends on the energy requirements of the pre-treatment employed, and hydrothermal pre-treatment of microalgae could significantly improve this yield. Fasahati, et al. [86] recommended the hot water wash as a more economical pre-treatment strategy for brown algae due to the lignin absence. This type of pre-treatment will put less burden on the plant economy, with improved yields rewarding for the economic surplus. Jambo, et al. [87]

suggested the application of enzymatic hydrolysis in the production of bioethanol, to reduce pre-treatment cost as a potential way to drive forward the bioethanol industry. This industry still required both economic and technical evaluation to determine the best fermentation methods for algae bioethanol. Silva, et al. [88] stressed the needs for extensive research on the structural, metabolic and genetic engineering. This is necessary for full assessment of the environmental risk associated with the industrial bioethanol processes, which involve the use of genetically modified microorganisms in place of the traditional fermentation process.

Brown algae biomass is considered as one of the best options for bioethanol production due to its high sugar content in the absence of carbohydrates, but the fermentation of the microorganisms involved must be effective in order to achieve bioethanol. Lee and Lee [14] indicated that higher bioethanol yields from brown algae is evident when there is an increase in the carbon source during fermentation. Ashokkumar, et al. [89] suggested bioethanol production after lipid extraction of biodiesel could be achieved by anaerobic fermentation process. Bioethanol could be obtained from residue biomass with the conversion of hydrolysate through fermentation, and a theoretical yield of 83.4% proves that brown algae can produce both biodiesel and bioethanol. However, this bioethanol commercialisation still depends on the development of cost-effective cultivation and processing methods.

4.2.5 Pyrolysis

This is one of the hottest thermochemical conversion processes during the last two decades, and it involves thermal cracking which can be used for converting algae biomass to bio-oil [64]. This is the thermal decomposition of biomass in the absence of oxygen [39], is used for the production of liquid fuel (bio-oil), solid fuel (biochar) and gaseous fuel products [64]. Pyrolysis is carried out at different temperatures and at different duration with or without catalyst, in order to recover biofuel within the medium to low calorific power range [2]. As illustrated in Fig. 12, this thermal cracking could be regulated by the temperature of both the furnace and condenser to achieve variable temperature for all potential product. The variability in the temperature and the duration of this process have led to the following classification [12]: 1) conventional pyrolysis; 2) fast pyrolysis and 3) flash pyrolysis.

Conventional pyrolysis: a slow heating rate at long duration and medium temperature to produce biochar [2], which can be used not only as fuel but also as a fertilizer for underground carbon sink [90]. With the carbon content over 50%, this conversion method helps in the reduction of the atmospheric CO₂ due to the highly porous structure of bio-char, which improves water retention in the soil as well as the efficient use of nutrients [91].

Fast pyrolysis: a fast heating rate at short duration and high temperature to produce bio-oil [2], which can be used directly as fuels, petroleum replacement or employed as a valuable source of chemicals [91, 92]. The temperature is around 400°C during high contact time with a yield of 35% that is rich in phytol, fast pyrolysis of algae biomass is easier than other lignocellulosic biomass because of the absence of phenolic compounds [92]. Bio-oil is perceived as the mid-way between energy and chemical products, suitable for further refining process in downstream operations [90].

Flash pyrolysis: a very fast heating rate at very short duration and very high temperature to produce a low calorific value gas called syngas [2], which is a promising fuel source. This conversion process is capable of producing algae-derived syngas with the energy density of approximately 50% of natural gas, which can be used as raw material in producing chemicals for direct synthesis of methanol [93].

Pyrolysis is the most tolerant conversion process when considering the high-level ash content of algae compared to another conversion method [41]. But the oil produced still faces some technical challenges like acidity, viscosity, and stability [16], as well as issues concerning residue disposal such as ash and carbon [39]. The 3 different processes involved were commended by Milano, et al. [12] for their potential to produce biofuel on the large scale. In particular, the production of bio-oil that has the capability to produce high-quality fuel oils with greater oil yields. The different pyrolytic stages for algae biomass is favoured by the protein and carbohydrate concentration of the species involved. Hong, et al. [93] recommended that protein-rich algae yield greater bio-oil composition due to their low PAHs content, while algae with high carbohydrate contents are more suitable for the production of syngas. The high protein content of most algae species was emphasized by Yang, et al. [64] as the reason for high nitrogen and oxygen content in bio-oil produced from pyrolysis which resulted in low heating value, low pressure, and low thermal stability. This high protein concentration and lipids could give a liquid that can be considered as a great addition to valuable compounds [92]. The heating value of bio-oil produced from this conversion process is lower than petroleum diesel and higher heating than other lignocellulosic feedstock, which defines its suitability for fuel oil use [67]. The microwave enhanced pyrolysis (MEP) was further recommended by Zhang, et al. [94] as a quick and efficient method for bio-oil production, due to the ability to ameliorate the environment while producing biofuels and chemicals at the same time. Some of the aforementioned technical challenges associated with this conversion process could be eradicated, by reducing the oxygen and nitrogen content before its application as a transport fuel [64]. The process of upgrading hydrogenation and catalytic

cracking could also be employed for further reduction of the oxygen content [16], while nitrogen on the other hand could be reduced in form of nitrogenated compounds by the addition of hydrotalcite catalyst during catalytic pyrolysis [95].

4.2.6 Direct combustion

This is a chemical process of converting algae biomass into hot gasses for energy production [12]. A chemical reaction between algae biomass and oxygen in a furnace, boiler, or steam turbine at around 1000⁰C, producing steam that is capable of powering a turbine which turns a generator to produce electricity [2]. Direct combustion of algae biomass can only be achieved when the moisture content is less than 50% to reduce air pollution [41]. This conversion process requires some level of preparation and processing as illustrated in Fig. 13. Pre-treatments such as drying, and grinding into smaller combustible particles after biomass storage is required prior to the combustion stage [39]. However, the composition of high ash and alkali residue tends to reduce the overall efficiency of this conversion process by fouling the system.

Milledge, et al. [96] recommended the fluidized bed method, as the best option to reduce the effect of the high ash and alkali content of algae biomass. But this method required smaller particle sizes, thus the grinding down the algae biomass will require another form of pre-treatment. Pre-treatment operation is usually an additional cost, which makes the conversion efficiency of this algae conversion process better than the coal-fired power plant [12]. Brennan and Owende [16] suggested this extra cost of pre-treatment could be reduced if the heat produced during the whole conversion process is immediately utilised.

5. Development of algae biofuels for transport and aviation

Algae biofuels could play a significant role in the improvement of global transport fuel and at the same time reduce the global emission of GHG [83]. This is because transport fuels are responsible for a quarter of the CO₂ emissions [65], which has resulted in the efficiency gains from biofuels as renewable fuel source, that is often used to justify every expansion in the transport and aviation industries with respect to climate change [81].

By the year 2070, renewable energy is expected to be the major global energy [83]. The European Energy Commission has set a flight path, that was aimed at getting aviation industries to use 2 million tonnes of biofuel by the year 2020 so as to reduce the 3% GHG emission in Europe [22]. This will improve the environmental performance of the transport sector through decarbonisation, along with the structured plan by the European Commission. If this plan is successful as illustrated in Fig. 14, there will be a drastic reduction of Europe's dependence on fossil fuel and it will be possible to reduce carbon emission from

transportation industries by 60% by the year 2050 [97]. However, the success of this plan will depend on the aviation sector meeting the projected biofuel requirements as illustrated in Fig. 15.

The exploration and implementation of greener alternatives to fossil fuels in the aviation industries have brought about the introduction of special algae-based hydrocarbons as additives [98]. The economic and ecological sustainability of aviation fuel has also led to the development of genetically modified algae-based bio jet fuel [99]. Presently “drop in” replacement is being produced in significant quantities to replace the traditional jet fuels. These are algae-based combined with the petroleum-based fuel as blends or emulsion [99]. There is a potential possibility of cost competition between algae-based and petroleum-based jet fuels due to the availability of the biomass involved, which could be economically viable through the scale of overhead production cost [82]. In September 2008 Solazyme, a California-based renewable oil producer produced the first ever algal-based jet fuel that passed all tested specification including the most challenging ASTM D1655 specification for aviation turbine fuel [100]. This development led to the two successful algae-based bio-jet powered flights the following year on 7th and 30th January, with the hope of more to come [98]. This could as well benefit the UK aviation sector in the reduction of up to 24% CO₂ emission by 2050, but there must be a step change adjustment in the policies and investment framework for sustainable aviation fuel [101].

5.1 Combustion and emission characteristics of algae biofuels

The combustion and emission characteristics of fuel determine the engine performance, and the environmental impact of such engine [10, 102]. Therefore, with all the stringent global emission regulation, it has become mandatory to combine both characteristics in order to evaluate fuel quality under operating conditions [103]. Algae biofuels tend to have different effects on lots of factors that define the combustion and emission characteristics. Such factors includes air/fuel ratio, fuel properties, cylinder pressure, brake mean effective pressure (BMEP), frictional mean effective pressure (FMEP), power, torque, brake specific fuel combustion (BSFC), brake thermal efficiency (BTE), exhaust gas temperature, heat release rate, particulate emissions (PN and PM), aldehydes, CO, CO₂, NO, NO_x and UHC [10].

5.1.1 Cylinder pressure

There has been a need for more emphasis on the effect of algae on the fuel properties of the blends during combustion and emission. Islam, et al. [10] analyzed the effects of the properties of pure microalgae oil methyl ester of *C. cohnii* on fuel blends, in compliance with

the biodiesel standards ASTM6751-12 and EN14214. The test rig was a four-cylinder, turbocharged common rail direct injection diesel engine. The very long chain polyunsaturated fatty acid gave a kinematic viscosity of 5.06 mm²/s and density of 0.912 kg/l. Which resulted in an evident increase in ignition delay due to lower cetane number and greater in-cylinder penetration of the fuel spray. The longer ignition delay means more fuel is injected before the ignition occurs and higher fuel mass is ignited in a short duration [104]. Therefore, lower cylinder pressure should be expected at the early stage of the combustion, and an increase in the later stage. The rate of pressure rise, as illustrated in Fig. 16, was associated with the commencement of the ignition, whereby algae and waste cooking oil biodiesel blends had higher pressure rise rate than petroleum diesel. Hariram and Kumar [105] also reported higher peak pressure for fuel blend with 15% algal oil methyl ester and 85% petroleum diesel when compared with 100% petroleum diesel at any load. The Kirloskar DM10 single cylinder direct injection engine was used, with the density and the kinematic viscosity of algae biodiesel to be 0.83 kg/l and 5.76 mm²/s respectively. An increase in cylinder pressure for all algae biodiesel blends was reported at any load condition, resulting in a better performance than petroleum diesel. This increase was associated with lower cetane number that caused longer ignition delay and improved the premixed combustion [105].

5.1.2 IMEP, BMEP, Power and Torque.

The optimal combination of unsaturated fatty acids and oxygen content of biodiesel that enables complete combustion was responsible for both the IMEP and BMEP variations. A slight increase in the variation of IMEP at 25% and 50% engine loads for Algae B20 blend was noticed when compared to petroleum diesel. IMEP for this blend later decreased at higher loads as illustrated in Fig. 17. It was similar for BMEP in Fig. 18 with a significant increase at 25% and 50% loads but the only reduction was at 75% load. The lower brake power and torque reported by Kumar, et al. [106] for algae biodiesel blend with butanol and petrol diesel was associated with the oxygenated level of algae biodiesel in the blend. High brake torque at low speed was expected, but as soon as the engine gathers momentum the torque reduces as a result of the inability of the engine to ingest full burst of air at higher speed. Al-lwayzy, et al. [8] linked the lower brake power of emulsified microalgae fuel when compared to petroleum diesel to its 20% water content, which reduces the lower heating value and increases BSFC.

5.1.3 BSFC and BTE

From the illustration on Fig. 19, the higher BSFC of algae biodiesel blends when compared to petroleum diesel could be a result of blend's oxygenation and lower calorific value [10]. The

lower BTE of algae biodiesel blends as shown in Fig. 20 could be associated with algae biodiesel's higher density and viscosity, coupled with lower cetane number that gives a longer ignition duration resulting in more fuel consumption [10]. Makarevičienė, et al. [107] linked the possibilities of higher BSFC and lower BTE of algae biodiesel blend to the lower calorific value of the blend, while using 30% microalgae biodiesel blend in a diesel generator on board of a ship. Lower BTE of algae biodiesel was also reported by Satputaley, et al. [108] as a result of lower calorific value. Ahmed, et al. [109] monitored a slight increase in BTE of algae biodiesel blend, which was the result of the better combustion efficiency of the biodiesel. However, Jayaprabakar and Karthikeyan [110] demonstrated the possibilities of higher BTE and BSFC compared to petroleum diesel using 20% of algae biodiesel. This was later supported by Nagane and Choudhari [111] for a similar blend ratio which resulted in an improved BTE, using the Kirloskar single cylinder diesel engine. Hariram and Kumar [105] also reported higher BTE when investigating algae biodiesel blends with petroleum diesel, which could be because of the oxygen content and the earlier release of oxygen in the combustion. Patel, et al. [112] pointed out that the reason for higher BTE in the algae biodiesel blends was due to algae's higher calorific values when compared with petroleum diesel, and this was argued by Piloto-Rodríguez, et al. [103]. Piloto-Rodríguez, et al. [103] based their argument on the fact that methyl esters are associated with lower heating value, therefore any difference in the calorific value will not necessarily affect the BTE. Mwangi, et al. [113, 114] reported an increase in both BSFC and BTE of different algae biodiesel blends, although butanol was blended with algae in water emulsion for some samples. The lower heating value of algae blends and emulsions was reported as the reason for BSFC increase, while better combustion efficiency was the cause of the BTE increase. Kumar, et al. [106] recently reported that low heating value of algae biodiesel was responsible for high BSFC in a blend of algae biodiesel with butanol and petroleum diesel. Where the BSFC values tend to increase with the increase in algae biodiesel composition of the blend.

5.1.4 NO and NO_x

The determining factors for the formation of NO_x during combustion are the combustion temperature, ignition delay and the oxygen content of the fuel. Islam, et al. [10] described the increase in NO and NO_x for the microalgae biodiesel blend as the effects of lower cetane number and ignition delay, which increases premixed combustion and peak heat release. Hariram and Kumar [105] stated that adequate atomization and improved combustion associated with the blend density reduction could lead to the increase in NO_x emission. The presence of oxygen which improves combustion and increases the in-cylinder temperature

could also enhance the formation of NO_x [116]. However, Fisher, et al. [115] reported that a decrease in NO emissions of algae biodiesel was accompanied by reduction in the premixed burn fraction. As shown in Fig. 21, lower NO_x emission was observed for lowest algae concentration blend of Algae B10 at low BMEPs, which later went higher than petroleum diesel as BMEP increases. Low cetane number, longer carbon chain length and the oxygen concentration of this microalgae blend could be responsible for this result. This is because NO_x tends to increase only when the FAME content of the fuel blend is above the 20% threshold. Jayaprabakar and Karthikeyan [110] demonstrated that the higher NO_x emissions were due to high combustion temperature caused by high oxygen content. Nagane and Choudhari [111] then suggested the 10% algae biodiesel blend ratio as a good composition due to the negligible increase in NO_x emissions. Kumar, et al. [106] recently demonstrated that adding butanol to algae biodiesel will reduce NO_x emission. Nurdin, et al. [117] confirmed that algae biodiesel has the lowest NO_x emissions compared to jatropha biodiesel blends as well as petroleum diesel. This is due to the combining factor of the lower in-cylinder temperature and an injection pressure as high as 130 MPa. The combination of both factors reduces the ignition delay period of algae biodiesel, which causes an increase in premixed combustion and gives enough energy for successive air-fuel mixing.

The use of emulsions instead of blends or neat biodiesel was highlighted by Piloto-Rodríguez, et al. [103], as feasible practice for the reduction of NO_x. However, important experimental information about algae biodiesel still requires adequate verification. Emulsified fuels tend to reduce the combustion temperature due to their water content, as revealed by Scragg, et al. [118] while fueling an unmodified single cylinder diesel engine with algae biodiesel emulsion. Wahlen, et al. [11] reported that the significant amount of palmitoleic and myristic methyl ester present in the emulsified microalgae biodiesel blend was responsible for the lower NO_x emission. Tüccar and Aydın [119] suggested that the less air drawn into the cylinder during combustion of microalgae biodiesel could be the reason for the reported reduction in NO_x emission, though the lower heating value of microalgae will lead to lower combustion temperature that could reduce NO_x emission [120]. Sun, et al. [121] stated that the reason for NO_x reduction might depend on the biodiesel oxygen content which affects the adiabatic flame temperature, depending on the level of unsaturation. Makarevičienė, et al. [107] highlighted that the kind of engine used for their experiment could have resulted in the insignificant difference in the NO_x emission, because the diesel engine used was optimized for different parameters. Lately, Zobel, et al. [122] suggested that

blending paraffinic and oxygenated biofuel could be a potential key step towards the reduction of NO_x in diesel engines.

5.1.5 UHC

The presence of unburnt hydrocarbons in exhaust gasses are due to the lack of oxygen to boost the ignition temperature of the fuel to be oxidized. Therefore, the oxygen presence in biodiesel fuel tends to reduce UHC emissions [123]. As illustrated in Fig. 22, UHC emissions of algae biodiesel blends were significantly lower than petroleum diesel, and this could be due to the composition of algae's very long chained fatty acids. Generally, a significant reduction in UHC emissions of algae biodiesel should be expected when compared to petroleum diesel [11, 108], but this reduction could be inversely proportional to the increase of NO_x emission [105].

5.1.6 Particulate emissions

The particulate emissions from microalgae biodiesel are one of the factors that determine the emission characteristics of this feedstock, this emission could be categorized into particle number (PN) and particulate matter (PM) for better understanding. Rahman, et al. [124] investigated the effect of the chemical composition of algae biodiesel on particle emissions. The brake specific particulate matter (PM) emissions of different biodiesel blends of algae, waste cooking oil, cotton oil were compared with petroleum diesel. The result of the PM calculation via a re-inversion tool in the DMS data analysis software as illustrated in Fig. 23, displayed an overall reduction in the PM emission of algae biodiesel blend. Fuel properties such as the higher density, viscosity, boiling point, surface tension and lower cetane number of this blends were stated as the reason for this obvious reduction [124]. Other biodiesel blends of waste cooking oil and cotton oil were in favour of the fuel properties that affect PM emission reduction when compared to petroleum diesel. However, the higher carbon chain length and unsaturation level of algae biodiesel blends were stated as the reason for the higher PM emissions at 25%, 50%, and 75% engine loads when compared with the same blend ratio of both, the waste cooking oil and the cotton seed oil. Though the reduction in PM emission was associated with slight increase in NO_x [105], effective reduction of both emissions could be achieved by using emulsions instead of neat blends [114]. The water content in the fuel will increase ignition delay coupled with the micro-explosion phenomena, thus reducing combustion temperatures with oxidizing soot to control NO_x formation.

Higher PN emissions were reported for 20% and 50% algae biodiesel blend concentration at 25%, 50%, and 75% engine loads as illustrated in Fig. 24. This significant increase was

associated with high algae biodiesel carbon content of C22:5 and C22:6. Which resulted in unburned fuel escaping the combustion chamber and staying in the exhaust with other partially oxidized substances such as volatiles or semi-volatiles [125]. The difference in the variation of the PN emission observed could be associated with the chemical composition of algae biodiesel blend defined by the overall fuel properties.

5.1.7 CO and CO₂

CO emissions are due to incomplete combustion of hydrocarbons, which are controlled by the air/fuel ratio and the engine temperature [119]. The oxygen content of algae biodiesel will obviously improve the air/fuel ratio, thereby permitting a complete combustion. This unique characteristic of biodiesel irrespective of the feedstock will potentially reduce the CO emission of any diesel engine [11]. Significant reduction in CO emission reported by [9, 11, 105, 107, 109, 112, 119] was due to the high oxygen content of algae biodiesel when compared to petroleum diesel. These additional oxygen molecules of algae biodiesel are responsible for the conversion of CO into CO₂ during the combustion process [119]. Therefore fuel-borne oxygen from algae biodiesel will reduce more CO emission than external oxygen supplied as air during the air-fuel mixing process [106]. Decrease in CO₂ emissions should be expected during the combustion of algae biodiesel due to the presence of oxygen [8, 9, 126], except for few cases where slight increase was reported [11, 112]. However, the performance of algae biodiesel should not be restricted to the combustion characteristics alone, because every step of the production chain of this fuel will reduce the overall greenhouse gas emission. Shirvani, et al. [127] analyzed the production of algae biodiesel, in order to find an alternative fuel to better the petroleum based transport fuel. It was suggested that CO₂ emission reduction could be extensively achieved with the full optimization and decarbonisation of the production process [128].

Tsaousis, et al. [129] acknowledged the feasibility of algae biodiesel as fuel in a diesel engine, based on acceptable combustion and emission characteristics even when compared with croton oil. Wahlen, et al. [11] compared the combustion characteristics of microalgae biodiesel, with other biodiesel in a double cylinder diesel engine based on the power output. They observed that even with lower heating values of biodiesel fuels, microalgae biodiesel achieved 96% of the power output of petroleum diesel, with the lowest exhaust gas temperature. The water content in microalgae emulsion could also reduce the exhaust gas temperature [8, 118], which may further reduce other high temperature associated emissions such as NO_x and Soot.

With the huge disparity in the recent research on the combustion and emission characteristics of algae biodiesel, it is evident that there are rooms for improvements. Concerning the combustion, the better brake specific fuel consumption should be expected with the quality of the fuel composition of algae biodiesel. Lower brake thermal efficiency due to longer ignition delay and lower cetane number should not be overlooked. The use of emulsions to reduce the high combustion temperature associated with NO_x emission should be comprehensively investigated.

5.2 Algae biofuel blends and emulsions

Different research and developments have been dedicated to the improvements of biofuels due to the adverse effects of fossil fuel on the environment [130]. However, the straight use of biofuels in a bid to replace existing fossil fuels have encountered various operational challenges due to their physicochemical properties [123, 130-132]. These challenges have led to the improvements of biofuel blends and emulsions in order to produce the fuel with desired physicochemical properties.

Fuel blends are developed as a result of improving the overall properties of the fuel, whereby different types of fuel are mixed together in different proportion to achieve a definite developmental purpose, mostly the overall engine performance [133]. Algae biodiesel can be blended with petroleum diesel and bioethanol or in some cases used as an additive [41, 123, 130, 131], to a diesel fuel without the need to modify the existing engine [134]. Nagane and Choudhari [111] established the possibility of blending algae biodiesel with petroleum diesel. Up to 20% of algae biodiesel was blended without any modification to the engine. This gave good overall results in both emission and engine performance, even when considering engine performance under variable engine compression ratios. Bioethanol up to 10% could also be blended with petroleum diesel and biodiesel without any modification to the existing diesel engine [130]. The oxygenating effect of algae biodiesel was complement with the addition of butanol to improve the performance efficiency of a four-cylinder diesel engine. The blend which consists of 10% algae biodiesel, 30% butanol and 60% petroleum diesel proved to be environmental friendly with reduced NO_x and CO emissions [106].

This is because using some of these fuels directly in a commercial engine may cause engine problems like engine fouling, incomplete combustion, low fuel atomization, and contamination of lubrication oil [135]. But whenever these fuels are mixed in blends, there are improvements in the properties of the blend [134]. This type of blends was stated by Mofijur, et al. [136] as one of the dependent factors of engine emission when both biodiesel-

diesel and ethanol-biodiesel-diesel blends were studied. Effective and efficient reduction in the exhaust gas emission such as CO, hydrocarbons, and particulate matter were evident due to the oxygenating effect of the blends. Instability of these blends is a major concern when using them in engines, because unstable blends may cause engine failure [137]. This is why good solubility of biofuel blends is highly required, and the durability of the soluble blends must be ensured taking into account its dependence on temperature, viscosity and specific gravity [137].

Algae biofuels can be blended by the following methods:

- *Splash mixing method:* this uncommon method is the least accurate of all the biofuel blending methods [135] because the fuel is pumped into a tank that already contains another fuel. This should be done when the temperature of the pumped fuel is between 18⁰ and 20⁰ C while the temperature of the fuel in the tank is colder than 8⁰ C.
- *In line mixing method:* this method involves an empty final product tank that stands as a collecting vessel, in which two or more different fuel are pumped in a precise ratio from either a pipe or hose [135]. This blending method is ideal for large volume of blends, but it is advisable not to keep the resulting blend in the tank for long and maintain at 6⁰ C above cloud point to avoid shock crystallization. Even with a better blend consistency compared to the splash method, the density and viscosity of final blend still require accurate adjustments.
- *Injection mixing method:* this method is the most accurate out of the three because it employs the technique of valve control to inject different fuels at required blending ratio, this method is commonly used at the manufacturing point before the delivery into the final tank [135].

Additives can also modify fuel properties such as the energy content, cetane number, viscosity, stability, and lubricity. Therefore reducing or eliminating biofuel blending challenges like fuel system corrosion, injector deposit, fuel foaming and water separation [5]. The corrosiveness or compatibility of the blends should be critically considered and analyzed along with properties that affect the safety of the diesel engine. Some selected additives known as cold flow improvers (CFI) or pour point depressors (PPD) were tested with biodiesel with the success of 10 wt% reduction in the cloud point [138].

Types of additives:

- *Oxygenated additives*: this tends to overcome the problem of incomplete combustion which is due to the lack of adequate oxygen [5]. The addition of oxygenated compound will improve the oxygen to fuel ratio and avoid the occurrence of incomplete combustion.
- *Metallic based additives*: these additives are to improve soot oxidation as well as lowering the oxidation temperature. They react with water to produce hydroxyl radicals and react directly with carbon atoms during soot formation.
- *Water*: water addition tends to reduce the temperature of the local combustion in the ignition chamber, therefore, reducing NO_x emission.
- *Antioxidants*: these additives are to inhibit the oxidation of other molecules, by terminating the chain reactions caused by radical agents that determine the oxidation reaction rate. Therefore, extending the fuel shelf life.
- *Polymeric based additives*: these additives tend to improve the engine performance as well as the emission parameters.

An additive supplied by Wintron Synergy, a combination of polymethacrylate compounds in a mineral oil solution, was used with biodiesel-diesel blends to address multiple idling conditions of a modern Tier 4 diesel engine Roy, et al. [138]. With the interest of combining two different multifunctional organic additives, it will be possible to have positive physicochemical effects on the injection, ignition and combustion of a diesel-ethanol blend. Satgé de Caro, et al. [139] studied the effects of the merging glycerol skeleton bearing heteroatoms with amino-ether, hydroxyl, nitrate, and nitramine functional groups, using them as non-ionic surfactants for the reduction of the interfacial tension in the fuel blends. The resulting emulsion improves the engine behaviour and reduces both, the overall emission and the ignition delay period. Roy, et al. [138] stated that chemical additives such as cold flow improvers or pour point depressors could obstruct the production of large crystal structures formed in biodiesel at low-temperature conditions. These chemical additives also lower the cloud point, pour point and cold filter plugging point of biodiesel by changing the shape of its crystal formation. Misra and Murthy [140] recommended that the cold flow performance of biodiesel could be improved by additive blending with short-chain alcohols such as ethanol, butanol, and isopropanol. Therefore, ethanol could be classified as a good additive for better combustion performance and emission in a diesel engine. Ethanol-blended biodiesel was commended by Bhale, et al. [141], as a complete renewable and feasible alternative fuel, due to its capability of better emission and improved cold flow behavior, without affecting the

performance of a diesel engine under cold climate. This is because of the significant reduction in both the pour point of the ethanol-diesel blends and the emission from the engine during experiments. Sadeghinezhad, et al. [142] highlighted the influencing factors of ethanol solubility in diesel oil, connecting the blend temperature to the water content. Dry ethanol can blend with diesel fuel at warm ambient temperature, but as soon as the temperature drops to 10°C, both fuels start to separate. This problem could be resolved with the addition of an emulsifier that can hold blends together by suspending the small droplets of ethanol inside the diesel.

The neat blending of biofuel such as biodiesel and bioethanol with petroleum diesel has become a major strategy in the reduction of diesel engine emission. However, these neat blends were unable to reduce all the pollutants simultaneously resulting in the development of the water-fuel emulsion method [143]. In the case of unblended fuel or in order to improve the thermodynamic stability of fuel mixtures, emulsions or more preferably micro-emulsions are employed [144]. These microemulsions are firmly dispersed liquid mixtures of a polar phase with a non-polar phase, using organic compounds called emulsifiers or surfactants for the reduction of the surface tension between the oil and water phase [145]. This is the production of a clear, isotropic and non-polarised thermodynamically stable mixtures [134]. Emulsions are sometimes referred to as hybrid diesel fuels because of the possibilities of mixing biodiesel with alcohols of low molecular weight, in order to reduce the viscosity with the aid of an amphiphilic compound otherwise known as surfactant [146]. This process employs co-solvents or emulsifiers to promote the required bonding for fuel blends in diverse conditions [142]. The creation of a successful emulsion is based on the ability of the emulsifier to facilitate the initial formation of the fine lipid droplets, during homogenization and to improve the stability of these lipid droplets after formation [147]. A collection of commonly used surfactants such as sorbitan monooleate (Span80) and cetyltrimethylammonium bromide (CTAB) were used with butanol and water as co-surfactants to improve the stability of algae biofuel blend, shown in Fig. 25, and engine emissions [145].

Hagos, et al. [148] tried to differentiate emulsification techniques from blending based on the difference in boiling points of the mixtures, stating that blending of a neat fuel mixture can only be convenient for fuels with relatively similar boiling points. Emulsion on the other hand, can only be used for fuel mixtures with different boiling points to demonstrate the benefit of micro-explosion in the fuel atomization. Al-lwayzy, et al. [8] described the mixtures of biodiesel and/or diesel with water in the production of emulsified fuels as another

way of utilizing microalgae and its elements. Emphasizing on the role of the emulsified water in facilitating the interaction between the mixtures, and extending emulsion stability. The ultrasound treatment employed improves disintegration of microalgae aggregates into dispersed cells, resulting in a slightly wider spray angle due to the fine droplet in the emulsion. The possibility of biofuels achieving a higher heating value than petroleum diesel was highlighted by Tan, et al. [123] via emulsion. The total heating value of petroleum diesel was just slightly higher than that of the biodiesel-bioethanol emulsion, resulting in low emission with lower brake power and torque. The inability of biofuel blends to simultaneously reduce all the pollutants in a diesel engine was stated by Hoseini, et al. [143] as the compromising factor for the deployment of a water-fuel emulsion. Whereby surfactant is frequently used as an emulsifier to hold the mixtures through the combustion process. This emulsion type is either micro-emulsion or macro-emulsion depending on the volume of emulsifier used. In order to stabilize the lipid droplets of biofuel blends during transportation, storage, and utilization, the emulsifier should facilitate the droplet fragmentation. This is done by decreasing the blend's interfacial tension and generating a protective coating to inhibit droplet coalescence within the homogenizer [147]. A novel emulsifier named CLZ was developed by Lei, et al. [149] for biofuels, based on the effects and stability of ethanol in biodiesel blends. It was observed that after testing the CLZ-type emulsifier in a diesel engine, there was a significant improvement in the overall engine performance. An increase in BTE and reduction in BSFC tends to improve the overall emission of the engine, but an increase in CO emission at light loads and a significant decrease at heavy loads were observed. Therefore, using emulsion in place of neat biodiesel blends could be very important to the potential reduction of CO₂ and NO_x [103].

6. Future of algae biofuel and its application

Based on this analysis, It could be established that algae biofuel gains surpass the setbacks, therefore a potential replacement of fossil fuel is established. The future of algae biofuel is based on developing cost-effective approaches for the most efficient technologies that will make the commercialization of this biofuel quicker and successful. Though all the production technologies involved are reasonably established but wastewater treatment is presently the only one that is economically feasible for domestic and industrial use. The commercialization of algae biofuel will start with the cultivation methods involved, considering better reviews from the artificial methods over the natural methods as regards production yields, environmental factors, and risk factors. However, while the most preferred method of artificial cultivation could be facing a decade or more delay due to technical limitation, the

natural method could be optimized in the most cost-effective way to achieve a significant percentage of the overall expectation. It will be very important to employ genetic engineering in order to identify super algae using the strain identification breeding process. This could produce high lipid content, higher growth rates, and growth densities.

As justified in this paper, biofuels from algae are technically feasible due to their sustainability, and this puts them in the best position to potentially and methodically displace fuels obtained from crude oil. Emulsified fuel blends should be recommended for algae biofuel production based on their ability to simultaneously reduce major pollutants, and improve the thermodynamic stability of fuel mixtures due to their water content. This water content facilitates the interaction between the blends and extends the stability of the emulsion, while surfactants also hold the mixtures together through the combustion process. However, significant improvement must be done on the current economics of algae biofuel production in order to permit a good competition with fossil fuel before the ultimate displacement. Some of these conversion methods are complex and economically expensive, but they can be commercially viable if all the by-products are optimally utilized. By-products that could be used for pharmaceutical and cosmetic purposes will definitely compensate for such conversion cost. Energy conversion methods like direct combustion and fermentation should be prioritized due to environmental feasibility as well as the economic possibility for both domestic and industrial use.

With the various technical challenges surrounding the production of algae biofuels for transportation. It is only by continuous research and development that the possibility of the cost-effectiveness and global availability of this remarkable organism as a renewable and sustainable fuel source could be achieved during the next decade. For example, in the International Energy Outlook 2016, the United State Department of Energy projected the possibility of 99% internal combustion engines for new cars in 2040 [21], this means that these engines will still be existing for the next 2-3 decades. Therefore to reduce the total emission generated in the transport sector, there is a need for advanced improvement on modern combustion strategies as well as renewable fuel design. Such improvement will facilitate the optimum configuration for the evolution of internal combustion engines into the environment, and this evolution can only be achieved by maximizing the sustainable algae feedstock to suit all the environmental requirements.

As of 1st May 2017, Singapore Airline's Airbus A350-900 flew 206 passengers from San Francisco to Singapore on a biofuel combination of hydro-processed ester and fatty acid. This was one of the series of 12 biofuel-powered flights by the Civil Aviation Authority of

Singapore to fly the San Francisco-Singapore route [150]. This operation was the first of its kind to combine the use of biofuels, fuel efficient and optimized flight operations, using waste cooking and conventional jet fuel to facilitate optimized flight operations towards the reduction of carbon emissions in passenger aircraft. The expensive fuel production process could be maximized to influence a significant reduction in GHG emissions from the aviation sector. Then, this development could be integrated with the knowledge from the Solazyme's algae-based jet fuel that passed all the eleven critical specifications for ASTM D1655 standard, to produce relatively affordable bio jet fuel for the aviation industries.

7. Conclusion

This review article discusses the current status and application of algae as a potential feedstock with a diverse benefit for the resolution of the global energy demand, and environmental pollution control. The limitations of first and second generation biofuel resources clearly demonstrate that these two generations are obviously insufficient to keep up with the global demands for transport fuels in a sustainable way. The significant potential production of synchronized valuable co-products with wide applications in medicine, food, and cosmetic industries, is obvious with the production of 3rd generation biofuel. The value of this paper is that it highlights the pros and cons of 3rd generation algae biofuel status and potential future applications.

Artificial cultivation system known as photobioreactor is the most effective, in terms of high production volume because of the improved cultured environmental conditions. However, the economic feasibility is still questionable due to the high operating cost, which makes genetic engineering cultivation method a potential innovation, but the environmental feasibility of this method is under heavy criticism.

Conversion technologies such as transesterification, pyrolysis, anaerobic digestion, hydro-treatment, fermentation and direct combustion for algae biofuel production were briefly discussed. Fuel blends and emulsion with algal biofuels can influence the physicochemical properties of the fuel, whereby giving positive results on both combustion and emission characteristics.

Improvement on the combustion and emission characteristics of algae biofuel is obvious, especially better brake specific fuel consumption due to the quality of the fuel composition, but lower brake thermal efficiency will be imminent because of the longer ignition delay and lower cetane number. However, improving algae biofuel blends and emulsions for better

physicochemical properties could give positive results on both the combustion and emission characteristics.

A significant portion of the total hydrocarbon fuel consumed by the world today can be potentially replaced by algae biofuels with minimum or no environmental footprint. However, the commercialization of the production is still in the developmental stage, and more research should be focused on the economic feasibility of the full-scale production. The commercialisation of algae production could redefine the future of global energy generation and GHG reduction through algae carbon capture.

Further works are required in order to identify the most energy efficient, cost-effective, and high yield extraction process, to enhance the economic feasibility of global algae biofuels sector. This will address all the major technical challenges affecting the various production processes involved. Hence, government emission policies combined with these aforementioned research and development will obviously fast-track the date when algal biofuel production can become a commercial initiative.

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