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Recent progress in catalytic conversion of microalgae oil to green hydrocarbon: A review

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ABSTRACT

The increase in greenhouse gas emission due to the burning of fossil fuels since the last century has led to global warming. This has triggered numerous researches in green hydrocarbon alternatives from renewable oil. Microalgae is one of the potential sources of green hydrocarbon, which will reduce the dependency on fossil fuel. This is because microalgae have a high oil or lipid content, rapid growth rate, and high ability to sequester carbon dioxide. Besides that, their cultivation does not require arable land and will, therefore not compete with global food production. The current biofuel production is based on the transesterification of triglyceride to biodiesel which suffered from several drawbacks such as high acidity, high viscosity, and low heating value, *etc.* A more efficient reaction route needs to be developed to produce biofuel which possesses similar properties as the fossil-derived fuel. Therefore, this review aims to encompass the conversion of microalgae oil towards green hydrocarbons *via* various catalytic reactions. The fundamental chemistry and mechanisms involved in the conversion of microalgae oil to useful chemical products are also discussed in detail.

1. Introduction

1.1. Current trend

For the last few decades, energy crisis has threatened the world due to excessive utilisation of the global depleting oil reserves by the ever-increasing human population. According to the United States Environmental Protection Agency (USEPA), 40% of the primary energy is consumed by transportation and contributed 71% of greenhouse gas (GHG) emission in 2010 [1,2]. Currently, fossil fuels supply about 90% of the global energy demand [3]. Apart from the fluctuating petroleum fuel prices, there are more worrying issues associated with the utilisation of these non-renewable fuels including deterioration of health standards and environmental issues [4]. To overcome the increasing demand for a new source of hydrocarbon, for various industrial applications as well as to reduce various environmental problems, researchers are focusing on developing sustainable alternatives. Biofuels have several advantages over fossil fuels, which include sustainability, non-toxicity, biodegradability, and extremely low CO_2 emissions [5]. As shown in Fig. 1, the evolution of biofuel from the first generation by using edible oil crops such as corn, rapeseed, soybean, *etc.* to the fourth generation with the development of engineered microalgae. In the first generation, both biofuels and biodiesel are produced from edible oil crops such as rapeseed, palm, sunflower, soybean, coconut *etc.*

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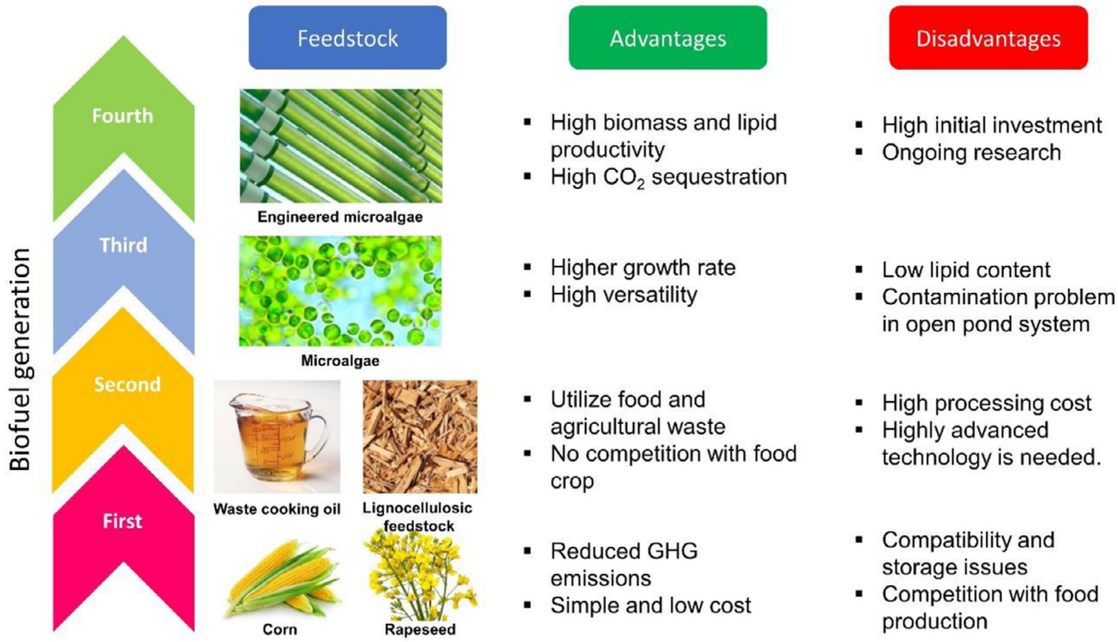

Fig. 1. Schematic diagram of biofuel evolution.

[6,7]. However, the first-generation biofuel has caused numerous debates in recent years, predominantly due to potential problems associated with the imbalance of the ecosystem and global food competition. This is mainly due to the large area of arable land that is required to grow these crops [8]. Besides, engine compatibility issues and storage issues have also limited its application. Furthermore, the costs of feedstock (80% of total cost) have contributed to the high biodiesel price [7]. Various non-food feedstock, such as agricultural waste and waste cooking oils (WCO), have been successfully converted into bioethanol or biodiesel (known as second-generation biofuels), however, the potential for this non-food feedstock to meet global energy demands remains limited [9–12].

It is, therefore, recommended that microalgae as one of the most promising alternatives (a so-called third generation feedstock) due to their simple growth requirement, higher growth rate, photosynthetic ability and most importantly it does not require arable land for production of food crops [13]. However, microalgae with a high growth rate is often accompanied with a low lipid content. Therefore, engineered microalgae which possesses high growth and lipid content has emerged as the fourth generation biofuels [14]. These unique features will be the future source of sustainable non-edible oil to be converted into green hydrocarbons.

1.2. Introduction of microalgae as a promising source for green hydrocarbon production

Microalgae is highly potential to be used as triglyceride feedstock owing to their high lipid contents and high biomass growth rates. Some microalgae species contain more than 60% lipid content by their dry cell weight and average at 35 wt% [15–17]. The lipid content and lipid productivity are dependent on the microalgae species and phenotypic factor such as culture conditions [18,19]. The yield of typical oil crops such as palm, corn, and coconut is below 1000 gallons per acre. In contrast, the oil yield from microalgae is approximately 5000 gallons per acre [20]. Furthermore, the microalgae biomass production can be accelerated through the utilization of wastewater and industry flue gas to supply a nitrogen source and CO_2, respectively [21–24]. Generally, 183 tons of CO_2 is consumed for every 100 tons of algae biomass [25]. Recently, Nascimento et al. [26] demonstrated that *Botryococcus terribilis* can fix 2.52 tons of CO_2 per ton of microalgae. The ability (1) to achieve high biomass, (2) produce high lipid yield, (3) easily cultivate on non-arable space, (4) to capture a high amount of CO_2, and (5) to grow on wastewater have made this biomass as a preferred oil feedstock for green hydrocarbon production.

The chemical composition of microalgae varies with algae strain and the cultivation conditions. In general, microalgae cells comprised of 20–40% lipids, 30–50% proteins, 0–20% carbohydrates, 0–5% nucleic acids [18]. The lipids from microalgae can be classified into two groups, storage lipids (neutral lipid) and structural lipids (polar lipid). The main function of structural lipid acts as a barrier to control the membrane's permeability. Storage lipids are mainly in the form of triglycerides (three fatty acid chains coupled to a glycerol molecule). The common fatty acids found in microalgae cells are stearic acid, palmitic acid, palmitoleic acid, vaccenic acid and linoleic acid (Table 1). The carbon chain length of these fatty acids is between the ranges of 12 to 18 which made them very suitable for green hydrocarbon production. As shown in Table 2, *Chlorella protothecoides*, *Desmodesmus* sp., *Scenedesmus* sp. and *Tribonema minus* possess a high lipid content (47.4–64.1%) and high lipid productivity (224.1–384.7 mg/L/d). It should be noted that the species mentioned above are cultured under different cultivation conditions.

In the past, biofuel production is based on the extraction of lipids from microalgae followed by transesterification to produce fatty acid methyl ester (FAME) [37,38]. This extraction method is applicable to microalgae strain with a high lipid content. Although transesterification is a well-developed process, the converted FAME contains large amounts of oxygenates which deteriorate the fuel quality. FAME is suffered from drawbacks as high oil acidity, high viscosity, and low heating value, hindering it to be used as a direct drop-in fuel. Alternatively, bio-oils can be produced from low lipid content microalgae *via* cost-effective thermochemical conversion such as hydrothermal liquefaction and pyrolysis [39]. However, low selectivity is a disadvantage of this conversion route as undesirable products—mainly oxygenates are produced. Therefore,