

Biodiesel Production from Algae via Transesterification Reaction: Challenges and Opportunities (Review)

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Received: 2023-01-23

Revised and accepted: 2023-03-25

Abstract

This study tries to review the methods and stages of biodiesel production from the extracted oil of algae through a transesterification reaction. Biodiesel is a clean, renewable, biodegradable, and eco-friendly fuel. Algae are considered the third-generation and the most promising biodiesel feedstock because of their advantages including that microalgae have the potential to produce 25–220 times higher triglycerides than terrestrial plants and the growth rate of algae is approximately 20- 30 times faster than food-yielding crops. Algae can grow almost in all kinds of water such as fresh or waste waters and on non-arable and marginal land and engine performance and exhaust emission of microalgae biodiesel investigated. Due to the higher oil content in microalgae than macroalgae, it is a better feedstock for biodiesel production. This work studied the steps of biodiesel production from microalgae including cultivation of microalgae, harvesting, oil extraction, and especially how to create biodiesel from microalgae biomass through transesterification reaction by focusing on

the kinds of catalysts that have been used for microalgal biodiesel production studied. Transesterification reactions are commonly catalyzed by acids or bases as chemical catalysts or carried out in the presence of enzyme catalysts as biocatalysts. Also, the advantages of using heterogeneous catalysts compared to homogeneous ones were investigated. Many efforts have been made to commercialize algae biodiesel but the high cost of producing algae and extracting its oil is challenging and it will still take some time before algal biofuels become a commercial reality in Iran and all the world.

Keywords: Catalyst, Biofuel, Microalgae, Oil extraction, Renewable energy

Introduction

Increasing the world population along with an improvement in the life standard has led to significant usage of energy consumption. only 7.8% of consumed energy is drawn from renewable sources. Due to the reduction of fossil fuels, efforts have been made to find alternative sources to meet the energy demand for the present and

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future. Biodiesel, a monoalkyl ester of fatty acids, is clean, renewable, biodegradable, eco-friendly, and nontoxic for nature. Also, biodiesel is considered as clean for the environment. The European Environmental Agency has reported a decrease in greenhouse gas emissions between 2018 and 2019 because of the implementation of biodiesel in the transportation sector.

Chemically biodiesel is a mixture of Fatty Acid Methyl Ester (FAME) derived from reacting either edible or non-edible oils with short-chain alcohol in the presence of a catalyst, producing a methyl, ethyl, or propyl ester by the process of transesterification (Fig. 1). The great challenge in biodiesel production for researchers is minimizing the production cost. Selection of the feedstocks and catalysts is so important as these require 75% of the total investment. Non-edible and waste oil sources like algal oil, microalgae, jatropha, waste cooking oil, and grease were reported to reduce the cost by 60–90% (Baskar and Aiswarya, 2016).

The biofuel feedstock has been classified into four generations (Aziz et al., 2020). The edible sources contain oil seeds and food

crops like soybean, sunflower, and rapeseed which are considered as first-generation feedstocks. However, due to the ‘food versus fuel’ conflict, the use of such feedstocks has been highly discouraged in recent years (Anto et al., 2020; Islam et al., 2017).

The second-generation biofuels, non-edible biodiesel feedstocks include crops like jatropha, Karanjaa, jojoba, salmon oil, tobacco seed, and animal fats, waste cooking oil, etc. can avoid problems faced by first-generation biofuels by producing biofuels from agricultural and forest residues instead of food stocks (Shah et al., 2018a). The second-generation feedstocks are more efficient and environmentally friendly. They eliminate competition for food and feed but the amount of these resource which is not enough to meet the world's fuel needs (Anto et al., 2020).

Third-generation feedstock, non-edible and non-agricultural sources, have come into view during recent years for the production of biodiesel. Microalgae are considered as the most promising choice for biodiesel production. The advantages of algae as biofuel feedstock are multifold. This matter

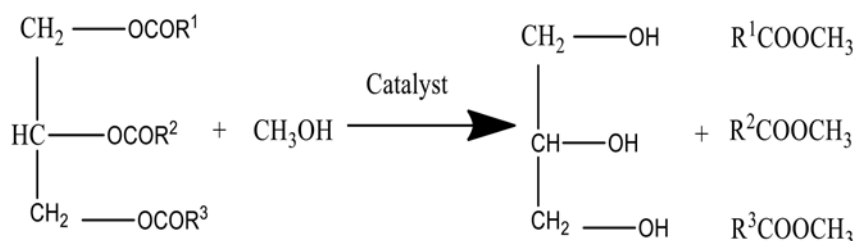


Fig 1. The process of transesterification

will be discussed further (Anto et al., 2020; Nautiyal et al., 2014b; Shah et al., 2018a).

Fourth-generation biofuel uses genetically modified algae to enhance biofuel production. Genetic modification is the key to improving oil accumulation and biomass yield, consequently developing the bioeconomy (Shokravi et al., 2022).

This review focuses on the properties of algae biodiesel and the process of transesterification of algae. Structurally, the paper comprises of 5 main sections. The overview of the biodiesel feedstocks and the advantage and disadvantages of algae as biodiesel feedstock is presented in Section 1. In section 2, microalgae and macroalgae are compared for oil content. Section 3 evaluates the properties, engine performance, and exhaust emission of microalgae biodiesel. Section 4 will focus on the steps of biodiesel production from microalgae and in the last section the kinds of catalyst that have been used for microalgal biodiesel production was investigated.

Advantages and disadvantages of algae as biodiesel feedstock

Advantage of algae

Researchers claim that due to the benefits of algae, it seems that algae be the most promising feedstock for biodiesel production. The most important benefit is that microalgae have the potential to produce 25–220 times higher triglycerides than terrestrial plants and they can produce 30–100 times more energy per hectare compared to terrestrial crops which is due to higher solar energy yield, and superior lipid productivity (Demirbas,

2010). Algae can grow almost in freshwater, seawater, and even in wastewaters (Baskar and Aiswarya, 2016). Algae act as cleaning agents because they can grow by using waste and cause to remove different types of pollutants and toxic chemicals as a nutrient such as nitrogen, phosphorous, potassium, nitrate, silica, iron, magnesium, and other chemicals from municipal and industrial wastewater. (Dharmaprabhakaran et al., 2020).

Studies showed that the growth rate of algae is approximately 20–30 times faster than food yielding crops (Demirbas and Fatih Demirbas, 2011). There is no need for the use of chemicals such as herbicides or pesticides and they do not need fertile soils for growing thus reducing costs and environmental impacts (Rodolfi et al., 2009). Microalgae can be grown on non-arable and marginal land which is not suitable for agriculture. In addition, they require significantly less land, an estimated 2% of the land required to produce the same amount of biodiesel from food crops. (Aransiola et al., 2014). They can adapt to desert conditions, and they can grow in nylon sacks or tanks (Aransiola et al., 2014; Cheng et al., 2013). Algal-based biofuel source is completely biodegradable. Microalgal biodiesel has properties similar to those of petro-diesel. These include density, viscosity, flash point, cold flow, and heating value. Also, from the environmental point of view, biodiesel from algae has greenhouse gas fixation ability as it has less emission of CO₂, NO_x, and other greenhouse gases and algae are capable to mitigate particulate

matter, CO, hydrocarbons, and SO_x (Anto et al., 2020; Atadashi et al., 2013; Chisti, 2007; Demirbas, 2010; Mata et al., 2010; Shah et al., 2018a).

Disadvantage of algae

For biodiesel to become the alternative fuel of choice, it requires an enormous quantity of cheap biomass. Using new techniques for cultivation, algae may allow biodiesel production to achieve the price and scale of production needed to compete with, or even replace, petroleum. Biodiesel production from algae is relatively a new technology which causes some challenges. One of the problems of using microalgae as biodiesel feedstock is the harvesting stage. Microalgae that store lipids are often unicellular, have low densities and there are in a suspension state that makes separation difficult. Consequently, extraction procedures for microalgal lipids in a large scale have challenges and researchers are trying to resolve this problem (Demirbas & Fatih Demirbas, 2011). Another disadvantage of microalgae for biofuel production is the low biomass concentration in the microalgal culture due to the limit of light penetration, which in combination with the small size of algal cells makes the harvest of algal biomasses relatively costly (Demirbas, 2010).

Comparison of microalgae and macroalgae

Algae are a diverse group of photosynthetic organisms ranging from unicellular microalgae to multicellular macroalgae forms. They are divided into two major groups based on their size and morphology

(Adeniyi et al., 2018; Anto et al., 2020; Demirbas, 2010; Demirbas & Fatih Demirbas, 2011).

Microalgae can be found in colonies or they may either live in a single form, living in saline or freshwater environments. They can convert sunlight and carbon dioxide to algal biomass. However, microalgae usually have higher lipid productivity per cultivation area and, as a result, a greater potential for liquid fuel production such as biodiesel. Because of this, the number of research on biodiesel production from microalgae is more than from macroalgae (Bharathiraja et al., 2015; Dharmaprabakaran et al., 2020; Mata et al., 2010; Shah et al., 2018a, 2018b).

Macroalgae or “seaweed are fast-growing multicellular organisms growing in salt or fresh freshwater that can reach sizes up to 60 m in length. Macroalgae possess plant-like characteristics, making their harvesting more easily compared to microalgae. Successful algal biotechnology mainly depends on choosing the right species. Therefore, the selection of strains with high lipid productivity is the key characteristic for successful biodiesel production from macroalgae (Abomohra et al., 2018; Aresta et al., 2005; Suganya et al., 2014; Xu et al., 2014). Due to the higher oil content in microalgae than macroalgae, it seems to be a better feedstock for biodiesel production, which is further investigated.

Algae lipid content and productivities

Many algae species can be induced to accumulate substantial quantities of lipids thus contributing to a high oil yield. The

average lipid contents of algae vary between 1 and 70% per dry weight but under certain conditions, some species can reach 90% of dry weight (Chisti, 2007; Mata et al., 2010; Singh et al., 2011). Table 1 compares the oil content of microalgae with other vegetable oil crops (Chisti, 2007; Demirbas & Fatih Demirbas, 2011; Mata et al., 2010; Singh et al., 2011). Although the percentage of the oil content in a dry weight of all crops is significant as it has been shown in Table 1,

microalgae can yield more oil per hectare of the occupied area compared to other crops.

According to Table 1, it has been concluded that using algae for biodiesel production seems more logical due to the high oil contents. In the following section, we will discuss why microalgae are used more than macroalgae for biodiesel production, and examples of the algae mentioned above in Table 1 containing approximately 30, 50, and 70% oil (L/wt) is introduced in Table 2.

Table 1. Comparison of microalgae with other biodiesel feedstocks

Crop	Oil content (% dry wt)	Oil yield (L/ha)	Land use (m ² year/kg biodiesel)
Palm	36	5366-5950	2
Soybean	18	446-636	18
Sunflower	40	1070-952	11
Corn	44	172	66
Rapeseed/ Canola	41	974-1190	12
Jatropha	28	741-1892	15
30% oil (L/wt) in algae (low oil content)	30	58700	0.2
50% oil (L/wt) in algae (medium oil content)	50	97800	0.1
70% oil (L/wt) in algae (high oil content)	70	136900	0.1

Table 2. Oil content of some microalgae

Microalgae species	Oil content (g/g dry wt%)	References
<i>Ankistrodesmus</i> sp.	24-31	(Mata et al., 2010)
<i>Chlorococcum</i> sp.	19.3	(Mata et al., 2010)
<i>Cryptocodinium cohnii</i> (Seligo) Chatton	20	(Chisti, 2007)
<i>Cylindrotheca</i> sp.	16-37	(Chisti, 2007)
<i>Dunaliella primolecata</i> Butcher	23	(Chisti, 2007)
<i>Dunaliella salina</i> (Dunal) Teodoresco	6-25	(Mata et al., 2010)
<i>Ellipsoidion</i> sp. F&M-M31	27.4	(Rodolfi et al., 2009)
<i>Haematococcus phuvialis</i> Flotow	25	(Mata et al., 2010)
<i>Isochrysis galbana</i> Parke	7-40	(Mata et al., 2010)
<i>Nannochloris</i> sp.	20-35	(Chisti, 2007)
<i>Pavlova lutheri</i> CS 182	35.5	(Rodolfi et al., 2009)
<i>Scenedesmus obliquus</i> (Turpin) Kützing	11-55	(Mata et al., 2010)
<i>Scenedesmus quadricauda</i> Chodat	1.9-18.4	(Mata et al., 2010)

Microalgae lipid content

It has been shown that the relative lipid content in microalgae is more compared to macroalgae and this is the main reason for applying microalgae for biodiesel production more than macroalgae. Table 2 displays the oil content per dry weight of several microalgae species. It is evident that the majority of these species produce oil ranging from 20% to 70% of their dry weight.

Microalgae have a high lipid content, which forms the foundation for producing biodiesel. In contrast, macroalgae tend to produce sugars and other carbohydrates instead of lipids. The oil content of macroalgae is typically less than 5% of their dry weight, making them an economically unviable source of biodiesel feedstock. Macroalgae have high water content rich in carbohydrates (25% - 50%), protein (7% -15%), and low lipid content (1% - 5%). Although the lipid content of seaweeds is generally low, certain species have a total lipid content exceeding 10% of their dry weight, making them promising candidates for biodiesel production (Abomohra et al., 2018). The quantity of biomass and lipids obtained from macroalgae varies depending on factors such as the type of macroalgae, light and temperature conditions, and geographical location. Table 3 displays the oil content per dry weight of various macroalgae species. Some of these species, like *Laminaria japonica* Areschoug, have a high oil content of approximately 10%, making them suitable for biodiesel

production.

Steps of biodiesel production from microalgae

To produce biodiesel from microalgae, the process can be divided into four major stages. Firstly, microalgae cultivation is required. Secondly, the microalgae must be harvested and concentrated. The third step involves the extraction of oil from the microalgae cells by disrupting them and extracting the intracellular lipids. Finally, the extracted oil is converted into biodiesel (Torres et al., 2013).

Microalgae cultivation

Open ponds and photobioreactors are two advanced technologies used to cultivate microalgae. Open ponds are constructed from inexpensive and widely available materials, making this method more cost-effective. Additionally, open ponds allow for mass cultivation of microalgae (Riahi, 2008; Torres et al., 2013).

Harvesting and concentration

Separating algae from its medium and in fact, its concentration is known as harvesting. Harvesting is a process and it is a combination of different chemical, mechanical, and thermal methods. The goal of biomass harvest is to achieve highly concentrated slurry with a minimum of 2%–7% of total solid matter. Harvesting of microalgae can be done by centrifugation, flocculation, membrane filtration, gravity sedimentation, flocculation, electrolytic process, flotation, electrophoresis techniques, and micro screens (Torres et al., 2013).

Oil extraction

After the algal biomass is harvested and dried, the next step is oil extraction. The choice of a certain method for extraction depends on its efficiency, cost-effectiveness, accuracy, applicability, robustness, extraction capacity, and most vitally precision and reproducibility, (Zhu et al., 2017). Extraction of algal oil from biomass can be done mechanically, chemically, or a combination of the two. Sharma et al. (2017) have well calculated the challenges of the oil extraction techniques. The considerable challenges in oil extraction from microalga were drying cost, high chemical consumption, less efficiency of extraction, rigidity of cell wall, and difficulty in separation between lipid and the medium (Sharma & Singh, 2017).

Conversion of oil to the biodiesel

The high viscosity of extraction oil from microalgae makes it unsuitable for direct use in diesel engines since it leads to poor fuel atomization and the formation of deposits, such as piston ring sticking, in the fuel transfer path. Additionally, the low volatility of the oil causes incomplete combustion, resulting in the production of significant amounts of ash. To address this issue, several methods have been proposed to reduce the viscosity of microalgae oils, including dilution, microemulsion, pyrolysis, cracking, and transesterification (Atadashi et al., 2013).

Transesterification

The most common method is the reaction of an ester with an alcohol in the presence

of a catalyst that produces a new ester and a new alcohol because one ester is converted to another ester. In the synthesis of biodiesel, methanol is mostly used as an alcohol due to its low cost, availability, and production of alkyl esters with low viscosity (Rashtizadeh et al., 2010). About microalgae oil, there are two transesterification methods. One method is direct transesterification or in situ oil extraction–transesterification that both extraction and reaction of the algae oil are performed simultaneously in the reactor and another one is a two-stage process or conventional transesterification involves the extraction of lipid and the removal of excess solvent followed by transesterification of extracted lipid (Karthikeyan et al., 2020).

Transesterification catalyst

Transesterification reactions require a suitable catalyst, which can be a chemical catalyst (acid or base) or a biocatalyst (enzyme). The catalyst used for the transesterification reaction can be either homogeneous or heterogeneous (Rashtizadeh et al., 2014). Figure 2 depicts the types of catalysts used for transesterification reactions.

The basic catalyst is most common since the process is faster and the reaction conditions are moderated. Traditionally, NaOH or KOH have been used as homogeneous basic catalysts for commercial transesterification processes. Compared to acids, methyl esters are produced with high yields under these basic catalyst conditions (Rashtizadeh et al., 2014).

The use of alkaline catalysts has some problems. A small amount of moisture can

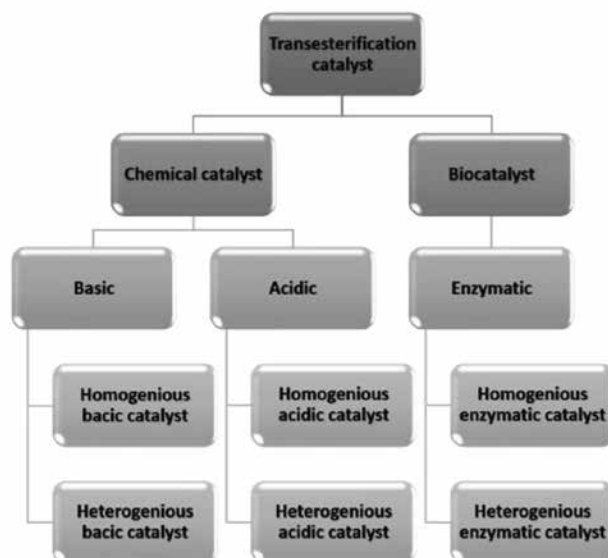


Fig. 2. Types of a transesterification catalyst

initiate hydrolysis of the oil to form FFA and glycerol. The subsequent reaction of the FFA with the base catalyst produces soap. The formation of an emulsifier between FAME and glycerol makes the separation process of the FAME-glycerol mixture more difficult and increases the purification costs. On the other hand, the presence of high FFA content also causes the saponification reaction. Basic catalysts are typically used to produce biodiesel from low-FFA oil. These adverse reactions consume the catalyst and prevent the separation of the biodiesel phase from the glycerol byproduct, which in practice leads to a decrease in yields (Farzaneh, Dashtipour, et al., 2016; Farzaneh, Moghzi, et al., 2016). The basic catalyst has a higher reaction rate than the acidic catalyst, but it can only be used in biodiesel production of lipids with lower free fatty acid content (<0.5%) (Han et al., 2019).

Acid catalysts are used for the conversion of oil with high FFA content like microalgae oil and transesterification of wet microalgal

biomass (Bharathiraja et al., 2015). Sulfuric or hydrochloric acid as a catalyst has been used in acid-catalyzed processes for algae feedstocks (Nautiyal et al., 2014a). In these reactions, a high molar ratio of methanol to oil is required and reaction times are usually longer (Rashtizadeh and Farzaneh, 2013). About algae, oil transesterification has been used as an acidic catalyst for in situ transesterification. But anyway, acidic catalysts are corrosive and non-green, generally (Rashtizadeh & Farzaneh, 2013).

Heterogeneous catalysts

The removal of catalysts in conventional homogeneous acidic or basic catalyzed transesterification reactions is challenging and produces a considerable amount of wastewater, which increases the production cost of biodiesel. Using environmentally friendly solid catalysts in the transesterification reaction can address these issues by eliminating the need for water washing, allowing for easy separation of the catalyst from liquid products, and

enabling catalyst reuse and regeneration in continuous processes. Solid catalysts also offer mild reaction conditions, no toxicity, and no corrosion (Moghzi et al., 2016; Rashtizadeh et al., 2014).

To increase the yield of biodiesel production, raw materials with more than 3% FFA content require a two-step catalytic process, esterification, and transesterification. Since algal oil contains high levels of FFA, the use of a basic catalyst in transesterification can lead to saponification, hydrolysis reaction, increased catalyst consumption, decreased catalyst efficiency, and reduced biodiesel yield. An acid catalyst is commonly used to overcome this problem (Chen et al., 2012). To increase the yield of biodiesel production, raw materials with more than 3% FFA content require a two-step catalytic process, esterification, and transesterification. Since algal oil contains high FFA, if a basic catalyst is used in transesterification, FFA will lead to saponification, hydrolysis reaction, increased catalyst consumption, decreased catalyst efficiency, and biodiesel yield. On the other hand, an acid catalyst is used to overcome this problem (Chen et al., 2012).

Discussion

This study reviews the methods and stages of biodiesel production from the extracted oil of algae through a transesterification reaction. Algae has some advantages including that microalgae have the potential to produce 25-220 times higher triglycerides than terrestrial plants and engine performance and exhaust emission

of microalgae biodiesel investigated. This work studied steps of biodiesel production from microalgae including cultivation of microalgae, harvesting, oil extraction, and especially how to create biodiesel from microalgae biomass by focusing on the kinds of catalyst and solid catalysts that have been used for microalgal biodiesel production studied.

The major cost factor in the production of biodiesel is the cost of the raw material. Conversion costs account for about 10% of large facilities and between 25% and 40% of small plants (Baskar & Aiswarya, 2016). In recent years, the search for a cheaper product has therefore largely been a search for the cheapest raw material, together with a quest for the most economical processing method (Aransiola et al., 2014). Microalgae have many advantages over traditional sources such as soybean, sunflower, and corn oil. This plant grows in open ponds and its demand is zero in agricultural land. It has the potential to produce biodiesel up to 100 times more than soy. Therefore, if the cost of producing algae is favorable, it offers an attractive option as a source of raw materials (Aransiola et al., 2014). However, the production of biodiesel from microalgae has been proposed for a long time and extensive research has been carried out in the last 20 years. But the high cost of producing algae means that, to date, it has only been possible to commercialize relatively high-value microalgae products and not low-value products, such as lipids for biofuels. The many attractive properties

of microalgae have led to significant efforts over the past few years to try and develop cost-effective production processes to make algal oil for biodiesel commercially viable. This task is very challenging and it will still take some time before algal biofuels become a commercial reality (Borowitzka, 2010).

Microalgae have the potential to meet the global demand for transportation fuel and replace fossil fuels entirely, making biodiesel production from microalgae an attractive option (Demirbas, 2008). However, the technology required for generating biodiesel from microalgae is still in its early stages of development, and microalgae production and oil extraction require significant investment and care, making commercialization of biodiesel production from microalgae challenging (Demirbas, 2010; Islam et al., 2017). Nonetheless, according to Briggs (2008), it may be possible to replace all vehicular fuel with biodiesel by utilizing algae with a natural oil content greater than 50% that can be grown in algae ponds at wastewater treatment plants.

In conclusion, the utilization of algae with high oil content and fast growth rates, along with cost-effective and easy cultivation conditions, can make algae a primary source of biodiesel production in the future. However, significant efforts are required to reduce the conversion cost and overcome the challenges associated with commercial-scale production. It may take some time before algal biofuels become a commercial reality in Iran and the rest of the world.

Acknowledgments

The author would like to thank Dr. Somayeh Keypour, assistant professor of Farhangian university, for her help and constructive criticism of the manuscript.

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