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Production of Biodiesel from Algae by Trans-esterification

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ABSTRACT

Energy is a crucial and vital thing needed for every living being everywhere every moment. It can be produced from various sources in different manners. But the necessity of clean, environment friendly, sustainable and renewable energy production is a burning question in recent years as petroleum-based fuels are depleting due to their excessive use. Among all other alternatives, biomass may be one of the primary and better choices as a sustainable renewable energy source. The motive of this research work was to identify a better feedstock for biofuel production. More specifically, the aim was to produce biodiesel from a specific species of algae. The production method involved in this work was trans-esterification which is an efficient method for biodiesel production. The findings of the experiment indicated that a total of 280 gm of dry algae powder chemically extracted 137 ml of algal oil and subsequently that algal oil was trans-esterified to 115 ml of biodiesel and 25 ml of glycerol as by-product. The conversion rate of dry algae to biodiesel was around 42%, while the conversion rate of algal oil to biodiesel was over 84%. Properties such as Cetane number, density, viscosity, boiling point, and calorific value of the derived biodiesel were 61.8, 0.8859 gm/cm^3, 3.83 cSt, 305.5°C and 35.71 MJ/kg respectively which are very similar to the properties of petroleum diesel or other biomass-derived diesel.

Keywords: Biodiesel, algae, algal oil, trans-esterification, chemical extraction.

1. Introduction

Energy is an essential need for life and all living organisms on the earth. For the developing nations, the necessity of reliable and affordable energy is a prime need. Energy consumption is experiencing an exponential growth today as a result of industrialization and urbanization along with the changes in life styles of people. Conventional fuels, the most vital sources of energy are depleting constantly and thus scarcity of these hydrocarbon deposits is rising [1]. Pressures on the global climate have prompted demands for the increased use of renewable resources in place of petro-chemical fuels in recent years. Among various renewable energy sources, biomass is one of the potential sources that can be converted to appropriate forms of energy, in general as liquid fuels for IC engines or electricity can be produced by employing various ways [2]. Biomass energy, also recognized as bioenergy, is the energy derived or produced from living or extinct biological organisms. Biomass is made up of energy obtained from the sun that is absorbed by plants through photosynthesis and converted into nutrients (carbohydrates). Direct and indirect methods may be used to convert the energy in biomass into useful energy. Biomass can be burned directly to generate heat, which can then be used to generate steam, which can further be transformed into electricity (direct). But heat is not the only way to use energy. In the transportation sector, we mostly need liquid fuel or gaseous fuel. So, it could be processed into biofuel (indirect) [3]. Thus, conversion of biomass is needed for achieving all forms of energy uses. There are mainly two key technologies for biomass conversions: thermochemical and biochemical. Mechanical extraction (with esterification) is considered another technology for biomass-based biofuel [2]. Biodiesel is made by trans-esterifying fats or oils and is chemically defined as simple mono-alkyl esters of long-chain fatty acids. Biodiesel is often made from animal fats, waste cooking oils, and algae which might help to reduce reliance on petroleum fuels. Algae are one of the greatest biomass sources for biodiesel production. Particularly, it is the most productive biodiesel feedstock [4]. Trans-esterification is amongst the most efficient methods of disseminating biodiesel from algal oil. Methanol is the most popular alcohol used in the trans-esterification of triacylglycerol (TAG), which produces fatty acid methyl esters (FAME). The molar ratio of oil to alcohol, catalyst concentration, reaction temperature, and duration all have a major impact on biodiesel yield and FAME composition. An additional influential factor that affects the fuel characteristics is the complete mixing of the reactants [5].

2. Biomass Conversion Technologies

Biomass to energy conversion (also known as bioenergy) covers a broad variety of biomass forms and raw materials, converting choices, final disposition, and framework necessities [2]. As mentioned before, there are a variety of methods for converting biomass into a usable source of energy such as thermochemical conversion and biochemical conversion technology.

As part of many ways to generate intermediate energy carriers or heat, regulated heating and/or oxidation of biomass are known as thermochemical conversion. Thermochemical conversion technologies,

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ranging from heating biomass in an oxygen-free environment (endothermic) to complete biomass exothermic oxidation, are classified according to their related oxidation status, particle size, and heating intensity (full exothermic oxidation) [6]. These procedures do not generate useful energy directly, but they do transform the original feed into more viable energy carrier types [7]. For thermochemical conversion of biomass, three main processes are used: combustion, gasification, and pyrolysis, as well as two less common choices such as liquefaction or hydro-thermal upgrading (HTU), carbonization, or torrefaction [2].

Biochemical conversion is a significant and cost-effective method for producing biomass-derived fuels, chemicals, and materials. The term "biochemical biomass conversion technology" refers to the process of converting biomass using biological pre-treatments. These pre-treatments aim to convert biomass into a variety of products and intermediates using a variety of microorganisms and enzymes. Biochemical conversion is the process of breaking down biomass liquids and gaseous feed stocks using bacteria, microorganisms, or their enzymes. For biomass with high water content, biochemical conversion is normally favored. Fuel, transportation fuels, and renewable chemicals can all be made from these feed stocks. Microorganisms are used to conduct the conversion process in the majority of cases: anaerobic digestion, and fermentation. The last method is chemical conversion, which involves a series of chemical reactions that extract energy from biomass. Mechanical extraction processes are another technology that can generate energy in the form of bio-diesel.

3. Trans-esterification Process

The process of trans-esterification, also known as alcoholysis, is characterized as allowing fat or oil to chemically react with alcohol. Trans-esterification refers to the method of substituting alcohol from one ester with another, analogous to hydrolysis but using alcohol rather than water. This method is commonly utilized for minimizing triglycerides' high viscosity. Fig. 1(a) represents the complete reaction of the trans-esterification process. Trans-esterification is a reversible reaction that is carried out by combining the reactants. The glycerol layer settles in the reaction vessel's rim. The intermediates in this phase are di-glycerides and mono-glycerides. Fig. 1(b) depicts the phases of the reaction. In order, three trans-esterification reactions occur during the trans-esterification of triglyceride by methanol. The triglyceride reacts with the alcohol first, forming a diglyceride and fatty acid ester. The diglyceride produced in the first reaction then reacts with the alcohol to form another fatty acid ester and a mono-glyceride. As this reacts with the alcohol, fatty acid ester and glycerol are formed.

Acid trans-esterification is usually catalyzed by sulfuric acid (H_2SO_4), while alkaline trans-esterification is catalyzed by sodium hydroxide (NaOH) and potassium hydroxide (KOH) [8].

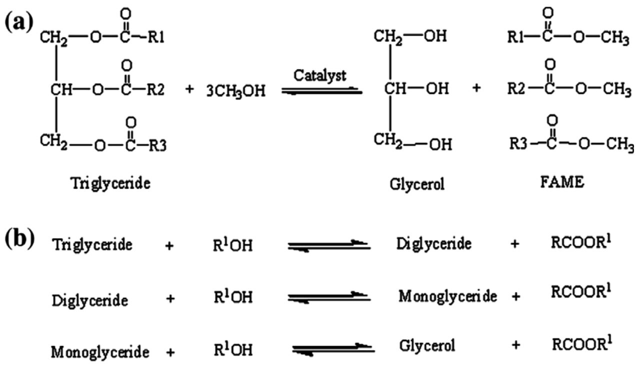

Fig. 1 FAME Production Equations (a) Complete Reaction for Trans-esterification of Triglycerides, (b) Phases Involved in the Whole Reaction [8].

4. Methodology

At first, fresh algae was collected from different sources which contains lots of water. So, for the purpose of drying these were spread on the roof under the open sky. These dried algae were then ground with a grinder as much as possible and evaporate in an incubator to release leftover water. After that, solvent n-hexane and methanol were mixed with the dry algae powder. Hereafter, the mixture was shaken by hands and mixed with NaCl solution. This mixture was further shaken by hands and heated. The solid biomass and algal oil were separated by filtration after hexane evaporation in a water bath. Henceforth, mixing of KOH catalyst with methanol is carried out and this mixture is poured into the algal oil. Finally, the trans-esterification process occurs due to this, and the products it leads to are Methyl Esters which are commercially known as biodiesel, and a little amount of glycerol as a byproduct. Afterward, biodiesel separation from the sedimentation was conducted.

The methodology of biodiesel derivation from algae by the trans-esterification process is shown in Fig. 2 with the help of a flow diagram.

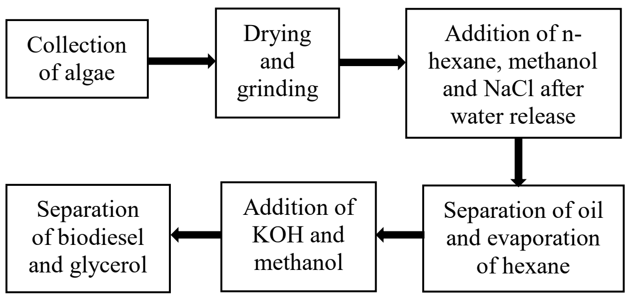

Fig. 2 Flow Diagram of Biodiesel Production.

5. Experimental Procedure

The entire procedure can be sub-divided into some steps which are briefly described below:

Sample Collection:

Microalgae species (*Chara vulgaris*) were collected from a local pond. To achieve better quality biodiesel, it is a prerequisite to remove any kind of unwanted aquatic organisms or human-made wastes. So, the samples were cleaned from any kind of foreign particles. Fig. 3 shows the collected wet algae sample.

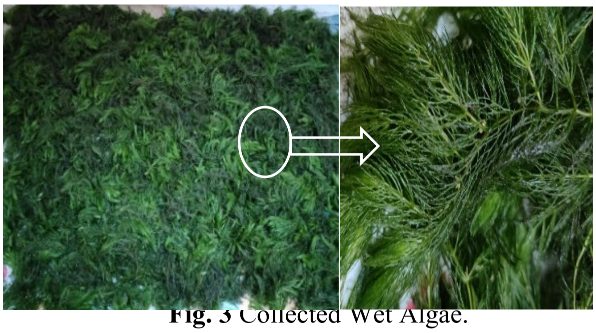

Fig. 3 Collected Wet Algae.

Drying:

Collected wet algae were placed on the roof under the sunlight for 48-72 hours to remove the loose moisture present in the sample. Fig 4 shows the sundried algae.

Fig. 4 Sundried Algae.

Size Reduction:

As smaller biomass size helps extracting the maximum amount of oil as well as increasing biodiesel yield, the dried algae sample was ground using a domestic grinder. The finest the powder is, the better the quality of biodiesel produced. Hereafter it was inserted in an incubator at 80°C for approximately 20-30 minutes to release leftover water. Fig. 5 shows the process of grinding the algae and the powders obtained.

Fig. 5 Grinding of Died algae and algae powder.

Oil Separation and Hexane Evaporation:

A total of 14 samples were investigated where each sample was prepared using 80 ml n-Hexane mixed with 5 ml methanol and poured into a sealed conical flask with 20 gm dry algae powder which was shaken by hands for about 10 minutes and heated in an incubator at around 60°C. After that, 70% NaCl solution was added to the mixture and again shaken by hands for another 10 minutes. The resulted mixture was filtered to remove solid algae. Then the liquid sample was kept for settling which led to two different layers of water-methanol (upper layer) and oil-hexane (lower layer). The upper layer was separated from the lower one and discarded. Then the oil-hexane mixture was evaporated in a water bath for about one hour to release hexane, at a temperature of around 58°C which is below its boiling point (~68.5°C). After evaporation, the smell of hexane disappeared and algal oil was found to be 10 ml on average in various samples investigated. Fig. 6(a) and 6(b) show filtration of solid algae and hexane evaporation respectively.

(a) (b)

Fig. 6(a) Filtration of Solid Algae and **6(b)** Evaporation of n-Hexane in a Water Bath.

Mixing of Alcohol and Catalyst:

The alcohol and the catalyst used in this work were: Methanol (CH_3OH) and Potassium Hydroxide (KOH) respectively. Methanol was used in a ratio of 6:1 to oil and KOH was used in an amount of 2% of oil. These two chemicals were mixed together properly which forms Potassium methoxide (CH_3KO). For 50 ml algal oil the mixture containing 10 ml methanol and 1 gm KOH was added.

<u>Biodiesel Production:</u>

The alcohol and catalyst mixture was poured into the preheated algal oil (at 50°C) and mixed thoroughly by shaking with hands. Then the mixture was kept at 60°C in an incubator for about 1.5 hours, while it was shaken by hands at intervals for the reaction to take place efficiently, as preheating was done near the boiling point temperature of alcohol (~64.7 for methanol) and moderate agitation increases the reaction rate and reduces the duration of reaction as minimum as 1.5 hours instead of 3 hours. Then the mixture was kept for about 1 hour for settling to ensure that the biodiesel and glycerol layers clearly appear.

<u>Separation of Biodiesel:</u>

The biodiesel was carefully isolated from the sedimentation using a separator which works due to density difference. Fig. 7 shows the separator containing clearly visible layers of biodiesel and glycerol. The upper layer is biodiesel and the lower one, relatively denser, is glycerol.

Fig. 7 Separator Containing Biodiesel and Glycerol.

6. Results and Property Analysis of Product

In this project, a total of 14 samples were prepared according to the process described in Section 5, more specifically under the title 'Oil Separation and Hexane Evaporation'. Each sample provided almost 10 ml of algal oil, thus the total amount of oil obtained was approximately 137 ml. Using this oil, 3 trans-esterification reactions were carried out and the results are presented in Table 1.

Table 1 Amount and Percentage of Biodiesel Production from Algal Oil

Algal oil (ml)	Methanol (ml)	KOH (gm)	Biodiesel (ml)	% of biodiesel production
50	10	1	43	86
50	10	1	44	88
37	7	0.5	28	76

The overall production was 115 ml biodiesel and 25 ml glycerol. Hence, the production rate of algal oil into biodiesel is about 84%. The products obtained are shown in Fig. 8.

Fig. 8 Biodiesel and Glycerol.

To ensure that the trans-esterified product is methyl ester or biodiesel, different properties such as cetane number, density, viscosity and the boiling point were analyzed by using a Fuel Analyzer apparatus in the Fuel Testing Laboratory of the Department of Energy Science and Engineering, KUET. The calorific value was determined by using a Bomb Calorimeter in the Heat Engine Laboratory of the Department of Mechanical Engineering, KUET. Table 2 shows the various properties analyzed and are presented in comparison with the standard values of those of conventional diesel and biodiesel [9].

Table 2 Data for Different Properties of Derived Biodiesel, Conventional Diesel and Biodiesel.

Properties	Derived Biodiesel	Diesel	Biodiesel [6]
Cetane Number	61.8	45 - 55	47 - 65
Density (gm/cm^3 at 15°C)	0.8859	0.820-0.845	0.88
Viscosity (cSt at 40°C)	3.83	2 - 4.5	4 - 6
Boiling point (°C)	305.5	180 - 360	315 - 350
Calorific Value (MJ/kg)	35.71	44 - 46	39 - 41

7. Cost Analysis

Approximate expenses of biodiesel production are briefly described below:

Cost of n-hexane (1120 ml) is Tk. 800/-
Cost of Methanol (97 ml) is Tk. 80/-
Cost of KOH (2.5 gm) is Tk. 5/-

Total cost of biodiesel is Tk. 885/-.

Approximate selling price of Biodiesel (115 ml) is Tk. 15/- [Assuming 1L diesel costing Tk. 109/-] Selling price of Glycerol (25 ml) is Tk. 40/-. So, total selling price is Tk. 55/-.

8. Discussion

In this study, n-hexane was mixed with methanol in a ratio of 16:1, in addition to 70% NaCl solution these were poured into dry algae powder which led to algal oil production. Subsequently, algal oil was transformed into biodiesel and glycerol by trans-esterification reaction. After separating these two substances, biodiesel was analyzed for various properties. On the other hand, the by-product glycerol was discarded as the crude glycerol contains methanol and fatty acids which has a high pH value of about 11-12. Hence, further processing, like complicated vacuum distillation process, of glycerol is needed for becoming usable glycerin. As the purification of glycerol on small scale is too expensive, it is not feasible [10].

According to the cost analysis, discarding some minor expenses the figure for approximate expense in this study was Tk. 885, whereas the approximate potential revenue is only Tk. 55 which is very negligible in comparison to the expense. The major cost is due to the high price of n-hexane. If a suitable substitute could be used instead of n-hexane, the overall cost of the whole production process could be reduced.

On the other hand, by observing the values of the properties shown in Table 2, it can be envisioned that the various fuel properties of the biodiesel produced are very similar to those of conventional diesel fuels. The cetane number of biodiesel is found to be 61.8 which is slightly higher than the conventional diesel. This also indicates that it is a better alternative fuel for compression ignition (CI) engines. The higher the cetane number, the lesser the ignition delays in CI engines [9]. Thus, the chance of knocking reduces in the engine. The density of biodiesel is higher so energy per unit volume may increase. As biodiesel has a higher viscosity than petroleum diesel, it may lead to improper atomization which in turn may cause incomplete combustion [11]. But it is lower than other biomass-derived diesel. On the other hand, having a higher boiling point, biodiesel evaporates much more slowly. The calorific value of the derived biodiesel is slightly lower than conventional diesel and other biodiesels, but it is high enough to be used as a fuel. It is better to blend biodiesel with petroleum diesel before using as B20 (20% biodiesel blended with 80% petroleum diesel) or B5 (5% biodiesel blended with 95% petroleum diesel). B20 is a better blend because it represents a good balance of cost, emissions, cold-weather performance, materials compatibility and ability to act as a solvent. Generally, B20 and lower-level blends can be used in current engines without modifications. In fact, many diesel engine original equipment manufacturers (OEMs) approve the use of B20. Engines operating on B20 have similar fuel consumption, horsepower, and torque to engines running on petroleum diesel. B20 with 20% biodiesel content will have 1% to 2% less energy per gallon than petroleum diesel [9].

Chemical extraction of algal oil and hence biodiesel from algae is an environment friendly process as there is no harmful emission like CO, CO_2, etc. But the handling of chemicals used in this process should be done carefully as n-hexane is a highly flammable chemical, KOH is irritating for skin when comes directly in contact.

9. Conclusion

The overall work could be concluded as follows:

1) Algal oil could be derived from green algae after drying and some processing and that could be used as a feedstock for trans-esterification reaction.
2) Chemical extraction of algal oil is better than mechanical extraction as the latter one has high power requirements and wear and tear on the equipment [10].
3) Algae-derived biodiesel has quite similar properties to petroleum diesel which also satisfies ASTM standards [5]. So, it could be used in similar applications [9] and thus reduce the dependency on fossil fuels and crude oil import.

10. References

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