Biodiesel production from spirulina microalgae oil

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Abstract. The present study, experimentally aimed to extract oil form spirulina microalgae then convert it to biodiesel via transesterification process. Different samples are collected from various locations. The samples are cleaned, dried and prepared for the process of oil extraction by soxhlet apparatus. The transesterification process is used to produce biodiesel fuel derived from spirulina microalgae oil, which is then used as an alternative fuel in diesel engine. The methanol along with sodium hydroxide as base catalyst used to minimize the raw oil's FFA content. The transesterification reaction is carried out at (1:6) oil to methanol molar ratio. Then the mixture is kept inside the separating funnel for 12 hours to separate the glycerine from mixture. The produced biodiesel algae methyl ester (AME) is subjected to gas chromatograph analysis as well as FTIR analysis. All the physical properties are measured and compared with ASTM standard.

Keywords: Spirulina microalgae, oil extraction, transesterification process, AME

1. Introduction
Due to the rapid increase in depletion of fossil fuels, environmental concerns and transportation fuel demand, scientists have to present vegetable oil-based derivatives having almost the same performance and properties of that of diesel fuel. Diesel engines cannot work on pure vegetable oils because of their high viscosity and density levels as compared to those of diesel (1, 2). Hence, transferring the vegetables oils into biofuels via transesterification process is strongly recommended. Biodiesel is a similar fuel to that of diesel and it has many positive features such as availability, renewable, low exhaust emissions and higher lubricity. However, by comparing with diesel, it has some drawbacks like lower heat content, higher density and viscosity, and higher NOx emission (3). Many various feedstocks are used to produce biodiesel. The production of biodiesel relies on both the quality and location of the feedstock (4). Replacing petro-diesel fuel with biodiesel results in many environmental advantages and some challenges such as the lower energy output which in turn increases the consumption of fuel to produce the same power as well as the increase in the NOx emissions(5). In recent years biodiesel derived from microalgae has gained a lot of attention. Because of its advantages, such as higher production of biomass, higher photosynthetic efficiency and faster growth compared to other energy crops, it can be considered best candidate for fuel production(6). The goal of this incoming review is to research biodiesel algae preparation methods, their effects on diesel engine performance, combustion and emissions.

2. Methodology:
Algae oil extraction: The oil extraction refers to an operation that transfers one or more components of a solid or liquid phase to another liquid phase. Several methods are used to extract the oil from microalgae, such as mechanical extraction and chemical extraction. Solvent extraction process is more common than mechanical as it extracts almost all the oil and leaves in the raw material just (0.5-0.7) percent of residual oil. The solvent extraction process which used in this study can be applicable to any raw oil content materials(7).

Collection of spirulina microalgae samples
The microalgae samples are collected from water treatment plant in Diwaniyah city (Diwaniyah large project, "Project No. 7") illustrating in Figure (1). The type of algae used in this research is spirulina.

Cleaning & Drying processes
The collected algae samples are washed to remove the remaining particle and insects as shown in Figure (2). Samples are subjected to sun light for 3 days to evaporate the amount of water, as shown in Figure (3).

Grinding process
The dried samples are pounded to fine powder with the helping of grinder and pestle grinder, as indicated in Figure (4). The algae powder is then placed in a sealed container in various jars for extraction purposes.
Oil extraction by Soxhlet apparatus
The Soxhlet device, as seen in Figure (5) is basically consists of a circular flask, with a capacity of 0.25 L, installed with a special tube by which the dry biomass (microalgae) are put with a capillary side tube which enables solvent circulation from the circular flask to the microalgae in a closed loop. A condenser is easily placed over this tube to avoid the leakage of solvent which helps it to condense which disperse by biomass.

Samples of 40 grams dried spirulina microalgae is placed in the filter paper of the Soxhlet extractor main chamber. In the circular flask, 200 ml of methanol is placed, and heated for 12 hours by using water bath supplied with a temperature control unit. The oil is separated from the solvent methanol by evaporation in the rotary evaporator to release methanol and obtained the microalgae oil, as seen in Figure (6). The removed solvent can be recycled for the next extraction. This process is repeated for several times. The amount of oil obtained is 5 grams in each process as shown in Figure (7). The percentage of oil extracted is calculated by using the equation (1).

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\text{Efficiency of oil extracted} = \frac{\text{Mass of oil extracted (grams)}}{\text{The total mass of dried algae}} \times 100
\]  

Biodiesel production and specifications
Transesterification process is used in the current research to produce biodiesel fuel that is derived from spirulina microalgae oil. The methanol used as a base catalyst along with sodium hydroxide to reduce the FFA content of the raw material. Figure (8) describes the base material used in the production of biodiesel. The experiment was performed in device of laboratory scale. The specific parameters influencing the transesterification reaction are: oil-to-methanol molar ratio, catalyst concentration, temperature of reaction and time.

The transesterification reactions are performed in "three neck round-bottomed flask" with a capacity of 1000 ml as a reliable laboratory reactor, provided with a reaction condenser, a hot palter stirrer, a thermometer and an oil bath to maintain a fixed temperature as seen in Figure (9).
The fatty acid methyl esters (FAME) are formed by the reaction mechanism which is described in equation (2) [Nakarmi, 2014 #171](6):

\[\text{(2)} \]
Firstly, 100 ml volume microalgae oil is selected for use in the conical round flask equipped with heater and magnetic stirrer elevated to 65 °C. A 25 ml of methanol with a 2 gram catalyst (NAOH) is mixed individually and heated for 15 minutes at a temperature of 60 °C. This mixture is then slowly added in the round flask to the 100 ml warmed spirulina microalgae oil. The transesterification reaction is performed at a ratio of (1:6) oil to methanol molar. The mixture is then put within the separating funnel as shown in Figure (10), and keep it for 12 hours to separate the glycerin from mixture. Glycerin should be removed from the biodiesel preparation unit by opening the tap provided on the bottom. After the stage of separation, the remaining mixture of the ester blend is washed more than 4 times with the distilled hot water till the water layer stays totally transparent as shown in Figure (11a). Since the purity level has strong effects on fuel properties, drying process is conducted by heating the biodiesel to 100 °C for 3 hours till bright color occurred, as shown in Figure (11b). Finally, filtering process is done to ensure that the end product is of excellent quality, as seen in Figure (11c).
Chemical properties

Gas Chromatograph Analysis.

The composition of fatty acid methyl ester (FAME) obtained from spirulina microalgae oil after transesterification process was analyzed by Gas Chromatograph- Mass Spectrometer (GC-MS) as shown in Figure(12). The analysis is done using a Porapak-Q column (2 x 2.5 m). The GC conditions are: temperature of the injector: 240 °C; column: 120 °C and temperature of the detector: 270 °C; Helium is used as the carrier gas with a 20 (ml / min) flow rate. The GC is focused on a specimen to detect the amount of biodiesel collected after transesterification process. Linoleic acid methyl ester, Oleic acid methyl ester and Stearic acid methyl ester are the major components of (FAME) at 39.92%, 28.89% and 9.50% respectively. As seen in Table (3.2), the mentioned components constitute 78.39% of the total fatty acid methyl ester. The approximated chemical formula for the algae methyl ester is C_{16}H_{29}O_{2}.

Table (1) The chemical composition of spirulina microalgae biodiesel.

| Chemical compound                  | Peak | Detention time Rs | Relative space Area % |
|------------------------------------|------|------------------|-----------------------|
| Palmitic acid ,methyl ester       | 1    | 13.735           | 7.70                  |
| n-Hexadecanoic acid               | 2    | 14.024           | 3.35                  |
| Linoleic acid ,methyl ester       | 3    | 15.123           | 39.92                 |
| Oleic acid , methyl ester         | 4    | 15.225           | 28.89                 |
| Stearic acid ,methyl ester        | 5    | 15.427           | 9.30                  |
| Oleic acid                        | 6    | 15.685           | 1.61                  |
| Eicosanoic acid ,methyl ester     | 7    | 16.956           | 0.43                  |
| Docosanoic acid methyl ester      | 8    | 18.372           | 0.27                  |
FITR analysis

The second inspection is the FITR test. The FTIR spectrum peaks or bands are due to the specific groups present in a given sample. It aimed to classify the functional groups in sample of biodiesel under test. Figure (13) reveals the FTIR spectra of microalgae methyl ester. The area in the spectra is between 3200 and 3400 cm$^{-1}$, that indicate overlaps the current absorption (OH). Appearance of the beams in the range of (2890 - 2980 cm$^{-1}$) is related to aliphatic bonds of CH in biodiesel structure. Characteristic beams at 1725 cm$^{-1}$, indicate (C=O) vibrations regarding ester group, moreover, aromatic (C=C) vibrations are indicated at 1548 cm$^{-1}$. Characteristic bonds in the range of (1375 - 1450 cm$^{-1}$) are result of (C-H) bonds for the (CH3)groups of biodiesel structure. Appearance of the beams in range of (1000 - 1100 cm$^{-1}$) indicated (C – O)vibrations.
The physical properties of the prepared algae biodiesel and ordinary diesel fuel are measured accurately at Al-Diwaniyah lab according to Table (2) reported below and detailed in Appendix B. The physical properties of diesel fuel, and biodiesel standards from American Society for Testing of Materials (ASTM). It can be seen that AME biodiesel meet the ASTM standards for biodiesel.

Table (2) The properties of diesel and microalgae methyl ester blends

| Property                | Diesel | 20% AME | 30% AME | 50% AME | 70% AME | 100% AME | ASTM D6751 standard |
|-------------------------|--------|---------|---------|---------|---------|----------|--------------------|
| Chemical formula        | $C_{13.77}H_{23.4}$ | $C_{14.22}H_{24.55}O_{0.6}$ | $C_{14.44}H_{25.11}O_{0.6}$ | $C_{14.88}H_{26.22}O_{1}$ | $C_{15.33}H_{25.11}O_{1.4}$ | $C_{16}H_{29}O_{2}$ | $C_{12}-C_{22}$ |
| Density at 15 °C (kg/m$^3$) | 830    | 837.8   | 842.7   | 849.5   | 857.3   | 869      | 880               |
| Viscosity at 40 °C (Pa.s) | 0.002241 | 0.002658 | 0.002867 | 0.003284 | 0.003702 | 0.004327 | 0.0019-0.006      |
| Calorific value (MJ/kg)  | 45.836 | 44.4528 | 43.7612 | 42.3785 | 40.9948 | 38.9200  | 36-39             |
| Surface tension (N/m)   | 0.028  | 0.028248 | 0.02837 | 0.02862 | 0.028868 | 0.02924  | -                 |
| Cetane number            | 53.4   | 52.69   | 52.335  | 51.625  | 50.915  | 49.85    | >47               |
| Molecular weight (g/mol) | 190    | 201.9688 | 207.9532 | 219.9219 | 231.8907 | 249.8439 | -                 |

Conclusions

1- Spirulina microalgae oil proved a bright alternative source of energy which can substitute diesel fuel after transesterification process.
2- Solvent extraction oil method is found to be successful with less amount of residual oil.
3- The properties of the produced biodiesel are found closer to original diesel than other biofuels derived from different sources.

References

1. Tüccar G, Aydn K. Evaluation of methyl ester of microalgae oil as fuel in a diesel engine. Fuel, 2013;112:203-7.
2. Edam MS, Al-Dawody M. Numerical Simulation for the Effect of Biodiesel Addition on the Combustion, Performance and Emissions Parameters of Single Cylinder Diesel Engine. Al-Qadisiyah Journal for Engineering Sciences. 2019;12(2):72-8.
3. Rashedul H, Masjuki H, Kalam M, Ashraful A, Rahman SA, Shahir S. The effect of additives on properties, performance and emission of biodiesel fuelled compression ignition engine. Energy Conversion and Management. 2014;88:348-64.
4. Appavu P, Madhavan VR, Venu H, Mariadoss A. Effect of fuel additives and exhaust gas recirculation in biodiesel fuelled CI engine: A review. International Journal of Ambient Energy. 2019:1-7.
5. Aregbe O. Biodiesel an Alternative fuel for a Cleaner Environment as Compared to Petroleum Diesel. American University of Nigeria Library.
6. Wu X, Ruan R, Du Z, Liu Y. Current status and prospects of biodiesel production from microalgae. Energies. 2012;5(8):2667-82.
7. Topare NS, Raut SJ, Renge V, Khedkar SV, Chavanand Y, Bhagat S. Extraction of oil from algae by solvent extraction and oil expeller method. International Journal of Chemical Sciences. 2011;9(4):1746-50.
8. Gutiérrez L-F, Ratti C, Belkacemi K. Effects of drying method on the extraction yields and quality of oils from quebec sea buckthorn (Hippophae rhamnoides L.) seeds and pulp. Food Chemistry. 2008;106(3):896-904.