Production and Fuel Quality Testing of Biodiesel from Algae and its Comparison with Conventional Fuel

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Abstract:

Due to fossil fuels source declination, atmospheric pollution increasing and climate changing attention to alternative fuels with lower polluted emissions is increased. One of The best alternatives is biodiesel which can be obtained from vegetable or animal oils. Biofuels production from edible oil seeds is complicated, so a new source as third generation is "Microalgae". In this case" Chlorella Vulgaris" as sources of biodiesel production was studied.

Beat beating method for Oil extraction, GC apparatus for extracted oil analyzing and transesterification method for biodiesel producing were applied.

Based on oil analysis 83% of fatty acids is 18-carbon while 60% of them are Oleic acid. Cloud Point, Cold filter plugging point and heating value calculated respectively: 0.33 (0C), -9.35 (0C) and 23.77(MJ/kg).

Microalgae proper characteristic such as mass rapid growth in short terms without spending arable land and fresh water and also producing more appropriate biodiesel make it one of the main choices for biodiesel producing in the world.

Keywords: Microalgae, Oil extraction, Biodiesel.

1. Preface

After internal combustion engines invention, fossil fuels like oil have become the most important sources of their energy.

Further technology development resulted to mass production and, of course more oil consumption. Disaster reduction or even check out fossil fuels resources threatening the whole world in near future. In other side oil combustion increases greenhouse gases, Ozone layer destruction and environmental pollutants such as unburned hydrocarbons(UHC), Nitrogen compounds(NOx), Carbon monoxide(CO) , Carbon dioxide (CO2) and of course respiratory disorders in large cities. In addition, dependency of consuming countries to oil exporting countries greatly increased and caused oil price boosting.

Since mentioned problems emergence extensive research has been done to find suitable alternative fuels in the world.

In the meantime, clean and renewable Biofuels allocated a special place in countries fuel-basket.

The most important Biofuels features are renewable and environment friendly without being worry about their termination.

Since biodiesel producing from edible oils conflicts with food security and environmental challenges and considering fossil fuels termination and their increasing pollution finding other raw materials such as Microalgae is essential[11].

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Biodiesel and bioethanol made great progress among the plant biomass Bioethanol is produced from sugar plants [1,2,7,10]. Biodiesel is Methyl or ethyl ester of animal or plants oil that extracted from biological materials such as vegetable oils, waste oils from restaurants and bars, animal fats and waste products collected from the plants and forests. Chemically, biodiesel is mono alkyl esters of long-chain fatty acid created by lipid renewable resources, which can be used in combustion engines and thermal machines as a fuel. For biodiesel production is necessary to break the triglycerides of natural oils structure which could be done by methods, such as Transesterifikasi, Pyrolysis and Microemulsions. Transesterification among mentioned methods is simply more practical. This process is similar to hydrolysis except, water is replaced by alcohol. For this purpose, oil or fat compounds molecules with an alcohol such as methanol or ethanol in the presence of an acidic or alkaline catalyst companied and alcohol OH substituted hydrocarbon chain in the oil. As a result new molecular structure ester with the name of fatty acid alkyl esters occurs [8].

As algae contain high oil, growth quickly and easily, do not need to farm land and fresh water, they could be a potential and economical source for biodiesel production [9].

Microalgae are the best algae type for producing biodiesel. They can produce oil 250 times more than soybeans per acre [4].

2. Materials and Methods

To produce biodiesel, provided Chlorella microalgae powder (Chlorella Vulgaris) dehumidified and dried with hot air and spray dryer. Microalgae cell wall was broken for oil extraction by Beat beating method.

- **Beat beating method**

First, microalgae mixed with distilled water and its cell wall was broken by this method. Then alcohol and solvent added to the reaction for oil extraction. For extracting oil and separating water, microalgae biomass and solvent the mixture placed into a centrifuge. After separating solvent from microalgae biomass and water phases, to remove the solvent and extracting oil the rotary machine used. Since the amount of oil in Microalgae is low, for complete extraction, it must be washed several times by solvent associated with centrifuge and rotary machine steps. In this case, to reduce the centrifuge, rotary operations and getting more complete extracted oil, microalgae biomass stored in solvent respectively 24, 48, 72 hours and necessary tests implemented. To ensure there is no more water in extracted oil, it was placed in an oven at a temperature above water boiling point. After finishing heat treatment oil properties identified by GC apparatus.

3. Fuel preparation

3-1. Mixing alcohol and catalyst

To prepare the fuel, alcohol and catalyst must be mixed. The mixture contains solid potassium/sodium hydroxide solved in methanol. High purity alcohol and catalyst with least possible percentage of water must be used, because the presence of water in the reaction will fail the production process that is why200 proof alcohol was used.

3-2. Transesterification reaction

This is the phase the main reaction to produce biodiesel takes place.Oil along with prepared alcohol and catalyst solvent mix and stir up together at temperature below methanol boiling point with atmospheric pressure. During Catalyst reaction fatty acids attached to glycerol structure converted to methyl ester by methanol in the presence of potassium monoxide. In this reaction glycerol, such a valuable material apart from fatty acids methyl ester is also

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produced. Difference density make two-phase mode in a way that methyl ester is above glycerol in separating funnel.Refining produced glycerin make it a commercial commodity as a byproduct which reduces general production expenses.

3-3. Catalyst Deactivation

To terminate reaction, facilitate separation and prevent any secondary reaction remaining catalyst should be neutralized. Du to environment PH is alkaline, acetic acid added as neutralizer.

3-4. Methanol recovery

As always extra methanol is added to the reaction mixture for exceeding production and it remains in both biodiesel and glycerin phases at the end of the reaction, the mixture heated to boiling alcohol in order to removed it from the environment.

3-5. Isolation

After the reaction, the glycerin (Saponification) and biodiesel phases were formed. Isolation required time depends on the quality of reaction. The greater Saponification the more isolation time required. After glycerin and derived fuel separation obtained biodiesel properties were tested.

The conducted experiments on the fuel consist of: calculating the density, kinematic viscosity, cloud point, cold filter plugging point, cetane index and heating value. The output results compared with conventional diesel and Salicornia biodiesel.

4. Discussion and Conclusions

Based on conducted experiments the best time for complete oil extraction is 48 hours.

4-1. Chromatographic test results

Chromatography results obtained from average of 5 times replication tests which shown in Table 1.

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Table 1: Various identified compounds specifications in Chlorella algae oil methyl ester

Detected article	Based acid name	Acid formula	Percentage
Hexadecenoic acid, Methyl ester	Palmitic acid methyl ester	$C_{16}H_{32}O_2$	10.11 ± 2.9
(Z)-9-hexadecenoic acid, Methyl ester	Palmitoleic acid methyl ester	$C_{16}H_{30}O_2$	1.068 ± 1.7
Octadecanoic acid, Methyl ester	Stearic acid methyl ester	$C_{18}H_{36}O_2$	2.524 ± 0.55
(9Z)-Octadec-9-enoic acid, Methyl ester	Oleic acid methyl ester	$C_{18}H_{34}O_2$	28.16 ± 16.8
(9Z,12Z)-9,12-Octadecadienoic acid	Linoleic acid methyl ester	$C_{18}H_{32}O_2$	7.702 ± 4.2
(9E,12E)-octadeca-9,12-dienoic acid, Methyl ester	Linolelaidic acid methyl ester	$C_{19}H_{34}O_2$	16.676 ± 20.9
(9Z,12Z,15Z)-9,12,15-Octadecatrienoic acid, Methyl ester	Linolenic acid methyl ester	$C_{18}H_{30}O_2$	10.546 ± 14.0
(5Z,8Z,11Z,14Z)-5,8,11,14-Eicosatetraenoic acid	Arachidonic acid methyl ester	$C_{20}H_{32}O_2$	0.18 ± 0
Saturated Fatty Acids	-	-	12.63
Monounsaturated Fatty Acids	-	-	29.23
Polyunsaturated Fatty Acids	-	-	18.43

According to detected compounds by GC the highest amount of fatty acid belongs to oleic acid, with 28.16% and the lowest one belongs to arachidonic, with 0.18%.

4-2. Fuel test results

Microalgae and Salicornia methyl esters and diesel characteristic measurement results are shown in the following table.

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Table 2: Microalgae methyl ester, Salicornia Methyl ester and diesel characteristic comparison chart

Characteristic	Unit	Microalgae methyl esters	Salicornia methyl esters	Diesel
Density	(g/cm^3)	0.52[(a)]	0.77[(b)]	0.8393[(c)]
Kinematic viscosity(40^0C)	Cst	0.79[(a)]	1.22[(b)]	3.09[(c)]
Cloud point	(^0C)	0.33[(b)]	- 0.41[(a)]	-2[(c)]
Heating value	(MJ/Kg)	23.77	35.11	45.938
Cetane Number	-	75.28[(a)]	58.43[(b)]	50[(c)]
Saponification Value	-	122.13[(a)]	177.33[(b)]	-
Iodine Value	g idone 100g	69.78[(a)]	82.88[(b)]	-
Degree of unsaturation	-	66.09[(a)]	89.28[(b)]	-
Long-Chain Saturated Factor		2.21[(a)]	12.79[(b)]	-
Cold Filter Plugging Point	(^0C)	- 9.35[(a)]	23.71[(b)]	-
Allyic Position Equivalents	-	65.18[(a)]	90.55[(b)]	-
Bis-Allyic Position Equivalents	-	29.14[(a)]	36.65[(b)]	-
Oxidation Stability	(hours)	9.06[(a)]	6.54[(b)]	-

As various repetitions showed the same results, so the error variance in the design statistic equaled to zero. The letters in each row is valid and different letters mean significant difference in meaning between them.

4-3. Cetane index test results

As Figure 1 suggests, net Algae Methyl Ester Cetane index is 75.28 which is relatively 29% and 50% higher than Salicornia methyl ester and diesel fuel. So Algae Methyl Ester Combustion quality is better than those two. Based on research done by “Harrington,1986”this high index can be related to the short length of carbon chain fatty acids[3].

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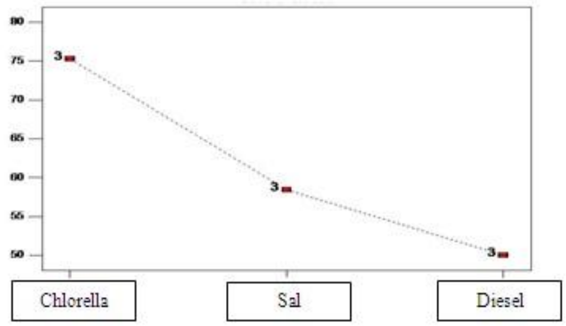

Figure 1: Cetane index comparison of Microalgae methyl ester with Salicornia Methyl ester and diesel fuel

4-4. Cloud point measurement results

As Figure 2 shows, Microalgae methyl ester cloud point ratio is relatively 74% and 116% higher than Salicornia methyl ester and diesel fuel. This is important in Cold regions and seasons. Due to Microalgae methyl ester higher cloud point in comparison to those fuels, it does not seem to be appropriate for cold climates. This feature based on -Harrington, 1986 & Knothe, 2003 researches- can be related to the presence of unsaturated fatty acids[3,5].

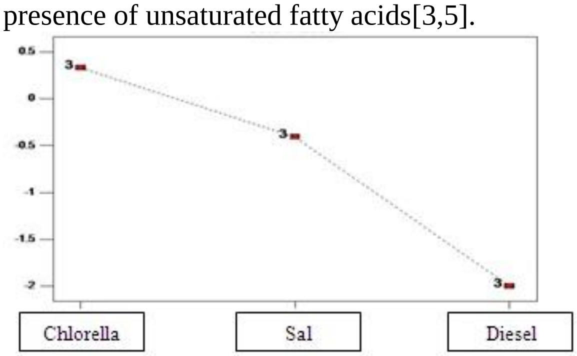

Figure 2: Cloud point comparison of Microalgae methyl ester with Salicornia Methyl ester and diesel fuel

4-5. Heating value measuring results

Experiments conducted on Microalgae methyl ester showed, its heating value is relatively 48% and 93% lower than Salicornia methyl ester and diesel fuel. Some reasons refer to Microalgae methyl ester high density and low hydrogen in the fuel. However, as fuels purchasing and consuming is volumetrically and B100 density is higher thanB00, the difference will be reduce by increasing the share of biodiesel.

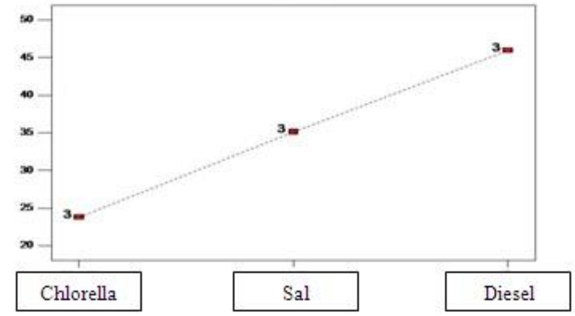

Figure 3: Heating value comparison of Microalgae methyl ester with Salicornia Methyl ester and diesel fuel

4-6. Kinematic viscosity

As indicated in Figure 4, Microalgae methyl ester viscosity is relatively 54% and 391% lower than Salicornia methyl ester and diesel fuel that indicates the superiority of Algae Methyl Ester. Viscosity is effective on powder quality when fuel injectors spraying. Higher viscosity disables injectors to make droplets turn to powder for effective evaporation and combustion. According to the research made by Knothe, 2005, the cause may be due to the short length of the carbon chain and using the methyl ester instead of ethyl ester in production process[6].

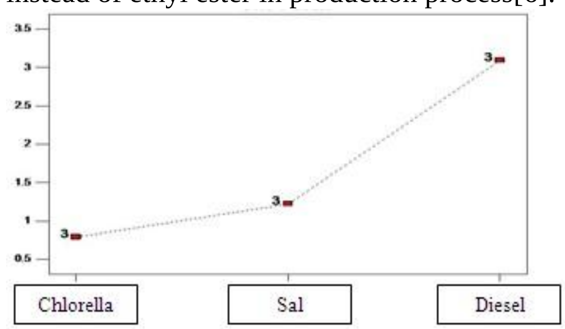

Figure 4: Kinematic viscosity comparison of Microalgae methyl ester with Salicornia Methyl ester and diesel fuel

4-7. Density

According to the experiments results, as seen in Figure 5, Microalgae methyl ester density is respectively 48% and 61% less than Salicornia methyl ester and diesel. High density (Increased density) is a limiting factor for using plant-derived fuels. In the current technology, without system changing, especially in the fuel system

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this factor creates additional pressure on system and cause problems in fuel injection.

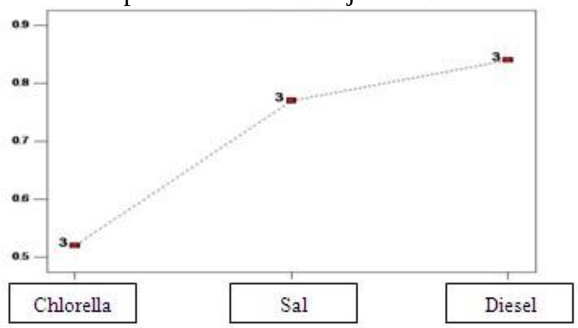

Figure5: Density comparison of Microalgae methyl ester with Salicornia Methyl ester and diesel fuel

5. Conclusions

Generally, by comparing algae methyl ester physical and chemical properties with Salicornia oil seeds and conventional diesel, its higher cetane index can be concluded. The higher cetane index leads to the better fuel combustion and engine durability.

Cold filter plugging point is lower than all of Salicornia Methyl ester and conventional diesel. Algae methyl ester cloud point is lower than Salicornia methyl ester and conventional diesel. This feature is important and does not seem to be appropriate for cold climate regions; it could be resolved by making changes in technology.

Algae methyl ester heating value is lower than those two, so more percentage in produced fuel combination is prevented. The high cost of plant fuel gives more importance to this topic. Because using high percentages of algae methyl esters make higher costs and consumers tend to reduce combination consumption. According to two different approaches, one increases the share of algae methyl ester, and the other demanding reduction. The logical solution is to use a lower percentage of the fuel in the current situation.

Algal methyl ester low kinematic viscosity improves the quality of fuel injector spraying, which reduces fuel consumption and better combustion. Algal methyl esters low-density, enables to be used with high percentages in mixed fuel.

Fuel Experiments show biodiesel from Microalgae includes more advantages than those two.

Microalgae oil production rate is 250 times more than soybeans per acre. So this can solve the country's annual biodiesel needs. Producing biodiesel from each type of fats has its own advantages and disadvantages. As the experiments show the low heating value and high cloud point are disadvantages of this type of biodiesel. All the advantages and disadvantages are influenced by different combinations of fatty acids.

Research on the effects of fatty acids and its influence on the properties of each fuel can be done in order to achieve the best combination of optimized fuel as alternative ones.

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