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Biodiesel Fuel Production from Palm, Sunflower Waste Cooking Oil and Fish Byproduct Waste as Renewable Energy and Environmental Recycling Process

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Authors' contributions

This work was carried out in collaboration between both authors. Author ABMSH designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MSA and ABMSH managed the analyses of the study. Both authors managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Significant of the Study: Biomass is renewable, organic, plant and animal derived source of biomaterial that can be converted into different forms of biofuel, bioplastic, bio-solvent, and bioenergy using different biotechnological procedures. Biomass derived bio-fuel is biodegradable, nontoxic, sustainable and substitute for fossil fuel as well as capable to reduce greenhouse gas emission. It is renewable and outstanding energy resource for the creation of steam and electricity, transportation fuel, manufacturing industries. Biomass derived from animal and plants like, fruits, vegetable, crops, fish, chicken and other animal byproducts or waste biomass which can be used for bioenergy production like biofuel and nano-catalyst for biofuel.

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Aim: The purpose of this study was to compare and investigate the suitable biodiesel properties produced from waste fish byproducts, palm and sunflower oil which were more economically viable.
Results: There was a total of 7, 5 and 4 types of fatty acid methyl esters presence in the fish, palm and sunflower biodiesel, respectively. The quality of biodiesel such as viscosity, total acid number, fuel consumption and emission rate was evaluated. The kinematic viscosity was maintained ASTM standard in case of all produced biodiesel. However, sunflower biodiesel was slightly viscous compared to palm and fish biodiesel. Metal elements such as phosphorus, magnesium, and calcium were present moderately in all biodiesel but it was limited range in fish oil. In the engine tests, the emissions of unburned hydrocarbons, oxides of nitrogen and carbon monoxide were lower in palm biodiesel than in sunflower and fish biodiesel. Fuel consumption was higher in palm biodiesel. Fish biodiesel had the lowest fuel consumption than that of palm and sunflower biodiesel.
Conclusion: It can be concluded that waste palm oil and fish oil can be considered as a great potential source for commercial biodiesel.

Keywords: Bienergy; biodiesel; fish and palm oil waste; engine emission.

1. INTRODUCTION

Biomass, hydro, wind, solar, hydrogen, geothermal are the types of natural energy that is readily available and sustainable [1]. By utilizing this energy wisely, it can be reduced the problem of air pollution, global warming, greenhouse effect and the detrimental consequences towards our health [2,3]. Biodiesel is produced when vegetable oil or animal fat is reacted chemically with an alcohol to produce fatty acid alkyl esters (transesterification) [2,3]. Biodiesel was produced by transesterification bioprocess using fatty acid methyl ester (from sunflower waste oil) along with methanol and sodium hydroxide as catalyst [4]. Biodiesel has a low emission profile and is environmental friendly, hence not danger to our vulnerable earth [4]. The reason that biodiesel is not utilized widely around the world due to the high cost of raw materials. To overcome this, it can be resorted from waste cooking oils and fish fats made from fish byproducts that are produced excessively in food processing industries. By utilizing these wastes oil, it could be helpful to overcome the problem of waste oil disposal [5].

Biodiesel has been chosen as one of the main alternative fuel because of its better characteristics and advantages such as: A renewable source, highly biodegradable (in soil and freshwater environments), high flash point, excellent lubricity, nontoxic, relatively low amount of polycyclic aromatics hydrocarbons as domestically available. Therefore this environmental friendly biofuel can be utilized in engines without any modification [4]. The main feature of this fuel was the low production of emission after the combustion due to the absence of sulphur [6]. It has been reported in engine emission analysis of biodiesel and showed that overall carbon dioxide emissions were reduced by 78% compared with petroleum-based diesel fuel [7]. A lot of research has been carried out on the production of biodiesel from vegetable oil sources but the used of fish fats, although often mentioned. Therefore, the objectives of the present research were to make a comparative study of biodiesel production from fish byproducts and waste cooking oil bio-resources and to test its characteristics such as chemical composition, viscosity, total acid number (TAN), multi element content and engine performance.

2. MATERIALS AND METHODS

2.1 Preparation of Oil Samples

Waste fish and its byproducts, palm and sunflower oil were utilized in this study to produce biodiesel. Waste fish and its byproducts (byproducts mixture of local fishes) were collected from open market in Pantai Dalam, Kuala Lumpur, Malaysia. Several simple processes were carried out to prepare the crude fish oil for the study. Firstly, the waste products were heated in the oven at 100℃ to melt it to fish oil for 4-5 hours per day until 5 days step by step to make more extraction of oil and stored in the beaker. Filtration was done by using a filter funnel with a piece of filter paper to filter off undesired waste particles. This oil was used for the subsequent biodiesel production (transesterification process). Palm oil was collected from household and sunflower oil was collected from University of Malaya cafeteria and then brought it to the Bioresource and Bioenegry laboratory, Biotechnology Division, Institute of Biological Sciences, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia for processing (Fig. 5).

2.2 Biodiesel Production through Transesterification Reaction

Biodiesel from fish, waste palm oil and waste sunflower oil was used at a reaction temperature of 55℃; a catalyst concentration of 1% (w/v); an alcohol, methanol (96%, v/v): oil ratio of 6:1, a stirring speed of 250 rpm with a 2 hours reaction time. NaOH was used as a catalyst to test its effect on biodiesel yield. Sodium methoxide is essential in enhancing the transesterificaation process which must be kept below 63℃ as the boiling point of methanol is 63℃ [8]. The filtered palm, sunflower and fish oil was preheated in the oven for approximately 15 minutes at 60℃ before subjecting it to the transesterification process. This was to ensure that all types of oil were mixed well and no sediments were left at the bottom. When the transesterification process was completed, the solution was separated into two distinct layers of crude biodiesel and glycerol. After transesterification process, the solution (both layers) was transferred into a beaker for evaporation of methanol at room temperature.

2.3 Biodiesel Filtration and Washing

There were three major steps involved in the purification of the biodiesel produced, namely, separation, washing and finally drying. Separation was done by pouring the solution into a separating funnel and settled down. Two distinct layers were formed; the lower layer containing glycerol was removed leaving only the methyl esters in the separating funnel. The methyl esters obtained was then washed with distilled water for at least four times to remove impurities such as pigments, excess alcohol, excess catalysts, glycerol, and soaps. The washing step was completed when the distilled water to methyl esters was used as 1:1. The washing step was carried out and soap was invariably formed and removed by using a weak acid. After that biodiesel was dried by using anhydrous sodium sulphate in the oven at 48℃. A little quantity of water was eliminated when biodiesel was dried in the oven whereas larger quantity of water was removed by using sodium sulphate anhydrous. Anhydrous sodium sulfate in the formation of hard crystals was filtered off by pouring the solution through a filter paper. Then the pure and dry biodiesel was sent to gas chromatography-mass spectrometer analysis.

2.4 Biodiesel Characterization

2.4.1 Identification of methyl esters present

The biodiesels have been sent for GC-MS analysis after drying. The main purpose of this analysis was to identify the presence of methyl esters in the produced biodiesel.

2.4.2 Total Acid Number (TAN) and viscosity

The total acid number is the amount of potassium hydroxide (KOH; mg) that is needed to neutralize the acids in one gram of oil.

2.4.3 Multi elements analysis

The produced biodiesel under optimum conditions was sent to the Engine Tribology Laboratory to determine the properties of the biodiesel and Multi elements (P, Ca, Mg, Na, Pb and Cu) content.

2.4.4 Engine tests

The biodiesel produced were sent for engine tests to the Tribology Laboratory of the Department of Mechanical Engineering in the Faculty of Engineering, University of Malaya, An engine test was carried out, which was the emissions test. The model of the engine was YANMAR TF120-M. This engine was horizontal, water cooled and single- cylinder. Bodiesel 20 (B20, 80% pure diesel and 20% biodiesel) was used in the engine test and compared with 100% pure diesel.

3. RESULTS AND DISCUSSION

In order to identify the fatty acid methyl esters presented in the biodiesel samples, the chromatogram and mass spectra obtained from the GC-MS analyzer had been interpreted. It was seen that there was a total of 7, 5 and 4 compounds that were present in the biodiesel sample produced from fish, palm and sun flower, respectively. Details of these compounds are shown in Table 1 containing the retention time (RT), possible identities, and the qualities of the compounds. Each of the peaks of solution had its unique retention time which was important in determining the chemical compounds in the biodiesel sample.

Table 1. Identification of methyl esters in fish, palm and sunflower based biodiesel

Total peak for different samples	Peak serial	RT (min)	Methyl ester of	Relative %	Total %
7 peak for fish	1	12.157	$C_{13}H_{24}O_2\ CH_3$	9.94	
	2	16.498	$C_{13}H_{30}O_2\ CH_3$	6.84	
	3	20.170	$C_{12}H_{30}O_2\ CH_3$	5,68	
	4	20.577	$C_{17}H_{34}O_2\ CH_3$	19.70	99.96
	5	23.767	$C_{19}H_{34}O_2\ CH_3$	14.20	
	6	23.886	$C_{19}H_{36}O_2\ CH_3$	40.60	
	7	24.330	$C_{19}H_{19}O_2\ CH_3$	3.00	
5 peak for palm	1	20.170	$C_{16}H_{29}O_2CH_3$	2.14	
	2	20.595	$C_{16}H_{31}O_2CH_3$	36.85	
	3	23.767	$C_{18}H_{31}O_2CH_3$	11.11	99.94
	4	23.898	$C_{18}H_{33}O_2CH_3$	44.00	
	5	24.330	$C_{18}H_{35}O_2CH_3$	5.24	
4 peak for sunflower	1	20.577	$C_{16}H_{31}O_2CH_3$	6.40	
	2	23.792	$C_{18}H_{31}O_2CH_3$	48.00	99.57
	3	23.898	$C_{18}H_{33}O_2CH_3$	42.10	
	4	24.330	$C_{18}H_{35}O_2CH_3$	3.00	

All of the 7, 5 and 4 compounds have been identified as fatty acid methyl esters, meaning all the triglycerides were successfully ethylated to methyl esters indicating conversion of TAG to FAME. The 99.96, 99.64 and 99.57% conversion proved that the given conditions used were correct. The identities and their molecular structures are shown in Table 1. Table 1 showed that the chain length of fatty acids composition ranged from 12 C to 19 C. The fatty acids with chain length of 19 carbons the major type of fatty acids. However, the viscosity and cold flow properties of the biodiesel got down regulated due to the higher chain length of bio diesel.

From the Table 1, it had been seen that the fatty acids presented in the fish oil sample was much lesser in comparison to the one reported [9]. Most of the reports in the literature showed the presence of C20 fatty acids. But in our results, we got C19 fatty acid. The results obtained in this study were different from the one reported by [9] although the amount of C22 fatty acids that were present in the fatty tissues was actually negligible. The major fatty acids that were identified in the samples were similar in some cases to the one reported by [9], which included oleic acid followed by palmitic acid and palmitoleic acid.

In case of palm oil, the five components were separated and have been shown as methyl palmitoleate, methyl palmitate, methyl linoleate, methyl oleate and methyl stearate (Table 1). This means the major fatty acids presented in the palm biodiesel were palmitoleic acid, palmitic acid, linoleic acid, oleic acid and stearic acid. This was similar to the components presented in the palm oil as referred by [10]. In addition, the palmitic acid and oleic acid were the two major components of fatty acid presented in the palm oil. As a consequence, the methyl palmitate and methyl oleate were the major components in the biodiesel.

Additionally, a good separation was obtained for sunflower oil, the yields of isolated fatty acid methyl esters (FAME) were methyl palmitate, methyl linoleate, methyl oleate and methyl stearate which eluted at 20.57, 23.79, 23.89 and 24.33 minutes respectively. This separation was sufficient for most classical oil characterization. This biodiesel from sunflower were composed of mainly 18 carbon fatty acids.

The viscosity was a basic design specification for the fuel injectors used in diesel engines [11]. Fuel with low viscosity may result in leakage of increased wear due to insufficient lubrication of the fuel injection pump. High viscosity however leads to poorer atomization of the fuel spray, incomplete combustion and carbon deposition on the injectors [11]. In this study, the kinematic viscosity was determined at 40℃ as this was the prime parameter required by American Society for Testing and Materials (ASTM) standard. From Table 2, the viscosity of biodiesel produced from transesterification of waste sunflower oil was 5.9 mm^2/s (or cSt). The kinematic viscosity at 40℃ accepted was limited between 1.9 to 6.0 cSt according to the ASTM. However, compared to the palm biodiesel, waste sunflower oil methyl esters was slightly viscous because of viscosity increased with higher contents of high molecular compounds like unreacted glycerides or polymers, which might be found in waste cooking oil. With reference to the above Table, it was seen that the viscosity of the fish based biodiesel was actually slightly higher than waste palm biodiesel and lower compared to the sunflower based biodiesel. Hence the biodiesel derived from fish possess was better quality biodiesel in terms of viscosity compared to sunflower biodiesel [2].

The total acid number is a direct measure of free fatty acids present in biodiesel. If free fatty acid content of the biodiesel is higher, then the oxidation stability of biodiesel would be less [3]. Free fatty acid can lead to corrosion of the engine due to its acidity and may be an indication of the presence of water in the fuel [12]. Palm oil has a low level of polyunsaturated fatty acids and almost half of them is saturated fatty acids. So, palm oil based biodiesel is less likely to oxidized if compared to other vegetable oil based biodiesel, such as sunflower based biodiesel, which is abundant in polyunsaturated fatty acids. In each source of waste sample was usually higher TAN value than pure sample due to the present of high free fatty acid content [13]. It was more likely the high acidity was due to excessive use of acid added to break the emulsion formed during cooking stage. Consequently, the biodiesel produced from sunflower oil has less oil oxidation and less causing corrosion too. So, the sunflower-based biodiesel is a better choice than other biodiesel.

ASTM D675I standard limits sodium, magnesium and calcium concentration to less than 5 ppm to prevent engine damage from deposits. The result shown in Fig.1 and showed that almost all metal contents followed the limits of ASTM D6751 except few. The high sodium level may be due to the residual sodium metals from sodium hydroxides and anhydrous sodium sulfate in the biodiesel produced. Sodium hydroxide was utilized as catalysts and anhydrous sodium sulfate was used as drying agent in the biodiesel production.

Metal elements contained in the biodiesel can lead to the deposition of ash after the combustion. Ash includes Na, Mg and Ca metals. Deposition of ash in the engine reduces the engine performance and high sodium content can induce metal corrosion and saponification of the methyl esters. Metal elements such as phosphorus, magnesium, and calcium that were present in the biodiesel might form ash deposited in fuel injection system and poison the catalytic converters of the engines and reduced its ability to decrease the exhaust emission [14].

The European norm as well as the American standard, also limits the maximum content of phosphorus in biodiesel samples to 10 ppm. However, phosphorus level was found very high, 20.5 in the biodiesel produced from sunflower oil.

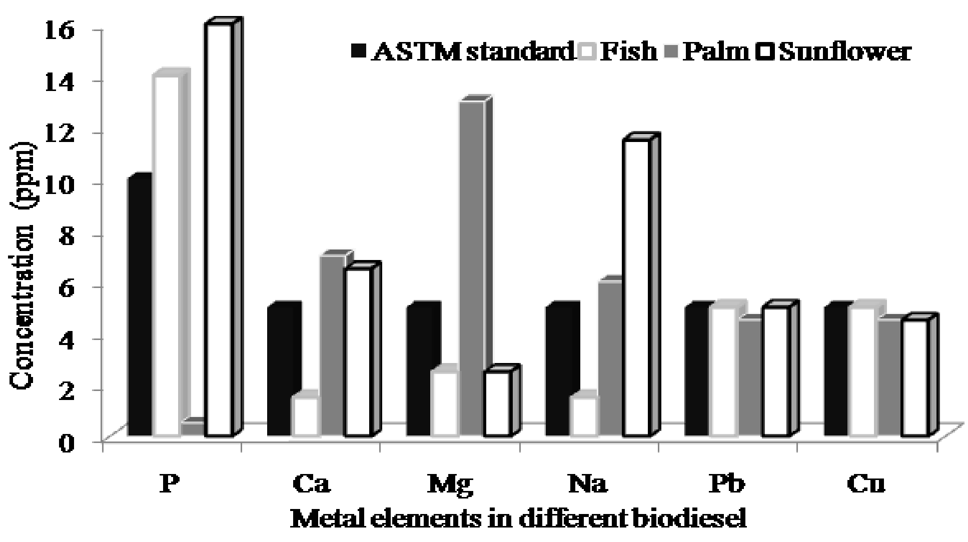

Fig. 1. Concentration of different elements present in biodiesel and comparison with ASTM standard

High level of phosphorus might be due to incomplete refining of the vegetable oil and from proteins encountered in the reading process. Phosphorus might also come from phospholipids (straight vegetable oil) and inorganic salts contained in the feedstock. In vegetable oils, the type of oil recovery strongly influences this parameter. As phospholipids might impede phase separation during the transesterification process due to their emulsifying properties. The transesterification process has been identified as an efficient means of lowering phosphorus.

From the results shown above it is obvious that fish oil biodiesel showed a lower SFC (0.581 ml/sec) in comparison with conventional diesel (0.613 ml/sec). The SFC value for waste cooking palm oil and sunflower oil biodiesel were 0.588 ml/sec and 0.612 ml/sec respectively. Fish based biodiesel had the lowest SFC, it might be due to its higher calorific value in comparison with the other samples. Table 3 shows the specific fuel consumption (SFC) in ml/sec. According to study done by [15], petro-diesel fuel showed higher fuel consumption per unit energy output compared to biodiesel fuels. They suggested this was because of the biodiesel, which was a biomass based fuel, contained higher oxygen.

As can be seen in Fig. 2, conventional diesel produced a higher amount of carbon monoxide than all produced biodiesel. During the combustion process, carbon dioxide are formed in the presence of sufficient oxygen from the air and as well as from the fuel itself. However, carbon monoxide is also produced due to the incomplete combustion of fuel in the combustion chamber of engine. Probably the lower cetane number of the petrodiesel results in the lower tendency of itself to autoignite, and hence higher emission of carbon monoxide. Biodiesel has higher cetane number causing higher ignition and lower Carbon emission. This might be due to the organic source derived fatty acid ester based biodiesel. Furthermore a higher viscosity and poorer atomization tendency can also lead to higher emissions of carbon monoxide. In addition, it might also possibly be because biodiesel itself has approximately 11% of oxygen content which may enhance the completion of its combustion [16]. Carbon monoxide concentration from waste palm oil derived biodiesel was much lower compared to other samples because of it possessed a lower acid and viscosity value.

Biodiesel fuel showed a lower production of unburned hydrocarbon compared to conventional diesel (Fig. 3). This might be due to the biodiesel had higher cetane number leading to faster vaporization and autoignition. Unburned hydrocarbon emission can also be known as partially oxidized hydrocarbon emission. Its emission can be caused by two main factors. It could increase due (a) the fuel injection that was occurred too early, causing an increased in delay time and hence more fuel can contact with the relatively cool cylinder wall, or (b) the combustion process in the engine occurring too late, causing an insufficient time for complete combustion. Al1 these factors enhanced the complete combustion of biodiesel and hence reduced the production of unburned hydrocarbon. The explanation of low carbon monoxide emission from biodiesel fuel applies for low production of unburned hydrocarbon as well because of its complete combustion. It was found that fish oil biodiesel showed lower hydrocarbon emission when compared with the waste palm and sunflower cooking oil biodiesel. This might be due to the fish oil biodiesel had better combustion properties.

Palm oil biodiesel showed a lower NOx emission in comparison with the other samples because it possesses lower exhaust gas temperature. NOx content is an important characteristic of engine fuel. NOx emission formation is highly temperature dependent. The amount of NOx emission is directly related to the exhaust gas temperature and engine combustion chamber temperatures. As the exhaust gas temperature increases, NOx emission also increases. Hence, biodiesel fuelled engines had a higher potential to emit more NOx because of the exhaust gas temperature increased as the biodiesel concentration increased [17].

Table 2. Determination of acid value and viscosity of different waste bio-source biodiesel

Property	Unit	ASTM value	Fish waste	Palm waste	Sunflower waste
Total Acid Number (TAN)	mg KHO/g oil	0.50	0.44	0.42	0.45
Viscosity	mm^2/s (cSt) at 40℃	1.9-6	5.40	4.2	5.9

** Not detectable*

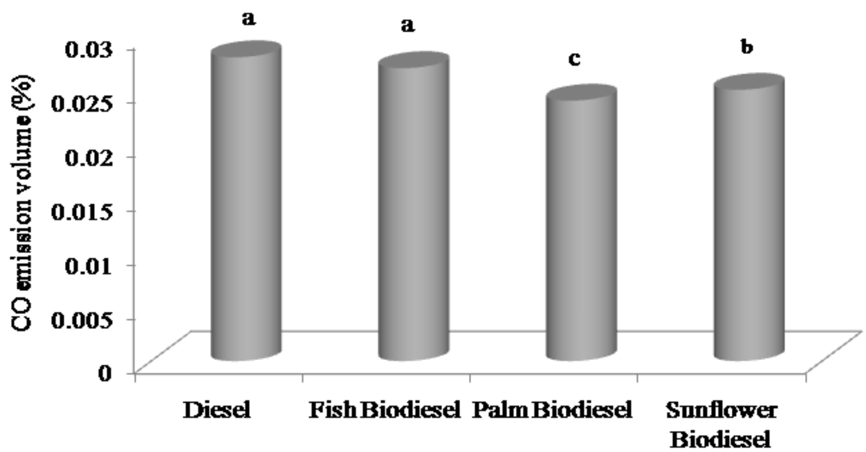

Fig 2. Engine emission (CO emission) test of biodiesel

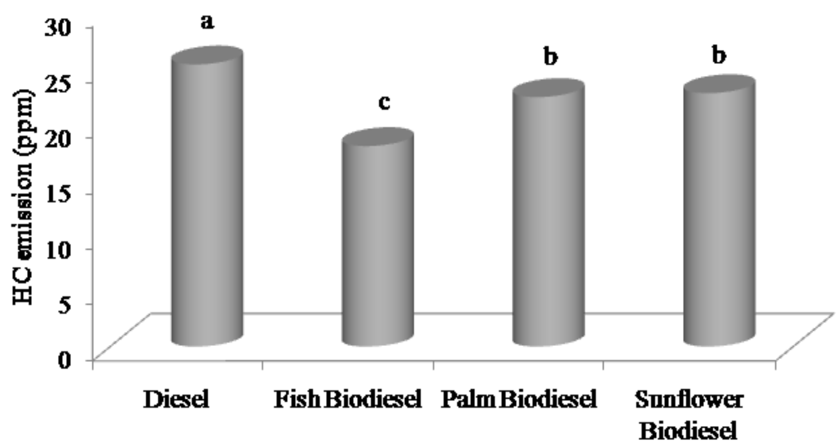

Fig. 3. Engine emission (HC, hydrocarbon emission) test of biodiesel

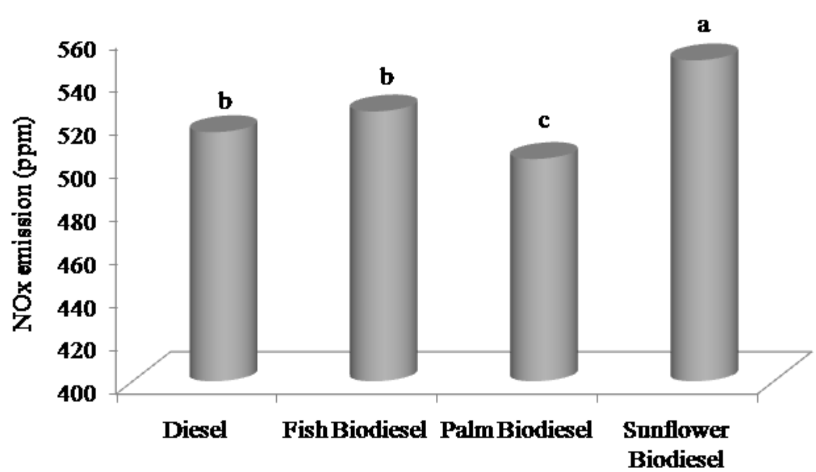

Fig. 4. Engine emission (NOx emission) test of biodiesel

Table 3. Measurement of fuel consumption using different types of biodiesels in diesel engine

Biodiesel sample	Load	Speed	Fuel consumption (ml/sec)
Pure diesel	15 Nm	2000 rpm	0.613
Fish biodiesel	15 Nm	2000 rpm	0.588
Palm biodiesel	15 Nm	2000 rpm	0.581
Sunflower biodiesel	15 Nm	2000 rpm	0.612

(A) (B)

Fig. 5.1. Fish byproducts: A, (fish byproducts), EB Heat at 100 ^{O}C in oven to extract oil for biodiesel production

Fig. 5.2. Waste cooking palm oil, waste palm oil collection, palm biodiesel (Upper layer) and lower layer is glycerin

A B C D

Fig. 5.3. Sunflower oil and biodiesel processing

Fig. 5. (5.1. Fish byproducts, 5.2. Waste cooking palm oil 5.3. A) Pure sunflower oil, B) Filtered waste sunflower cooking oil, C) Phase separation, upper layer is biodiesel, lower layer is glycerol and D) Formation of emulsion (washing of biodiesel)

4. CONCLUSION

From the studies it can be concluded that the produced biodiesel conversion was little bit higher in fish byproduct and waste palm oil than in waste sunflower oil. Biodiesel 20 (B20) showed less CO, HC and NOx emission and fuel consumption compared to the 100% pure diesel. Finally it can be concluded that biodiesel 20% (B20, 80% pure diesel and 20% biodiesel) can be used in the engine without any modification and reduced the engine emission. It can be recommended that by using this biotechnology for biofuel, waste can be managed and environment can be saved from pollutions of waste fish byproducts and waste cooking vegetable oil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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