



Characterization and Glycerine Analysis of Mustard (*Brassica juncea* L.) Seed Oil and Biodiesel

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Authors' contributions

The work was carried out in collaboration among all authors. Author EIB designed the study, wrote the protocol and prepared the first draft of the report. Author OZA designed the experiments and prepared the equipment for the experiments. Author SO conducted the experiments and analyzed the results. Author KB carried out the literature survey. All the Authors read and approved the final manuscript.

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ABSTRACT

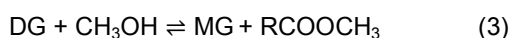
Due to increased global warming and pollution, the use of biodiesel as alternative to biodiesel has become a widespread. The use of Mustard (*Brassica juncea* L.) oil as a possible feedstock for biodiesel production was evaluated. The biodiesel was produced through transesterification with sodium hydroxide and gave a biodiesel yield of 94 wt.%. The fatty acid profile obtained by chromatography analyzer was mainly erucic acid 45.7 wt.%, linoleic acid 14.2 wt.% and linolenic acid 13.0 wt.% acids. The distillation characteristics show higher distillation temperature than diesel and the mineral elements in the oil and biodiesel are within the ASTM limits for biodiesel. The oil and biodiesel were characterized and they gave properties that are similar to those of fossil diesel and within the ASTM D6751 and EN 14214 limits for biodiesel, which led to the conclusion that mustard seeds can be a viable source of feedstock for biodiesel production. The glycerin analysis shows the completeness of the transesterification process.

Keywords: Mustard seed oil; *Brassica juncea* L.; fatty acid profile; biodiesel; transesterification.

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1. INTRODUCTION

The increasing global warming and consequential effects such as draught and flooding has brought to the fore front the need for alternative fuel for diesel engines that is more environmentally friendly and this has led to increasing interest in biodiesel [1]. Biodiesel is derived from vegetable oil or animal fats by reacting them with low density alcohol such as methanol and ethanol as reagent with aid of a catalyst such as sodium hydroxide and potassium hydroxide [2,3]. The transesterification reaction is as shown in equation 1 and leads to the production of a mono alkyl esters and glycerol. The reactions are reversible and occur in three consecutive steps as shown in equations 2 - 4. Between the stages, it is possible that conversions of triglyceride (TG), diglycerides (DG) and monoglycerides (MG) are not completed thus allowing small amounts of the compounds to be present in the biodiesel.



An important application of the result is that, by measuring the amounts of these compounds present in the biodiesel, it is possible to determine the degree of completion of the transesterification reaction. These intermediate compounds are very unstable and can affect the storage stability of the fuel and are hence limited in biodiesels by ASTM D6584 and EN 14105 standards.

Glycerol, because of its high viscosity, can attract solid particles in the fuel to form very viscous mixture that can block fuel pipes and cause blockage of filters. Such fuels are prone to coking and may thus cause the formation of deposits on injector nozzle, piston and valves that can affect engine fuel economy and performance.

Several vegetable oils have been converted to biodiesel and tested as alternative fuels for diesel engines [4]. One of such oils is that obtained from mustard plant, which is an annual herbaceous plant that belongs to the Brassicaceae family. It has lyre-shaped leaves about 16 cm long. The seeds are 1 - 2 mm diameter and the main varieties are black

(Brassica nigra), brown (B. juncea) and white (B. hirta/sinapis alba). The oil content varies from 43-46 wt% [5] and is hence a potential source of feedstock for biodiesel production.

2. MATERIALS AND METHODS

2.1 Materials

Mustard seeds were procured from a local dealer in Akure, Nigeria. The normal hexane, methanol and sodium hydroxide used were of analytical grade and procured from Pascal Laboratory in Akure, Nigeria.

2.2 Oil Extraction

The oil was extracted using normal hexane as solvent by leaching for 8 hours in a Soxhlet extractor. The hexane in the oil extracted was removed using a rotary evaporator under reduced pressure (20 mbar at 30°C). The oil content was calculated by first measuring the weight of mustard seeds used and then dividing by the weight of oil extracted after the hexane had been removed.

2.3 Transesterification Process

Transesterification was carried out in a 500 mL table top mounted biodiesel processor. 300 g of sodium methoxide was mixed with 50 g of the oil to give a molar ratio of 6:1. It was heated to 60°C and stirred at 450 rpm for 2 hours after which the mixture was poured into a separatory funnel and left for 8 hours for the reaction to reach equilibrium and the biodiesel and glycerol to separate into two distinct layers. The glycerol at the bottom was drained off by gravity and the excess methanol in the biodiesel was removed using a reduced pressure (20 mbar, 30°C) rotary evaporation. The crude biodiesel was washed with distilled water until a neutral pH value was obtained and then dried by passing over magnesium sulfate. The biodiesel yield is the volume of biodiesel produced divided by the volume of oil and methoxide mixture.

2.4 Fatty Acid Profile and Glycerine Analysis

The fatty acids of the oil and biodiesel were separated using the HP 6890 Gas Chromatography analyzer powered by HP Chem. Station Rev a 09.11 [1206] software. It has a split ratio of 20:1 and was equipped with a flame

ionization detector and HP INNO wax column (30 m x 0.25 cm x 0.20 µm film thickness). Nitrogen was used as the carrier gas and the initial temperature of the oven was set at 60°C. The first ramping was at 12°C/minute for 20 min and maintained for 2 minutes. The second ramping was at 15°C/minute for 3 minutes and maintained for 8 minutes. The detector temperature was 320°C while hydrogen and compressed air pressures were 22 and 35 psi respectively.

Total and free glycerol were determined according to ASTM standard D6584 using the same equipment. However, the carrier gas was helium, flow rate was 1.0 mL/minute and inlet temperature 60°C. The Elite-biodiesel M column used has dimensions (14 m x 530 µm x 0.16 µm film thickness). Initial oven temperature was 60°C and was held for 2 minutes. The first ramp was set at 10°C for 2 minutes and second ramp was at 8°C/minutes to 300°C and held constant at 5 minutes. The detector temperature was 380°C. Flow rates of hydrogen and compressed air were 45 and 450 mL/minute respectively.

The sample solutions were injected into the gas stream and transported into the column where separation occurs and the quantity of each component that exits the column was measured by the flame ionization detector. The sample concentration was determined by injecting a standard sample of known concentration. The standard sample peaks, retention time and area are compared to the test sample to calculate the concentration. The free and total glycerol quantifications were made by comparison to external calibration curves according to the official method.

2.5 Distillation Characteristics

The vacuum distillation temperature experiments were conducted according to the ASTM D1160 method using the reduced pressure advanced distillation curve apparatus. The set up consists of a distillation unit and a vacuum pump. The distillation pressure was set at between 1 kN/m² and 83 kN/m² and the temperatures were recorded for 5%, 50% and 95% distillations. The reduced pressure was used because the boiling temperatures of the fatty acid contents of biodiesel are so high at atmospheric pressure that the compounds can decompose (crack) during the distillation test and give incorrect results.

2.6 Characterization

Density was determined using a densimeter with necessary corrections. Cloud and pour points were determined following ASTM standards D5773 and D5949 respectively and using a cloud point meter. Flash point was measured according to method ASTM D6751 using Kehler Model K-16270 (Pensky-Martens Closed Flash Tester). Kinematic viscosity was determined with a capillary type viscometer immersed in water bath at 40°C in accordance with ASTM D445. Heating value was measured by Glenton apparatus. Cetane number was calculated using the distillation characteristic and equation 5 [6].

$$CI = -420.34 + 0.016G^2 + 0.192G(\log T_{50}) + 65.01(\log T_{50})^2 - 0.0001809 T_{50}^2 \quad (5)$$

where G is the specific gravity as specified by the American Petroleum Institute, while T₅₀ is the distillation temperature at 50 vol.% fuel sample distilled and condensed in a unit of °F. To determine the Carbon Residue, 1.0 g of the sample was placed in a crucible and subjected to destructive distillation. The residue undergoes cracking and coking reactions during the heating. At the end of the heating, the test crucible containing carbonaceous residue was cooled in a desiccator and weighed. The residue remaining was calculated as a percentage of the original sample. To determine the sulphated ash, each residue was treated with sulfuric acid and heated in an Isotemp muffle furnace to 750°C for the carbon to be completely oxidized before allowing it to cool down to room temperature. The ash formed was again treated with sulfuric acid and heated to 750°C until the weight became constant. The percentage ash content was calculated by dividing the final weight by the initial weight and multiplying by 100.

Acid value titrations were carried out according to AOCs official method Cd 3d-63.0. 40 g of the oil sample was dissolved in 5.0 ml of 1:1 mixture of ethanol diethyl ether in 100 ml flask. The mixture was homogenized, swirled and phenolphthalein indicator was added. The acid value was calculated using equation (6)

$$\text{Acid Value} = \frac{56.1X \text{ NXV}}{w} \quad (6)$$

To determine the iodine value, 0.25 g of the oil sample was dissolved in the 20 mL of carbon tetrachloride in a 100 ml flask. The Wiji's solution was added to the content of the flask. It was

stopped and allowed to stand for two hours in the dark at room temperature. 20 mL of potassium iodide solution was added and the mixture was titrated against sodium thiosulphate solution using the starch indicator. The same procedure was repeated for the blank and the iodine value was calculated using equation (7)

$$\text{Iodine Value} = \frac{12.69 N (V_2 - V_1)}{w} \quad (7)$$

Sulfur content was measured in a Horiba sulphur- in- oil analyzer, model SFLA-20 while phosphorous (P, mass %) contents were measured with Magellan Midstream Partners, L.P. (Kansas City, KS) according to ASTM standards D5453 and D4951, respectively. The mineral analysis was done using atomic absorption Spectrophotometer.

The copper strip corrosion test (ASTM D 130 in ASTM D 6751: ISO 2160 in EN 14214) was used for the determination of the corrosiveness of copper in the samples. It involves dipping a strip of copper into Koehler K25330 Copper Strip Test

Bath for 3 hours at 110°C and observing the corrosive action of the fuel on the strip. The pattern was compared with standard to determine the classification.

3. RESULTS AND DISCUSSION

The fatty acid profiles are shown in Fig. 1.

The biodiesel contains mainly 42.5 wt.% erucic acid (22:1, 13(Z)-docosenoic, 24.2 wt.% linoleic acid 18:2 (9(Z), 12(Z)-octadecadienoic, 16.5 wt.% linolenic acid 18:3 (9(Z), 12(Z),15(Z)-octadecatrienoic, 9.96 wt% oleic 18:1 9(Z) - octadecanoic acids,. The biodiesel is 95% unsaturated. The results are similar to previous works on fatty acid profile reported by [7,8,9, 10,11].

3.1 Characterization

Table 1 shows the properties of the samples (oil and its biodiesel) and all subsequent discussion on characterization refers to the Table 1.

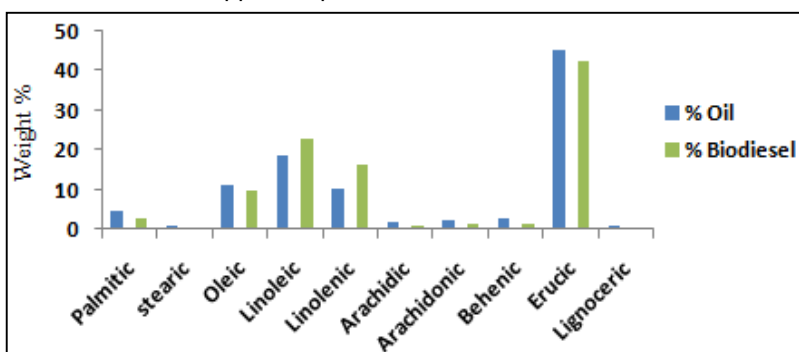


Fig. 1. Fatty acid profile of mustard seed oil and biodiesel

Table 1. Properties of mustard seed oil, its biodiesel and ASTM limits

S/N	Parameter	Oil	Biodiesel	ASTM limits
1	Density (g/mL)	0.908	0.883	
2	Cloud Point (°C)	-4	-6	
3	Pour Point (°C)	-16	-18	
4	Flash Point (°C)	282	142	130 Min.
5	Kinematic Velocity (@ 40°C (mm ² /s)	68.50	4.44	1.9 – 6
6	Lower Heating Value (kJ/kg)	39.2	40.4	
7	Cetane Number	42	62.5	47 Min
8	Water and Sediment (mass %)	1.50	0.02	
9	Acid Number (mgKOH/g Oil)	0.65	0.61	0.08 Max
10	Iodine Value (mgI ₂ /100g)	108	52.46	
11	Oxidation Stability @110°C (Hrs)	20	16	
12	Sulphated Ash (mass %)	0.012	0.008	0.020
13	Carbon Residue (mass %)	0.041	0.020	0.050
14	Free Glycerin (mass %)	0.002	0.046	0.020
15	Total Glycerin (mass %)	0.086	0.242	0.240
16	Copper Strip Corrosion classification@50°C 3 hr	3	1	3 Max.

Density: The density reduced after transesterification from 0.9080 to 0.883 kg/m³, which is within the limits for biodiesel and diesel. Density is important because it affects fuel properties that vary with the mass of fuel. The oil contains 42.5% erucic fatty acid (22:1) which is a monounsaturated long chain fatty acid with a single double bond.

Cloud point: This is the temperature at which the fuel becomes cloudy in preparation for solidification. It reduced from 10.20°C to -2.80°C after transesterification. The biodiesel can hence be used in regions where the temperature can fall below the freezing point of water.

Flash point: The property is the temperature when the vapour arising from the fuel sample when heated, is high enough for the vapour to flash when exposed to a standard source of ignition. It affects the safety in handling and storage of the fuel. It reduced from 282°C to 142°C, which is higher than the flash point of diesel and thus makes it a safer fuel than diesel.

Kinematic viscosity: This is a measure of the resistance of fuel to flow and affect parameters such as flow rate, power required for pumping and fuel spray pattern from the nozzle. The kinematic viscosity of the oil was very high at 68 mm²/s and reduced to 4.80 mm²/s after transesterification which is within the limits for biodiesel. The oil contains 42.5% long-chain erucic acid (C22:1) which has a kinematic viscosity of 7.33 mm²/s [12] and is responsible for the high kinematic viscosity of the oil.

Cetane number: This is a measure of the ease with which the fuel can be ignited, the rate of pressure rise during combustion, the completion of combustion and noise level. The cetane number increased from 42 to 62.5 both of which are above the minimum for biodiesel and can be attributed to the high content of erucic fatty acid content.

Heating value: This is the amount of heat released in KJ when a kg of the fuel is burned. The values did not change much after transesterification and are about 10% lower than that of diesel. The heating value of the biodiesel is lower than that of fossil diesel because the oxygen in biodiesel, which occupies about 10% of the volume and has lower heating value than the carbon and hydrogen molecules displaced by the oxygen.

Water and sediments: Fuel contains naturally occurring water and that remains after water washing. Sediment also occurs naturally and as a result of reaction between elements. It can also result from the degradation of the fuel. Water is detrimental to the fuel system as it can solidify and inhibit fuel flow, it can also promote corrosion in the fuel system and must hence, be reduced as much as possible. The value reduced from 1.50% to 0.02% after transesterification.

Iodine value: This is a measure of the degree of saturation and dryness quality of the fuel. Unsaturated fuel can easily react with other elements thus creating storage stability problem and can also readily polymerize to form deposits. The value reduced from 108 to 52.46 (gl₂/ 100 g) which is quite low compared to other biodiesel fuels. Although not on ASTM list, it is lower than EN 14214 maximum value of 120.

Acid value: This is a measure of the amount of potassium hydroxide required to neutralize the free fatty acids present in one g of the sample. High amount in the fuel can promote the formation of deposit in the fuel system. The value reduced from 0.65 to 0.61 mgKOH/g for the oil but still well above the maximum ASTM value of 0.50 mgKOH/g; this shows that transesterification can reduce metallic components in the oil.

Sulphated ash: This is the residue of alkaline catalyst left after the sample was carbonized and the product treated with sulphuric acid and heated to a constant weight. The test enables the metallic components of the samples remaining in the product of combustion to be determined. The value reduced from 0.012% to 0.008% after transesterification.

Carbon residue: This test enables the determination of the remnant when samples are subjected to thermal degradation. It is a measure of the tendency for coke or carbon formation. The carbon residue reduced from 0.041% to 0.020% after transesterification.

Copper strip corrosion test: The test is used for assessing the corrosive effects of biodiesel on copper components in fuel systems. It has a value of 3 on a scale with maximum value of 5 making it averagely corrosive, but it reduced to 1 for the biodiesel that has the same effect as fossil diesel. The degree of tarnish on the corroded strip correlates to the overall corrosiveness of the fuel sample.

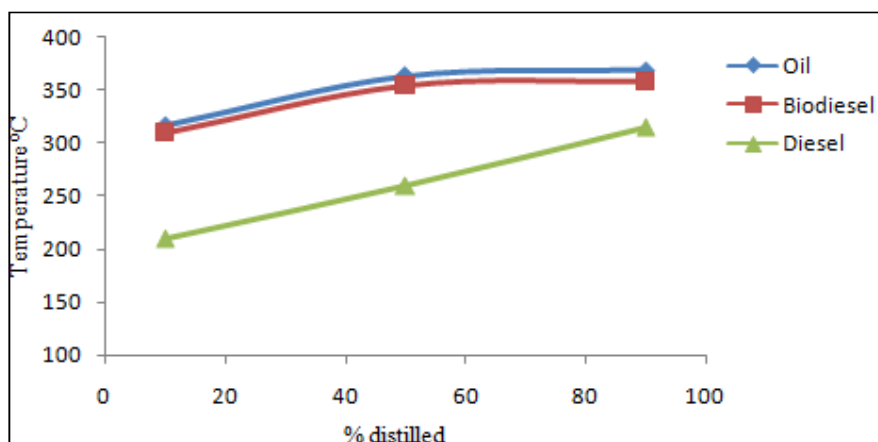


Fig. 2. Distillation characteristics of mustard seed oil, biodiesel and diesel

Fig. 2 shows the distillation characteristics of the samples and diesel. There are few differences between the distillation characteristics of the oil and biodiesel which is a reflection of the closeness of their cloud and pour points as well as the densities. They distilled at higher temperatures than diesel because of their high molecular weight. While the distillation rate is high for diesel, those of the samples are fairly steady. Distillation characteristics are dependent on the fatty acids composition, volatility, boiling range distribution and hence flash point. It has important effects on the injection timing, combustion characteristics, engine performance, fuel storage and safety. The oil did not meet the T-90 360°C standard in ASTM D6751 but can be corrected by blending with diesel fuel.

Fig. 3 shows the mineral elements in the samples. Sulphur is the most prominent in the biodiesel but is still below the 15 ppm of ASTM D6751 maximum value for biodiesel.

Potassium and sodium are alkaline metals that are used as catalyst and tend to increase after transesterification. Potassium, sodium, calcium and magnesium can form soap in the fuel which although, promotes cleanliness of the fuel system but can inhibit biodiesel yield. Phosphorus and sulphur are carry over elements from vegetable oils with phosphorus originating from the phospholipids while sulphur originates from glucosiolates in vegetable oil and both have been reported to reduce effectiveness of the rare metals in exhaust systems catalytic converter. Sulphur confers lubricity on diesel fuel and is mandatory in diesel in the US. Sulphur dioxide in the exhaust emission can increase atmospheric pollution and cause adverse environmental

effects such as soiling when deposited on the soil and can cause acid rain. Sulphur can also affect catalytic converter's effectiveness.

3.2 Glycerine Analysis

A triglyceride is a mixture of different glyceride esters of fatty acids in which each glycerol molecules has attached to it three molecules of long chain monocarboxyl fatty acids. Glycerol is a trihydric alcohol (containing three-OH hydroxyl group) that can combine with 1, 2 or 3 fatty acids to form monoglyceride, diglyceride and triglyceride respectively. Free glycerol is when the fatty acids have been detached. Total glycerol is the sum of bounded glycerol and free glycerol.

The free glycerin increased from 0.002% (20 ppm) to 0.046% (460 ppm) after transesterification. While total glycerol decreased from 0.086% (860 ppm) to 0.245 (2450 ppm). Glycerol has high boiling point and is responsible for the high viscosity of vegetable oils. If the glycerol level in a fuel is high, because of its high viscosity, some of its contents will settle out at the bottom of the fuel tank to form very viscous mixture, which can attract solid particles, increase the viscosity of the fuel and may cause blockage of filter and consequently restrict fuel flow. Such fuels are prone to coking and may accelerate the formation of deposits on injector nozzle, piston and valves that can affect fuel economy.

Fig. 4 shows the variation of MGE, DGE and TGE with retention time for mustard seed oil. The most unstable component in terms of retention time, is the DGE while TGE is most stable. Fig. 5

shows the variation of monoglyceride, diglyceride and triglyceride esters in the biodiesel. Triglyceride is dominant in the oil with traces of monoglyceride and diglyceride. However, the biodiesel contains only the fatty esters and as

such shows the completeness of the transesterification process. During transesterification, a delay period before conversion occurs and could last about 0.7×10^{-3} minutes.

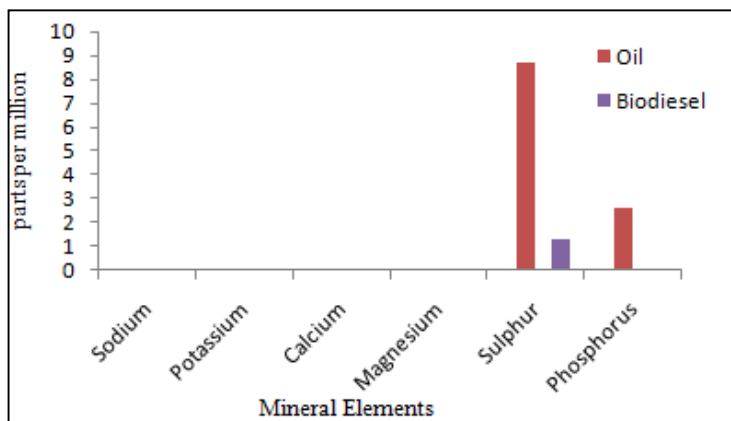


Fig. 3. Mineral elements in mustard seed oil and biodiesel

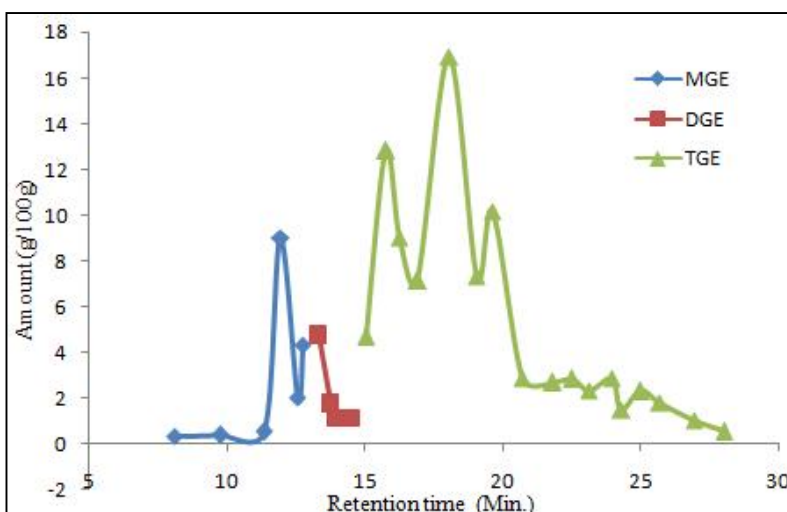


Fig. 4. Variation of MGE, DGE and TGE with retention time for mustard seed oil

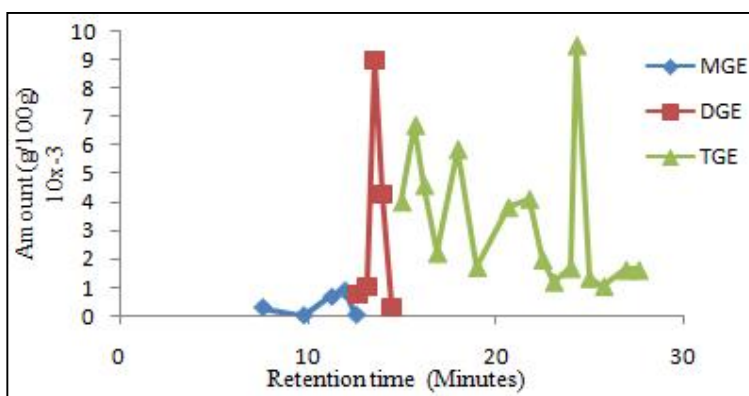


Fig. 5. Variation of MGE, DGE and TGE with retention time for mustard seed oil and biodiesel

MGE is 0.8 (g/100 g) in the oil, 0.45 (g/100 g) of DGE which occurs over a duration of 1 minute. TGE is the most dominant and has a retention time of 16 minutes. MGE, DGE and TGE are in trace amount in the biodiesel and a confirmation of the completeness of the transesterification process.

4. CONCLUSIONS

Mustard seed oil contains 25% oil and the main fatty acid is erucic fatty acid, which constitute 45% of the weight of the seed. The cloud and pour points of the biodiesel are below freezing point of water thus allowing it to be used in cold regions. Most of the properties are within the ASTM limits for biodiesel and similar to those of fossil diesel. However, the T-90 temperature is outside the limit but may be corrected by blending with lighter diesel. Glycerine analysis shows trace amount of glycerine in the biodiesel thus confirming the method as a veritable tool for ascertaining the completeness of the transesterification process.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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