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Research Article

COMPARATIVE STUDY OF BIODIESEL PRODUCE FROM ASH GOURD SEED OIL USING METHANOL AND ETHANOL

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ABSTRACT

Biodiesel as a sustainable and alternative energy source can be applied directly to industrial and automobile fields even as fuel source for power plant. Therefore, this paper seek to study the use of ash gourd seed oil as feed stock to produce biodiesel using methanol and ethanol, using standard method. The results indicated that the acid number of the two biodiesel range between 12.90±0.02mgKOH/g -- 16.83±0.02mgKOH/g, pH range between 6.50±0.01 -- 6.51±0.01, iodine number range between 250±0.2gI2/100g --- 275±0.2gI2/100g, flash point range between 100±0.1oC -- 110±0.1oC, sulphur content range between 0.01±0.1ppm -- 0.23±0.1ppm, viscosity range between 18.85±0.02mpa/S – 24.14±0.02mpa/S and density range between 0.875±0.2gcm3 -- 0.922±0.2gcm3 . In conclusion, when the result was compared with European standard and thermal test conducted the biodiesel produce perform well with auto devices when used and compatible with petrol diesel.

Keywords: Transesterification, seeds oil, spectrum and, thermal test.

INTRODUCTION

The demand for petroleum is increasing at geometrical rate everyday due to uncontrollable population while the petroleum resources are limited even decreasing everyday therefore, it becomes necessary to search for alternative fuel sources for proper selection, sustainability and renewable. Singh (2010). Actually, biofuel is a real solution with biodiesel as an alternate to petroleum based diesel, while biogas is alternative to petroleum based gas. Geaffad (2010) and website (2011). Despite other methods of operating automobile like battery motor, gas generation motor, petroleum sources and biodiesel is still the best because of rate of burning, load and speed involved. Moreover, since biodiesel is produced from vegetable oil and are available everywhere for easy access and cultivation with good soil. In addition biodiesel is simply, a fuel derived from vegetable oil and fat which has similar combustion properties to regular petroleum base fuel. Sayyed *et al.,* (2017). Biodiesel as a suitable alternative energy can be applied directly to industrial and automobile fields and even as fuel. Antaram *et al.,* (2015). Generally, biofuel are divided into two, namely primary and secondary biofuel. The primary biofuel include: fire wood, animal waste, landfill gas, wood ships pellets typically used in unprocessed form for cooking, heating even electricity production. While the secondary biofuel consist of biodiesel and bioethanol which are used as fuel and various industrial processes. Initialy biodiesel was produced using feed stock in the form of edible vegetable oil such as palm oil, soybean oil, and sunflower oil, this period are called first generation biodiesel production. The second generation feedstock include: various types of non edible vegetable oil such as jatropha, mahua, jojoba oil, cooking oil and urban agricultural waste, they also has similar fuel characteristics and performance with the conventional diesel in terms of chemical structures and and performance while the third generation include the micro algae, cyano bacterial and other single called oleaginous microorganism but research are still going on in most country of the world. Like Europe and USA. The fourth generation of biodiesel feedstock began to developed massively through the use of technology in engineering. They require feedstock include: the use of pyrolysis, gasification, purification and genetic process in certain organism to obtain hydrocarbon compound. Dulqarnain *et al.,* (2021). Biodiesel is produce by technology called transesterification reaction which is carried out on various types of raw materials including various animal fat and plant oils, and reaction with methanol and ethanol so that this can be used as fuel in internal combustion engine. The reaction occurs when vegetable oil or fats is chemically reacted with alcohol to produce fatty esters, a catalyst like sodium, potassium or calcium ethoxide is required, glycerol is also formed in the process but the ester can be separated using separating funnel. of which the ester is lighter in weight to the glycerol. But these research is using sodium methoxide, calcium ethoxide as a catalyst which is more effective, Solomon (2005). Others explained it as a chemical reaction between triglyceride and short chain alcohol in the presence of a catalyst to produce monoesters the long and branch chain triglyceride molecules are transform to mono-esters and glycerin. The commonly used short chain alcohol are: methanol, ethanol, propanol and butanol, Marwan *et al.,* (2022). Ethanol is more preferred because it is renewable, non toxic, eco- friendly and can be produce from Agricultural resources. The fatty acid ethyl ester is far better than fatty acid methyl ester in terms of fuel properties, cetane number, oxidation stability and cold flow properties, Dulqarnain, *et al.,* (2021). The major resources use are sourced locally like gourd seed oil and the seed can be planted, maintained, harvested and put to use. The concept of using vegetable oil as an engine fuel is likely dated back to when Rudolf diesel (1858 - 1913) develop the first engine to run a peanut oil. Tang *et al.,* (2010). There was fuel shortage experience in the middle 1970. This lead to renewed interest in diversifying fuel resources with biodiesel as alternate to petroleum diesel emerge Majoy *et al.,* (2008). Other examples of transesterification reactions are:

a. n- Butylacetone + alcohol ⟷ $CH_3COOC_2H_5$ + n C_4H_8OH

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b. methylcyclopentacarboxylate + $C_6H_5CH_3OH$ ⟷
Benzylcyclopentane carboxylate + CH_3OH

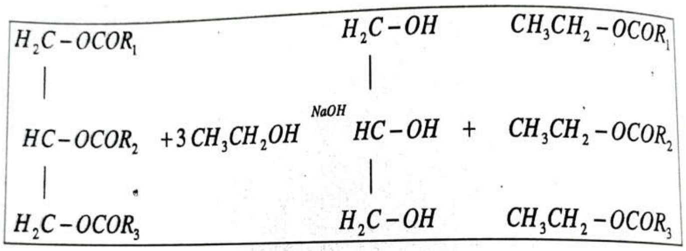
The type of reaction that exist in transeterification reaction is pseudo first order reaction.

Ash gourd: Ash gourd belongs to the cucurbitaceae family of gourd with 25 general and 825 species among them is the ash gourd which is one of the oil seed crop, because there seed produces oil and therefore has the potential of generating energy in term of biodiesel production. Gourd are generally grow as food majorly, and for ornamental while some are cultivated for their rich oils. The fruits are large stalked 20 – 35 cm by 15 - 20 cm spherical to long oblong, hairy at first becoming glaborous dark green, cover with waxy deposit which easily removed, and flesh white spongy in the centre. It grows within 80 to 160 days from the day of sowing. The outer layer of the fruit becomes hard and dried at maturity.

Transeterification : When an ester refluxed with an alcohol other than the one used in its preparation preferablyin the presence of small amount of acid or sodium alkoxide as catalyst, the original alcohol residue in the ester get replaced by the new alcohol. This ester interchange which is actually alcoholysis. (splitting by alcohol) of an ester is known as Transesterification. The reaction is useful for the preparation of ester derived from insoluble acid Solomon (2005). It can also be define as process for biodiesel synthesis that involve the reaction between oil feed stock with short chain alcohol, most likely methanol, in the availability of catalytic medium. Methanol is the commonly used solvent for biodiesel synthesis, Some researchers have suggested the use of ethanol for biodiesel synthesis due to minimized cost with easier availability. NaOH and KOH catalyst are enormously used. Zulqarnain *et al.,* (2021).

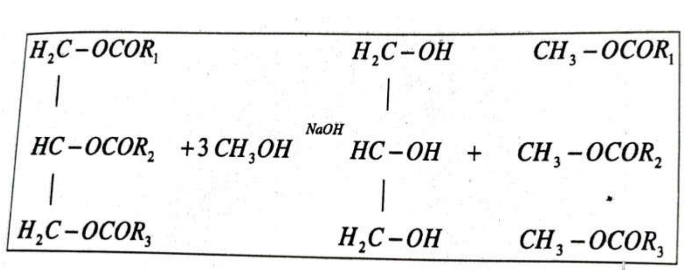
$$RC00R + R'OH \xrightleftharpoons[\Delta]{H^+ \text{ or } {}^-OR} RCOOR" + ROH$$

Fig 1



Vegetable oil Ethanol Glycerol Ethyl ester (Biodiesel)

Fig 2



Vegetable oil Methanol Glycerol Methyl ester (biodiesel)

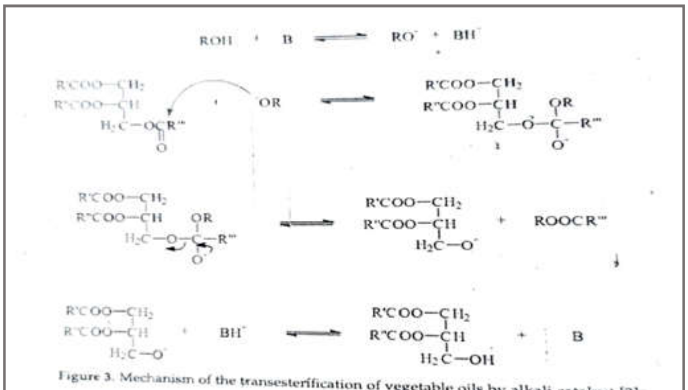


Figure 3. Mechanism of the transesterification of vegetable oils by alkali catalyst [2].

The mechanism of transeterification is most probably analogous to the hydrolysis of ester. In the case of hydrolysis, water act as a nucleophile and displace alcohol whereas in transesterification, the alcohol act as a nucleophile and displaced another alcohol. It is an equilibrium reaction that is thermodynamically control. It becomes necessary either to use large excess of the added alcohol or to remove one of the product from the reaction which is the best, both for stability and yield increase of the major product of interest, Yanhui *et al.,* (2021). Furthermore when the alcohol use is of higher boiling point than the one produced then the removal of the latter by distillation offers a useful method for increasing the yield of ester. Solomon (2005).

JUSTIFICATION: The problem associated with fossil fuel in terms of global warming and other environmental related problem, like oil spillage during extraction of crude, impact of high price of fuel on economic growth demands a transition to renewable sources of energy. Several reports has also being put in place for successful decision making but some of the feed stock has not be properly put to use such, feedstock are gourd species that belong to 25 general with 825 species of cucurbitaceous family and has a substantial amount of oil content in the seed and were underutilized. Therefore, this research seek to study one of such species call ash gourd for its seed oil as one the potential for biodiesel production. This will allow other varieties to be exploited and their planting, be encourage in our environment, especially for industrial use.

EXPERIMENTAL MATERIAL AND METHOD

Sample preparation: The cultivated gourd in University premises was harvested when matured. The ash gourd was wash with water and latter with distilled water and dried in an oven at 105 ^{0}C for 1 hr and was latter brought out from the oven and allow to cool and cut into two using clean dried knife, this will allow the seed to be properly removed and dried again at 50^{o}C for 3 -- 4 hr for the seed coat to be removed easily. After proper removal, the seeds were blended with kenwood blender and the powder was kept in dried PVC plastic, it was latter packed in a thimble and placed inside the soxhlet extractor for the extraction of the oil for 2 – 4 hour where the oil was taking to rotary evaporator for concentrate of the oil. making it ready as feed stock for biodiesel production.

Catalyst preparation: Sodium hydroxide crystals and calcium oxide powder was made to react with methanol and ethanol respectively by reacting 4g of each crystal and dissolved in 250ml of methanol and ethanol and allowed to dissolved inside volumetric standard flask of 250ml capacity. Mixed thoroughly and make up to mark with the alcohol, and then store in a well cork plastic bottle until when needed.
Extraction: The powder ash gourd seed was packed inside the thimble of the soxhlet extractor and placed on heating mantle and extract with petroleum ether (60^{o}C - 80^{o}C) for 2 – 4 hours and allow

to cool and concentrate the oil solution with rotary evaporator, and store in glass sample bottle until when needed.

Methods: The transesterification reaction was performed as follows: 50ml of the extracted ash gourd seed oil +30ml of animal fat (butter) and 20ml of poultry fat. were pour inside a clean dried 500ml separating funnel and add the prepared catalyst solution into each, (methanol and ethanol), and stirred for two hours before taken to the water bath section. The funnel was place inside a thermostatically control water bath regulated to heat at 60°C and heated for two hours with intermittent shaken. After the stipulated time, they were removed and hanged with tripod stand and clamp on the laboratory bench until when cool. The separated two layer inside the funnel the upper lighter layer is the fatty acid ester (biodiesel) and the lower layer is the glycerol. The separated biodiesel can be store in a thick 25ml glass container (pyrex) for drying, first by adding 0.01M acetic acid (10-50ml) and the pH measured with indicator paper and monitored until it neutral to the acid solution, then humidity is removed by adding 10g of sodium sulphate and latter heated on hot plate at 110°C for 0.5hour (30 minutes) and cool making ready for analysis and use.

Statistic Analysis: Observed data was subjected to analysis of variance (ANOVA) to ascertain the source of variance. Least significant difference (LSD) test was use to determine if there was significant different between the mean. The significant was at $p < 0.05$.

DETERMINATION OF IODINE VALUE

1.0g of the biodiesel was weight on a balance (M301). Inside a cleaned dried beaker and 4ml of carbon tetrachloride was added and shaken vigorously until clear solution formed. 100ml of iodine monochloride was also added to the clear oil solution and shaken properly and allow to stand for two hour inside a dark environment. After 2 hours about 1-2g of potassium iodide was added in other to convert the unused reagent to iodine. The librated iodine was titrated with standard solution of 1.0M sodium thiosulphate ($Na_2S_2O_3$) to a colorless end point.

Calculation: $\text{Iodine value} = \frac{C \times B \times M}{W}$

C = volume of iodine monochloride added

B = Volume of thiosulphate used (titre value)

M = Molarity of thiosulphate.

W = mass of oil used.

Determination of Density.

A measuring cylinder cleaned and dried in an oven, cool and of 10ml capacity was weigh on analytical balance, and value recorded as w_1. !.0ml of biodiesel was pour inside and re-weight and final value given W_2. The density is calculated as follows.

$$\frac{W_2 - W_1}{\text{Volume of oil}}$$

W_1 = weight of measuring cylinder empty.

W_2 = weight of cylinder plus the oil.

Acid value determination.

1.0g of biodiesel was weight inside a volumetric flask (250ml) and 50ml of hot ethanol was added and two drop of phenolphthalein was also added as indicator, and the mixture boiled on a heating mantle. The hot, mixture was titrated against 0.1M KOH in a burette untilled permanent pink color appeared. The number of milligram KOH needed to neutralized one gram of the oil was calculated as acid value.

$$\text{Acid value} = \frac{\text{Titre value} \times 56.1}{W}$$

W = weight of oil.

Determination of pH value

5ml of the biodiesel was pour into a clear, cleaned and dried 25ml beaker and 10ml of ethanol was added. The content stirred slowly and the pH electrode probe was immersed into the solution. The pH of the oil sample was read on the pH meter.

Determination of the Ash content

1,0g of the biodiesel oil was weight inside a cleaned, dried crucible on a weighing balance (M301). The content was placed inside a furnace heated to a temperature of 550°C for two hours. Then latter removed and placed inside a desiccators for cooling, and reweight.

Calculation as follows: $\frac{W_1 - W_2}{\text{Weight of oil}}$

W_1 = weight of empty crucible.

W_2 = weight crucible + oil.

Sulphur content:

10ml of biodiesel was measured into a cleaned dried 100ml volumetric flask and 10ml of alcohol added. 25ml of gelatin barium chloride solution wads added, The content was left for 30minutes for color development. The solution color was read on the spectrophotometer set at 425nm. The sulphate content was determined using standard graph. Then the sulphur content of biodiesel was calculated from the amount of sulphate present.

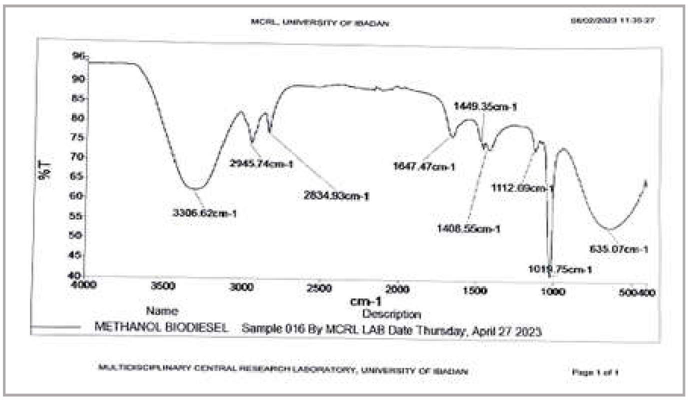
Determination of Viscosity: 60ml of the biodiesel was measure inside a cleaned, dried 100ml beaker and was placed on the working laboratory benches. The viscosity of biodiesel was measure with the viscometer digital machine (M. fission).

RESULTS AND DISCUSSION

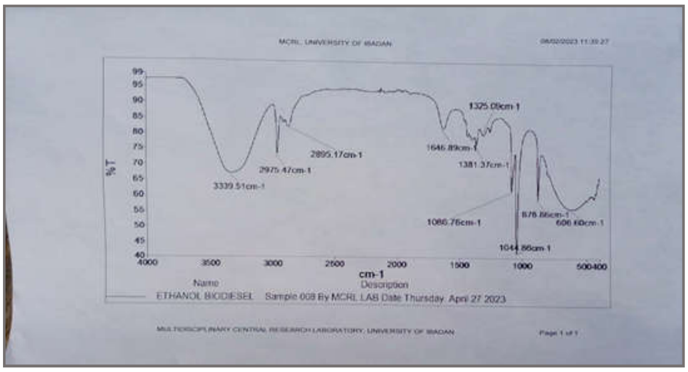
Table 1 Characteristics of biodiesel produce from ash gourd using methanol and ethanol

Parameters	Methanol	Ethanol	Europe Biodiesel standard
Acid number (mgKOH/g)	12.90±0.02	16.83±0.02	
pH	6.5±0.01	6.51±0.01	-
Iodine number (gI_2/100g)	250±0.02	275±0.02	120
Flash point (min.)	105 -110±0.01	100 – 105±0.01	120
Sulphur content (ppm)	0.10±0.01	0.23±0.01	-
Ash content (%)	*0.70±0.1*	0.69±0.1	0.02
Viscosity (mpa/S)	18.85±0.02	24.14±0.02	3.5 – 6-0
Density (g/cm^3)	0.875±0.2	0.922±0.2	860 – 900
Moisture content (%)	0.06	0.054	0.05

± = Standard deviation. Mean are in triplicate value.



Methanol Biodiesel spectrum



Ethanol biodiesel spectrum.

Table 1 above shows the results of the biodiesel analysis and it indicated the acid number: 12.90±0.02(mgKOH/g) for methanol biodiesel and 16.83±0.02 (mgKOH/g) and were far higher than the biodiesel standard requirement of 0.80(mgKOH/g) by ASTM and 0.270 (mgKOH/g) for sunflower biodiesel as reported by Gheorghe *et al.,* (2019) The value is also higher than Mahua oil biodiesel (0.29mgKOH/g) as reported by Antaram, *et al.,* (2015). The iodine value observe : 250 ±0.02 (gI$_2$/100g) and 275±0.02(gI$_2$/100g) for methanol and ethanol biodiesel respectively, of which the value for ethanol biodiesel is higher than that of methanol biodiesel, The high iodine number for ethanol biodiesel indicated its stability since iodine number shows the level of unsaturated present in the ester. The values were also higher than the value require as the maximum :120±0.02 (gI$_2$/100g) as reported by Zakir (2016). The viscosity reveals the value for methanol as 18.85±0.02mpa/S and 24.14±0.02mpa/S for ethanol biodiesel, the values were higher than value recorded for jatropha biodiesel 2.37mpa/S, soybean biodiesel 4.5mpa/S and oil palm 5.7mpa/S as reported by Zakir (2016). While Sumit *et al.,* (2019) reported : 3.7 -- 5.8mpa/s for jatropha and 20.5 - 48.5mpa/s for neem. The density values are: 0.875±0.2g/cm^3 and 0.922±0.2g/cm^3 for methanol and ethanol biodiesel respectively, the value for methanol biodiesel is similar to the value reported for Mahua biodiesel (0.871g/cm^3) by Antaram (2015), but lower to that of ethanol biodiesel. The values were also similar to value reported for candle oil biodiesel (871±6Km^3), jatropha biodiesel (879Km^3) JoJoba biodiesel (871Km^3) by Marwan *et al.,* (2022). All are within the EN14214 standard. The flash point values: 105 -110±0.01 and 100-105±0.01min. for methanol and ethanol biodiesel respectively. The valhes were lower than the value reported for sunflower biodiesel: 168min. and ASTM value of 130 min. by Ghearghe *et al.,* (2019). Generally, the stability of biodiesel can be improve to meet the require minimum standard by the application of improver these substance include acetone, diethylether, ethylaceto acetate, iso-octyl methacrylate etc, and antioxidant like tocopherol, galic etc, may be added usually when just being produced that is before use which display hydrophobic and hydrophilic properties. The spectrum of methanol biodiesel was similar to that of ethanol biodiesel with almost the same peaks . The broad peaks between 3200cm-1 ---- 3550cm-1 is for alcohol stretching (hydrogen bonded), and from 2500cm-1 --- 3000cm-1 for carboxylic acid (hydrogen bounded), from the spectrum, peaks at 3306.62cm-1 and 3339.51cm-1 are for methanol and ethanol biodiesel respectively, both shows the present of alcohol and peaks at 2945.75cm-1 and 2945.74cm-1 in ethanol biodiesel spectrum and 2975.47cm-1 and 2895.17cm-1 in methanol spectrum indicated the present of acid as a broad peaks while peaks between 1630cm-1 -- 1780cm-1 indicate C== 0 stretch for ketone, esters and aldehyde. from the spectrum, peals at 1647.47cm-1 and 1646.89cm-1 for methanol and ethanol biodiesel spectrum and it is within the range therefore esters, ketone are also present.

CONCLUSION

In conclusion, the characteristics of biodiesel from ethanol are somehow similar to that of methanol because they have properties that has a slight differences in which that of ethanol was higherand different but both are within the ASTM standard, and that the toxicity of methanol makes it not be recommended but can be monitored during use, compare to ethanol and that is eco-friendly, stable, less expensive and easily produce from agricultural source, and burnt easily when tested thermally.

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