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Production of Biodisel from Melon Seed *(Citrullus coloncythis L.)*

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Abstract

Oil from Melon seed was extracted using methanol and converted to biodiesel by sodium methoxide catalyst at the reaction temperature of 60^0C for the duration of thirty minutes. The pacentage oil yield was 41%. The physicochemical parameters of the melon oil were found to be: specific gravity, saponification value, acid value, free fatty acid and pH were 0.92, 190.04, 12.67, 6.37, and 7.67 respectively. And physicochemical parameters of the produced biodiesel : specific gravity and pH were found to be 0.885 and 7.53., and for the blends biodiesel (B_{90}, B_{80} and B_{70}) are 0.806, 0.843 and 0.915, with pH of 7.85,7.82 and 7.86 respectively, this shows an excellent miscibility. The fuel properties of the melon seed biodiesel compared with the conventional petrol diesel showed that biodiesel from melon seed oil could be used alone or in blends with petrol-diesel to power compression diesel engines.

Keywords- Biodisel, Transeterification, physicochemical parameters, Melon seed.

Introduction

Biodiesel is an alternative fuel for diesel engines. It is primary advantages is one of the most renewable fuels currently available in the world that is non-toxic and biodegradable. Biodiesel can be produced from any biological carbon source, but the most common sources are photosynthetic plants. The process used to convert this oil to biodiesel is called trans-esterification (Pahl, 2005).

The process biodisel production from fat is not a new process, it was discovered as early as 1853, when scientists Duffy and Patrick conducted the first transesterification of a vegetable oil, many years before the first diesel engine became functional. Transesterification is a process of using an alcohol, such as ethanol or methanol in sodium hydroxide or potassium hydroxide, to chemically break the molecule of the raw renewable oil with glycerol as a by-product (Gerpen, 2005).The increase in population of both the developing and developed nations of the world are the consequence which increase the fuel consumption and the non renewability of diesel source (petroleum), as well as the adverse environmental effects of diesel burning are some of the factors that have made alternatives to petrol diesel very attractive. (Jaturang et al .,2004)..

Blending cracking, pyrolysis, emulsification or transesterification of vegetable oils to produce biodiesel may overcome these problems. Heating and blending of vegetable oil may reduce the viscosity and improve volatility of vegetable oils but the molecular structure remains unchanged, hence poly saturated character remains. Blending of vegetable oil with diesel however reduces the viscosity drastically and the fuel handling system of the engine can handle vegetable oil diesel blends without any problems. On the basis of experimental investigations, it is found that converting vegetable oils into simple esters is an effective way of overcoming all the problems associated with the vegetable oils (Srivastava and Prasad, 2004).

Biodisel Production Processes

The production processes for biodiesel are well known. There are three basic routes to biodiesel production from oil and fats, these are; Base catalyzed transesterification of the oil ,Direct acid catalyzed transeserification of the oil and the Conversion of the oil to its fatty acids and to biodiesel.

Most of biodiesel produced today is through base catalyzed reaction because it operates at low temperature and pressure, high yield conversion (98%) with minimal side reactions and time, It is a direct conversion to biodiesel with no intermediate compounds and no exotic materials of construction needed (Hanna, 1999)

Product Quality

Biodiesel is a better solvent than petrol diesel and has been known to break down deposits of residue in the fuel lines of vehicle that has previously been run on petroleum. Fuel filters may clog with particular test if a good transition to pure biodiesel is made, as biodiesel cleans the engine with the change of fuel filter must be replaced within 600-800 miles after first switching to a biodiesel blend (Hanna, 1999).

Prior to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated equipment to ensure that it meets required specifications for a biodiesel's commercial fuel quality measured by the ASTM standard: D6751 (American standard for testing materials). This ensure that biodiesel is pure and the fuel production process are satisfied by; Complete reaction, Removal of glycerine, Removal of alcohol, Absence of free fatty acids and Low sulfur content (Koraosmanoglu, 1999).

Therefore, biodiesel can be defined as monoalkyl esters of long chain fatty acids derived from vegetable oil or animal fats, for use in compression ignition engine (Pahl, 2005).

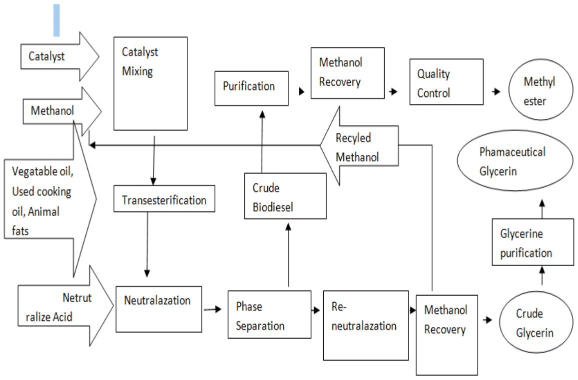
Feed Stock Used in Biodiesel Production

The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled grease. These materials contain triglycerides, free fatty acids and other contaminants depending on the degree of pretreatment they have received prior to production. Since biodiesel is a mono-alkyl fatty acid ester, the primary alcohol used to form the ester is the other major feedstock (Allen, 1997). Most processes for making biodiesel use catalyst to initiate the esterification reaction. The catalyst is required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalyst used are strong mineral bases such as sodium hydroxide and potassium hydroxide. After reaction, the base catalyst must be neutralized with a strong mineral acid (Williams, 1997).

The alcohol and catalyst are mix is then charged into a closed reaction vessel where the oil or fat is added. The system is totally closed while the reaction mixture is kept just above the boiling point of the alcohol (around 71.1^{O}C) to speed up the reaction. The reaction needed about 1 to 8 hours and some systems recommend the reaction to take place at room temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to ester. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil fat. If the free fatty acid level or water level is too high it may cause problems with soap formation (Garpen, 2005).

Production Process

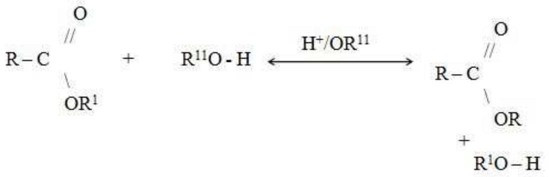
An example of a simple production flow chart is provided with a brief explanation of each step.



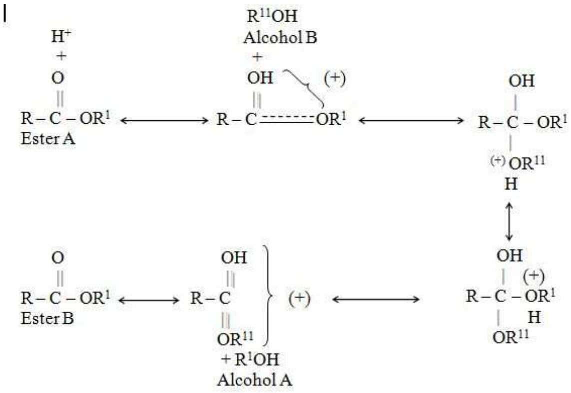
(Hanna.,1999)

Mechanism of Transesterification

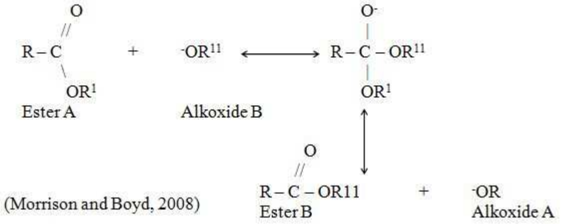
In the esterification of an acid, an alcohol acts as a nuecleophilic reagent; for the hydrolysis of an ester, alcohol is displaced by a nucleophilic reagent .This process is called tranesterification.



Transesterification is catalyzed by a (H_2SO_4 or dry HCl) or base (usually alkoxide). For acid catalyzed;



For base-catalyzed transesterification.



(Morrison and Boyd, 2008)

Experimental

Sample Collection and Preparation

Melon seeds were bought from Malumfashi market, Katsina State. Nigeria , The collected sample of melon seeds was reduced into a smaller piece by Pounding in a mortar using a pestle.

Oil Extraction using soxhlet Extraction Method

Sample of different weight were used for the extraction. 10g of each sample was wrapped in a filter paper, stapled and then weighed. 300ml of methanol was poured into 500ml round bottom flask containing 500ml round bottom flask containing six pieces of anti bumping granules. Each weighted sample was inserted in the center of the extractor.

The round bottom flask containing the solvent that is methanol was heated at 60^0C when the solvent was boiling, the vapour rises through the vertical tube into the condenser at the top. The liquid condensate drips into the filter paper thimble in the center, which contains the sample extracted. The extracted seeps through the pores of the thimble and fills the siphon tube, where it flows back to the round bottom flask. This was allowed to continue for 2 hours 30 minutes. The sample was then removed from the extractor, dried in an oven, cooled in desiccators and re-weighed to determine the amount of oil extracted. Further extraction was carried out using the same procedure for 2 hours 30 minute interval until the required oil needed was obtained. At the end of the extraction, the mixture of the methanol and oil in the round bottom flask was then heated in the reflux where the solvent was recovered and the oil was left in the round bottom flask.

The percentage oil yield was calculated using the formula

$$\%\text{yield} = \frac{\text{weight of extracting oil}}{\text{Weight of oil before extraction}} \times 100$$

Production and Purification of Biodisel

The transesterification reaction was carried out in 1000cm^3 beaker equipped with a thermometer, condenser and magnetic stirrer with a magnetic hot plate at 60^0C.

Heating and mixing

The extracted oil was pre-heated on a hot plate from 48 – 54^0c in 1000cm^3 beaker, a stirrer was inserted into the beaker, and the oil was stirred for 5 minutes. The sodium methoxide solution was then added gently to the oil while stirring continues for 1 hour. The reaction reaches completion in 30 minutes, but longer time is better (that is heated using reflux and condenser for 6.5 hours). Heating speeds up the reaction but the temperature should be maintained at 60^0C.

Setting and separation

The solution was allowed to cool for at least 8 hours, preferably longer. The methyl ester (Biodiesel) was floating on top while the denser glycerine was congealed at the bottom of the separating funnel, forming a hard gelatin. The Biodiesel was carefully decanted into a separate container keeping the reaction mixture above 38^0C will keep the glycerine in a semi-liquid because it solidifies at a temperature below 38^0C.

Washing and drying of fuel

The biodiesel was washed in order to remove products like soap, catalyst and impurities. After separating the unwashed biodiesel from the glycerin, warm water was added to the biodiesel and stirred well. During stirring, a white cloudy solution was formed at the bottom of the container. This cloudy liquid was carefully separated from the washed biodiesel by decantation. The washed biodiesel was then heated to a temperature of 100^0C to derive off the remaining water. The resulting biodiesel was golden yellow in colour.

Physico-chemical analysis of melon seed oil

This analysis was carried out in order to assess the quality of the oil extracted. This is to ascertain the acceptability, stability and other characteristics of the extracted oil in terms of biodiesel production.

Determination of Acid value of the oil

Acid value is the number of milligram(mg) of NaOH required to neutralize the fatty acid in 1g of the fat. 2.8g of the melon seed oil was accurately weighed in 25cm^3 conical flask. 50cm^3 of the solvent mixture (25cm^3 ethanol + 25cm^3 ether in 1:1 v/v) was added. The mixture was then heated gently on a hot plate until all the oil dissolves completely.5 drops of phenolphthalein indicator was then added. The solution was titrated against 0.1N NaOH solution with constant agitation until the end point was reached which was marked by a pink colouration. The titer value T was then recorded. The above steps were repeated 3 times and the average titer value T was calculated and recorded. The acid value was calculated using the following relation.

Acid value = $\underline{40 \times N \times T}$

Where :40 = molar mass of NaOH, N = normality of NaOH, T = titre value , M = mass of oil used

Determination of free fatty acid

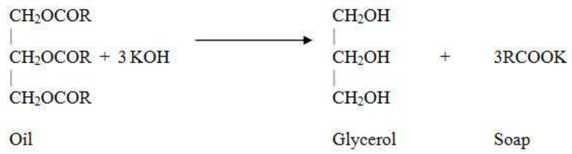
The free fatty acid (FFA) is the percentage by weight of a specified fatty acid for example percentage oleic acid. Acid value and FFA may be converted from one to the other using a converting factor. FFA is calculated after knowing the acid value. It was then determined using the following relation.

$$FFA = \frac{\text{acid value obtained}}{2}$$

Determination of saponification value

Saponification value of an oil is defined as the number of milligram(mg) of potassium hydroxide (KOH) required to saponify (i.e breakdown) 1g of oil into glycerol and salt of fatty acid.

The saponification reaction is represented as follows:



2g of melon seed oil sample was weighed into a conical flask.25cm^{3}of 0.5M ethanolic potassium hydroxide was added to the sample.The sample was then heated with constant stirring for 60mins under reflux.5 drops of phenolphthalein indicator was added to the warm solution .The solution was then titrated against 0.5M HCl to the end point until the pink colour of the indictor disappears blank sample was also prepared and back titrated accordingly. The above steps were repeated 3 times and the sample result (V_1) and that of blank (V_2) were recorded. The saponification value of the melon seed oil sample was then calculated using the equation:

$$S.V = \frac{56.1 \times N \times (V_2 - V_1)}{M}$$

Where: S.V = saponification value , V_2 = volume of the HCl used for the blank test, V_1 = volume of the HCl used for the titration , N = actual normality of HCl used and, M = mass of the oil sample

Determination of specific gravity

A clean and dry density bottle of 50cm^3 capacity was weighed (M_0) .The bottle was then filled to mark with distilled water, corked and reweighed (M_1)The water was poured out and the bottle was dried in an oven and allowed to cool in dessicator. The bottle was again filled with the oil sample to the mark and reweighed (M_2).The whole procedure was repeated 3 times and the result was calculated using the formula

$$\text{gravity} = \frac{\text{mass of the substance}}{\text{Mass of an equal vol. } H_2O}$$

$$= \frac{M_2 - M_0}{M_1 - M_0}$$

Determination of pH of biodiesel

Biodiesel sample was agitated, then the pH value of the sample biodiesel was determined using Jenweh pH meter, model 3320. The pH value was then recorded.

The meter was set to the pH mode and adjusted to the temperature to 25^{0}C, after calibration of the meter. 30cm^{3}of the oil sample was placed in a beaker. The electrode of the meter was immersed into the beaker containing the oil sample. The p^H of the oil sample appears in the display and the reading was taken when the display stabilized.

be 41% 12.74, 6.37, 0.921, 190.04 an7.67 respectively, and the colour was found to be golden yellow are within the ASTM6751 standards, as shown in Table 1

Table 1 Physico-chemical parameters of melon seed oil (MSO) in relation with their corresponding standards.

PARAMETER	MSO	STANDARD
Percentage yield	41%	25 – 45 %
Acid value	12.74	<20.00
Free fatty acid	6.37	-
Specific gravity	0.921	0.87 – 0.9
Saponification value	190.04	175 – 205
Colour	Golden yellow	-
p^H	7.67	-

Table 2 Physicochemical properties of MSO-Biodiesel and commercial fossil diesel

Properties	MSO-Biodiesel	Petro-diesel	ASTM 6751
Colour	Golden yellow	Golden yellow	-
Specific gravity	0.885	0.857	0.87 – 0.9
p^H	7.53	8.56	-

Table 3 Specific gravity and pH of blends Biodiesel

Sample	Specific Gravity	p^H
B_{90}	0.806	7.85
B_{80}	0.843	7.82
B_{70}	0.915	7.86

Discussion

The oil yield estimation after extraction was found to be 41% and it is in the range of the standard oil yield 25 – 45%. As such melon seed oil as non-edible vegetable oil can be used as a feed stock in oil chemical industries (biodiesel, fatty acid, soap, detergent etc.).

Specific gravity has been described as one of the most basic and most important properties of fuel (Alawu et al., 2007) because of its correlation with cetane number, heating values and fuel storage and transportations (Ajab and Akingbehin 2002). The specific gravity obtained for melon seed oil lies within the standard range 0.87 – 0.9 and that of the produced biodiesel was 0.885 slightly higher than the petrodiesel standard range 0.81 – 0.86 as shown in Table 2. the petro-diesel used in this study gave specific gravity of 0.857 lower than that of the melon seed oil 0.921.

The near-neutral pH of the biodiesel produced of 7.67 as shown in Table 1 and that of the produced biodiesel of 7.53 is a welcome development to circumvent the corrosion problems associated with extremes of pH in the metallic component of engines.

Acid value is the measure of the free fatty acid(FFA) content in the biodiesel and is the measure of mg of NaOH required to neutralize FFA in 1g of the sample. The acid value of melon seed oil biodiesel produced in this work was 12.67 as shown in Table 1 hence, this value is an indication of good biodiesel quality.

Saponification values of oil was between the range of the standard 175 – 205mg KOH/g oil. It was found to be 190.04mg KOH/g oil, this high value indicates that the melon seed oil is normally triglycerides and can be used in the production of soap and shampoo.

The specific gravity of B90, B80 are found in the petro-diesel standard range 0.81 – 0.86 while that of B70 was in the biodiesel standard range of 0.87 – 0.9 as shown in Table 3. This indicates that melon seed oil biodiesel could be used in blends with petro-diesel to power compression (diesel) engines.

The pH of B90, B80 and B70 are 7.85, 7.82 and 7.86 respectively as shown in Table 3 which indicate that the blends of melon oil biodiesel could prevent corrosion problems since the pH is near neutral.

Conclusion

The physicochemical parameters of the produced biodiesel and blend biodiesel are very close to that of petrol diesel. This shows that melon seed oil is suitable for industrial production of biodiesel, use of non edible plant seeds that produced high percentage yield of oil for biodiesel production is one of the significant of this research so that the problems like global warming , environmental pollution and energy security will be addresses.

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