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Biodiesel Production by Transesterification of Used Vegetable Oil

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Abstract:

In this research, biodiesel was produced by transesterification of Used Vegetable Oil (UVO) via two stage process. Esterification of the Free Fatty Acid (FFA) in the UVO was carried out in the first stage, using methanol in the ratio of 1:3 and 2wt% tetraoxosulphate (VI) acid as catalyst at 50°C. In the second stage, transesterification of the triglycerides (TGs) in the UVO was done using methanol in the ratio of 1:6 and 1wt% Sodium hydroxide as catalyst at 50°C. The physicochemical properties estimated also gave 158°C, -2°C, 8°C, 0.863g/cm³, 32.462 and 0.5% for Flash Point, Pour Point, Cloud Point, Density (at 15°C), API Gravity and Moisture Content respectively. These values were compared with that of fossil diesel and ASTM Standards. The overall result shows that Used Vegetable Oil is a good alternative feedstock for biodiesel production.

Keywords: Used Vegetable Oil (UVO); Esterification, Transesterification, Biodiesel

1. Introduction

1.1. Current Energy Scenario

Energy sources are the main driver of economic growth and social development of a country. With the exception of hydroelectricity and nuclear energy, the majority of the world's energy needs are supplied through petrochemical source, coal and natural gas (Meng X. *et al.*, 2008). There is an exponential increase in the consumption of fossil fuel both in developed and developing nations; and it is estimated that these fuels shall be exhausted by the turn of 22nd century (Naveen, 2007). The first oil crises of 1973 forced policy makers, scientists and technologists throughout the world to search for alternative sources of energy for the future (Naveen, 2007). With the rapid rate of environmental degradation, present emphasis is essentially focused on the renewable, low cost and environmentally friendly energy sources.

1.2. Need for Alternative Fuels

Rapid escalation of fuel prices and shortage of conventional petroleum based fuels in the world has forced us to look for appropriate technology and alternative fuels to cater for the ever increasing demands of energy. In view of the need for identifying alternative fuels, it is essential that main reasons for depletion of fossil fuels and the related environmental degradation are closely looked into (Meng X. *et al.* 2008). The demand for world energy continues to rise due to two main reasons; the continuing increase in the world population and the growing demand by developing countries for their growth. The world's energy reserves are in finite quantities and at current usage rates will be consumed one day in the near future. These stimulate the need for an alternative to petroleum based fuels.

1.3. Environmental Issues

Indiscriminate use of fossil fuel in various sectors has been a major issue as the significant contributor of environmental degradation (Naveen, 2007). Technologies for fossil fuel extraction, transportation, processing and particularly their combustion, have harmful impacts on our environment. During the extraction, transportation and storage of petroleum fuels, spills and gas leaks cause land, water and air pollution (Ngobiri C. *et al.* 2007). However, major environmental damage occurs during the combustion of the fossil fuels. Fossil fuels, which mainly constitute carbon and hydrogen in addition to traces of sulphur and quality enhancer additives like oxygenates, produce various gases, soot, ash and other organic compounds during combustion which when released into the atmosphere cause complete loss of air quality (Zhang Y. *et al.* 2003). Efforts have been made in the recent past to reduce vehicle pollution by improving vehicle technology and fuel quality. Use of alternative fuels could also be important means of achieving lower exhaust emissions. Global warming is a very serious concern worldwide and has made it imperative that sources and mitigating

options to reduce anthropogenic emissions worldwide are immediately identified. Thus, introduction of a renewable clean-burning alternative fuel is the best option.

1.4. Biodiesel as an Alternative Fuel

Biodiesel, derived from vegetable oil or animal fats by transesterification with alcohol like methanol, is recommended for use as a substitute for petroleum based diesel, mainly because biodiesel is an oxygenated, renewable, biodegradable and environmentally friendly biofuel with similar flow and combustion properties and low emission profile (Zhang Y. *et al.* 2003).

Because of the good properties and the environment improvement credited to it, many countries pay much attention to Research and Development of biodiesel industry and constitute favourable legislation for it (Meng X. *et al.*, 2008). The main advantages of using this alternative fuel are its renewability, better quality exhaust gas emission, its biodegradability and given that all the organic carbon present are photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and consequently, to the greenhouse effect.

1.5. Used Vegetable Oil (UVO) as a Feedstock

Currently, compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization (Meng X. *et al.*, 2008). It is reported that approximately 70% - 85% of the total biodiesel production cost arises from the cost of raw material. Use of low cost feedstock such as used vegetable oil (UVO) should help make biodiesel competitive in price with petroleum diesel. This opens a golden new way and opportunity for the use of UVO as its production feedstock. From the viewpoint of chemical reaction, refined vegetable oil is the best starting material to produce biodiesel, because the conversion of pure Triglyceride (TG) to fatty acid methyl ester (FAME) is high and the reaction time is relatively short (Wang Y. *et al.* 2007).

The purpose of this work is to produce biodiesel from waste cooking oil obtained from restaurants and fast food shops in Nigeria, on a laboratory scale and also compare the physicochemical properties of the biodiesel with that of fossil fuel and standards.

2. Materials and Methods

2.1. Sample Collection and Preparation

Used Vegetable Oil (UVO) was obtained from a Fast Foods restaurant in Owerri, Imo state, Nigeria. The used vegetable oil was mainly contaminated with water, solid particles and Free Fatty Acid (FFA). Since water and FFA create a problem during transesterification, UVO was pre-treated before the reaction. Solid particles in the UVO were removed by heating the oil mildly and leaving the particles to settle, then the oil was decanted out. The oil was washed using warm distilled water. This was to take away dissolved salts. Water was removed by pouring the oil in a separatory funnel. The oil and water layers were allowed to separate under gravity, and the oil was collected. This step was conducted twice to ensure complete removal of salt and water.

2.2. Biodiesel Production

Two stage acid and base catalysis was adopted in the production process. In the first stage, 100g UVO was weighed into a 500 ml beaker and was placed on a hot plate. In another beaker, 2wt% of tetraoxosulphate (VI) acid with respect to UVO was mixed with methanol and then poured to the UVO. The methanol-UVO ratio was 3:1. The mixture was continuously stirred using a glass rod. The reaction temperature was maintained at 50°C. The esterification reaction was continued for 5 hours to ensure the FFA was neutralized to a large extent. The mixture was then allowed to cool. Water formed was removed using separatory funnel.

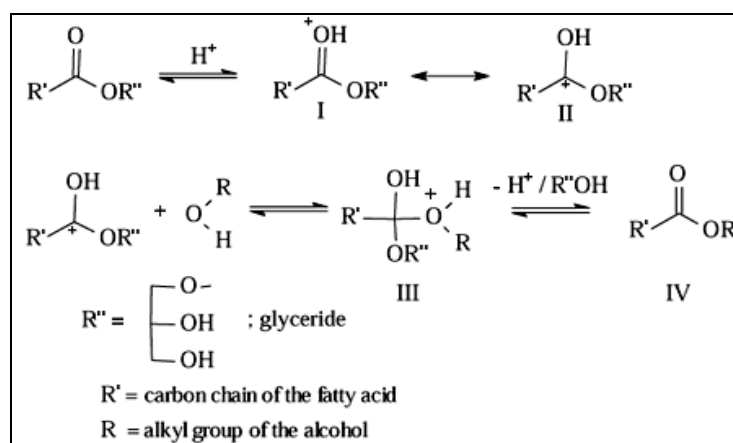


Figure 1: Mechanism of acid catalysed transesterification of vegetable oils.

Source: http://www.scielo.br/scielo.php?script=sci_arttext&pid=s0103-50531998000300002

In the second stage, the upper layer (oil) was collected and weighed. 100 ml of the pre-treated oil was measured into a 1litre pre weighed round bottom flask. The flask with the oil was weighed using Mettler electronic weighing balance (Model LT 502 d = 0.01g

Max 500 g). 1% weight Sodium hydroxide was dissolved in 100ml methanol which after dissolution was made up to 600ml with methanol. This was mixed with the oil in the round bottom flask and was agitated. The mixture was refluxed at 50°C for 1hour. The mixture was then removed and allowed to cool after 1 hour. This was later transferred into a 500ml separatory funnel and allowed to separate under gravity. The upper layer which contained methanol, biodiesel and little amount of soap was recovered. The biodiesel was washed with distilled water in a separatory funnel until the lower phase became clear. The biodiesel was then recovered and stored in an air tight container.

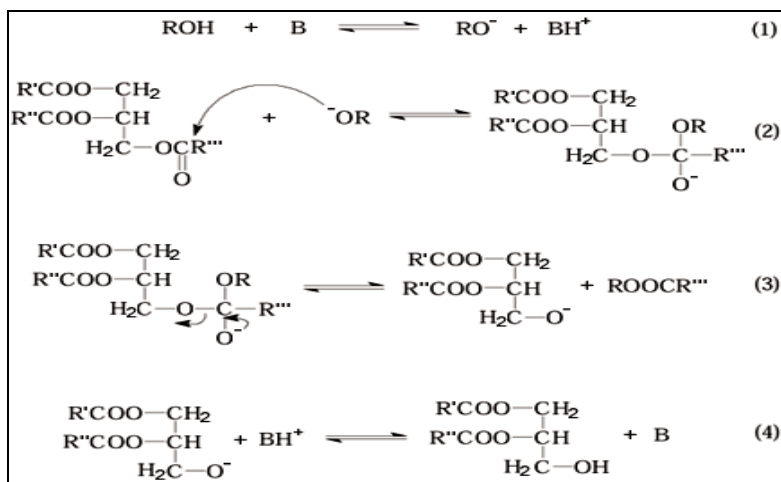


Figure 2: Mechanism of base catalysed transesterification of vegetable oils

(Source: http://www.scielo.br/scielo.php?script=sci_arttext&pid=s0103-50531998000300002)

2.3. Physicochemical Properties Determination

2.3.1. Colour Determination

A sample of the ester was placed in a transparent reagent container and the colour was compared with coloured glass disk until a matching colour was found using a standard light source (ASTM D1500).

2.3.2. Water Content Determination

10g each of the sample was weighed in a previously weighed crucible. The samples were dried in the JP Selecta Electric Oven operated at 105°C, for one hour, cooled in a desiccator containing silica gel overnight before re-weighing (AOAC, 1990).

2.3.3. Density/Api Gravity Determination

10 cm³ of purified biodiesel was cooled in a refrigerator to 15°C. A clean and dry density bottle was weighed (w_1). It was filled with the biodiesel, covered, cleaned and reweighed (w_2).

2.3.4. Flash Point Determination

10grams of the purified biodiesel was put in open cupdevice and heated on a hot plate. At every increase of 5°C a burning splint was placed above the crucible for possible ignition. After the initial temperature was recorded, the procedure was repeated at regular intervals until an ignition was observed. The temperature at that point was recorded.

2.3.5. Cloud Point Determination

50ml of the sample was measured into a 500 ml beaker and the sample placed into a deep freezer. The sample was inspected at intervals. When the bottom of the container became hazy, the temperature was recorded.

2.3.6. Pour Point Determination

The sample was cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9°C above the expected pour point, and for every subsequent 3°C, the test jar is removed and tilted to check for surface movement. When the specimen does not flow when tilted, the jar is held horizontally for 5seconds. 3°C is added to the corresponding temperature and the result was recorded. (ASTM D5853)

3. Results and Discussion

3.1. Results

The results obtained from the transesterification of used vegetable oil are summarised in the table 1.

PARAMETERS	RESULTS
COLOUR	Light brown
FLASH POINT	158°C
POUR POINT	-2°C
CLOUD POINT	8°C
DENSITY (at 15°C)	0.863g/cm ³
API GRAVITY	32.462
WATER CONTENT	0.5 %

Table 1: Qualitative results of the purified biodiesel

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC ^a (C10-C21)	FAME ^b (C12-C22)
Kin. Viscosity at 40°C	1.9-4.1 mm ² /s	1.9-6.0 mm ² /s
Specific gravity	0.85 g/ml	0.88 g/ml
Flash point	60-80°C	100-170°C
Cloud point	-15 to 5°C	-3 to 12°C
Pour point	-35 to -15°C	-15 to 16°C
Water	0.05vol %	0.05vol %
Carbon	87wt %	77wt %
Hydrogen	13wt %	12wt %
Oxygen	0wt %	11wt %
Sulphur	0.05wt %	0.05wt %
Cetane Number	40 – 55	48 – 60
HFRR ^c	685µm	314µm
BOCLE ^d scuff	3600 g	>7000 g

Table 2: Values for the American Society for Testing and Materials (ASTM) standards of maximum allowed quantities in Diesel and Biodiesel. ^a Hydrocarbons, ^b Fatty acid methyl esters, ^c High frequently reciprocating rig, ^d Ball-on-cylinder lubricity evaluator.

Source: (Lotero E. et al. 2004)

The results are compared with American Society for Testing Material standards for biodiesel in table 3.

Property	Results	Standards	Petroleum Diesel
FLASH POINT	158 °C	100-170 °C	60-80 °C
POUR POINT	-2 °C	-3 to 12 °C	-15 to 5 °C
CLOUD POINT	8 °C	-15 to 16 °C	-35 to -15 °C
DENSITY (at 15°C)	0.863 g/cm ³	0.860 – 0.900 g/cm ³	0.82 – 0.845 g/cm ³
API GRAVITY	32.462	NA	NA
WATER CONTENT	0.5 %	0.05	0.05

Table 3: Correlating Results with Standards

Source: (Lotero E. et al. 2004) and (Umunakwe C. 2009)

3.2. Discussion

In the acid esterification of the UVO, it was observed that with methanol oil ratio of 3:1 and 2wt % of the acid with respect to the UVO reduced the FFA to a large extent hence reducing the side reaction (saponification). Similar work done by T. Issariyakul *et al.* (Issariyakul T. *et al.* 2007) and N. Ozbay *et al.* (Ozbay N. *et al.* 2008) have shown that esterification of the waste fryer grease reduced the FFA also bringing the acid value down from 25 to 15. This is in conformity with the result in this work; hence esterification of the UVO was necessary.

Flash point of fuel is the minimum temperature at which it gives enough vapours to form a flaming mixture that ignites for a moment, when a tiny flame is brought near it. Interestingly, the flash point of the UVO methyl ester was found to be 158°C. This is in conformity with ASTM standard for diesel; values ranging between 60°C- 80°C and 100°C – 170°C for diesel and biodiesel

respectively. Similar works by Xiangmei *et al.* (Meng X. *et al.*, 2008) and also by Yong *et al.* (Wang Y. *et al.*, 2007) show that the UVO methyl ester has a flash point falling within international standards and will therefore imply good ignition properties.

Cloud point is the temperature at which a cloud of wax crystals first appears in the oil when it is cooled. Pour point is the lowest temperature at which the oil specimen can still be moved. Cloud point and pour point are used to measure the cold temperature usability of ester as fuel. According to the ASTM standards of maximum allowed quantities in diesel and biodiesel (Loterio E. *et al.*, 2004), Cloud point of esters was in the range of -3°C to 12°C while pour point range was -15°C to 16°C . In this work, the cloud point was determined to be 8°C and the pour point determined to be -2°C which fell within the range of ASTM standards, implying good cold weather usability.

Density is the ratio of mass of a given volume of liquid at a specific temperature. API gravity determines fuel density and along with distillation, is used to calculate Cetane index. The density according to the ASTM standards for the maximum allowed quantities has the range $0.860 - 0.900 \text{ g/cm}^3$ at 15°C (Umunnakwe C. 2009). Density was determined to be 0.863 g/cm^3 and the API gravity calculated to be 32.462 in this work. Similar work done by C. Umunnakwe (Umunnakwe C. 2009) has shown the density of the purified biodiesel to be 0.8776 g/cm^3 at 15°C , which also is in consonance with the ASTM standards.

3.3. Conclusion

The results in this research, has so far shown that used vegetable oil could be a good alternative feedstock for biodiesel production. Acid pre-treatment is necessary to reduce the interference of FFA during the transesterification reaction. This two-step catalysed process provides a simple and economic method to produce biodiesel from UVO. The by-products of glycerol and soap stock in this process can be easily handled.

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