Production of Biodiesel from spent cooking oil and Oxidative stability Improvement using Onion scale extracts

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Abstract- The need for a clean and cheap source of energy is ever increasing in our world today. Biodiesel has become a topic of interest for some time and researches are still on-going on how to obtain cheaper feedstock for biodiesel production. Moreover, there is need to improve the oxidative stability of biodiesel which is a measure of its shelf life, seeing that biodiesel is biodegradable. This research work considers the production of biodiesel from a cheap and viable feedstock; spent cooking oil. The feedstock was subjected to acid etherification reaction which reduced its free fatty acid level from a value of 2.16% to 0.9% which is suitable for biodiesel production. A transesterification reaction catalyzed by Sodium Hydroxide was carried out on the oil at $60^{O}C$, using a methanol to oil ratio of 6:1 for a period of 60 minutes. The biodiesel yield was 89.4% and the product was subjected to physicochemical characterization which showed that its properties closely approximate the standard values. Furthermore, the ethanolic extract obtained from waste onion scales were introduced into some of the biodiesel after which the acid and peroxide values were monitored for a period of seven weeks. The results obtained showed that the onion extract was able to fairly inhibit the rate of increase in the acid and peroxide values of the biodiesel produced which are parameters that were used to measure the oxidative stability of biodiesel and hence its shelf life. It was therefore concluded that onion extract is a viable natural antioxidant for improving the oxidative stability of biodiesel and hence its shelf life.

Keywords- biodiesel, oxidative stability, onion scales, peroxide value, acid value, transesterification

I. INTRODUCTION

In the world today, there is a great need for energy; one that is clean, safe and environmentally friendly. There are many sources of energy such as solar, wind, hydro, geothermal energy, fossil fuels, etc. The use of fossil fuels has greatly increased over the years, and these fuels account for more than fifty percent of the world's energy supply. The probable scarcity of fossil fuels in the near future, combined with concerns over the consequences of dependency on this type of energy source, in terms of changes in the Earth's climate, has forced the world to find alternatives that are less harmful to the environment. Renewable energy sources, especially vegetable fuels, have appeared as an important alternative. (Santana et al., 2010).

One of such renewable energy sources is biodiesel, which can be produced from the transesterification of various types of vegetable oils and animal fat. The emissions produced from the combustion of biodiesel are cleaner compared to petroleum-derived diesel fuel and has the potential to solve many of the current social problems and concerns from air pollution and global warming to other environmental improvement and sustainability issues.

However, a great economic challenge for the biodiesel commercialization is the high cost of pure vegetable oils, which represents 70% to 85% of the overall production cost (Haas & Foglia, 2005).
Among the sources of feedstock for the biodiesel production are rapeseed, palm, sunflower, and soybean oils. However, their availability to be used in the biodiesel production is limited due to competition with edible oil markets and consequent price increase (Kansedo et al., 2009).

Therefore, the search for new sources of biodiesel production is necessary, such as spent cooking oil that can be acquired at little or no cost. Therefore, the use of this feedstock for the biodiesel production is a promising alternative as it combines economical aspects, due to the low cost of feedstock acquisition, with environmental preservation, as it prevents water sources contamination at the same time producing a less pollutant fuel.

Furthermore, research has shown that biodiesel does not last as long as the petroleum derived diesel due to biodegradation as a result of oxidation. In response to this, several synthetic antioxidants have been developed

to help improve the oxidative stability of biodiesel and hence improve its shelf life. However, some of these substances are costly, toxic and non-biodegradable and for this reason it has become important to derive antioxidants from plant sources which serve the same purpose as the synthetic antioxidants while minimizing cost and reducing pollution to the environment.

II. ALKALI CATALYZED TRANSESTERIFICATION

The chemical reaction by which a lower alcohol reacts with a triglyceride to yield a fatty acid alkyl ester is known as transesterification. Transesterification occurs more easily with alcohols like ethanol and methanol. Even though it is a slow process, it can be accelerated with the help of a catalyst. Traditionally, an alkaline catalyst such as sodium or potassium hydroxide is used to catalyze and accelerate the reaction at standard temperatures and pressures. Catalysts provide a phase-transfer as well as an ion exchange effect which reduces reaction times by many orders of magnitude (Mittelbach & Remschmidt, 2004). The triglyceride is converted in consecutive steps from a triglyceride to a diglyceride, to a monoglyceride, and finally to glycerol.
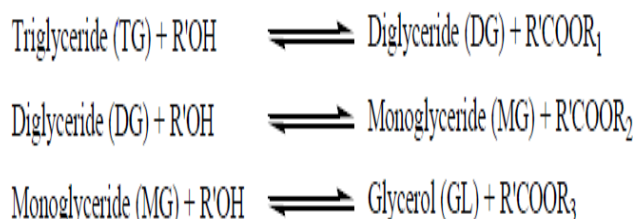

Fig. 1 The transesterification reactions of vegetable oil with alcohol to esters and glycerol. (Freedman et al., 1986).

Alkali transesterification is the most widely used process because it uses moderate temperature and lower pressures when compared to other transesterification methods, it also has high conversion efficiency.

III. MATERIALS AND METHODOLOGY

Spent cooking oil was collected from Sunic restaurant at Federal University of Technology, Owerri, Imo State, Nigeria, for the research project and the experiments (i.e. physicochemical analysis, esterification and transesterification reactions) were carried out in the Chemical Engineering Laboratory at Federal University of Technology, Owerri, Nigeria.

1. Determination of free fatty acid (FFA) of the oil for the production of biodiesel

1g of the spent cooking oil was dissolved in a conical flask containing $25cm^3$ of propanol. 3 drops of an indicator (phenolphthalein) was then added to the dissolved oil. Titration was carried out on the mixture of oil and indicator against 0.1M potassium hydroxide. The average titre value after three titrations was used to calculate the acid value and FFA value of the oil using the following formula adopted from Kabiru et al., 2016:

$$Acid\ value = \frac{Titre\ value\ x\ Conc.of\ KOH\ x\ 56.1}{Weight\ of\ Oil} \quad (1)$$

$$FFA = \frac{Acid\ value}{2} \quad (2)$$

2. Esterification Reaction of FFA in the oil

In order to reduce the free fatty acid content of the oil to a value less than 1%, the etherification reaction procedure adopted from Kabiru et al., 2016 was used. 400g of spent cooking oil was poured into a beaker and placed in a constant temperature water bath which maintained a temperature of $60^{O}C$. Methanol corresponding to 20%w/w of the oil was also added. Sulphuric acid was also measured whose amount was 5%w/w of the oil. The methanol and acid were mixed thoroughly and then added to the oil. The whole mixture was continuously heated and stirred for 60 minutes. After one hour, the mixture was poured into a separating funnel and allowed to separate. After separation, two layers were observed; the upper layer is the methanol-acid mixture while the lower layer is the oil. The oil was tested again to ascertain reduction in FFA, and if the FFA is still greater than 1%, another round of esterification was done as described above, once the FFA became less than 1%, the process of esterification was suspended and the oil was then ready for biodiesel production

3. Transesterification reaction procedure (Biodiesel production)

The procedure used for the transesterification process was adopted from Ojolo et al., 2011. 200ml of oil was measured and poured into a beaker; this oil was pre-heated to a temperature of $60^{O}C$ with the aid of a magnetic heater/stirrer. 40ml of methanol was measured with the aid of a measuring cylinder and poured into a beaker. 0.7g of Sodium hydroxide was also measured and added to the methanol. The mixture was stirred vigorously using a magnetic stirrer until the sodium hydroxide pellets were completely dissolved in the methanol.

The mixture of methanol and sodium hydroxide now known as sodium meth oxide was poured into the pre-heated oil. The whole mixture was then stirred continuously with continued heating at a temperature of $60^{O}C$ for a period of one hour. The mixture was then poured into a separating funnel where the biodiesel was separated from the glycerol. The glycerol which is a by-product was run off from the bottom of the separating funnel while the biodiesel was then collected separately for storage.

4. Physiochemical Characterization of Biodiesel

After the production of biodiesel from spent cooking oil, the biodiesel was subjected to the following physical and chemical properties analysis.

4.1 Colour Test- The colour test was carried out by inspecting the product visually.

4.2 Viscosity- The viscosity was determined using the angler viscometer, and the formula:

$$V = 0.226t - \frac{19.5}{t} \qquad (3)$$

Where t = time taken for the biodiesel to flow from the viscometer completely.

4.3 pH Test- The pH was measured using the pH meter at room temperature.

4.4 Density and Specific Gravity/API Gravity- This was measured using the pycnometer.

Density was calculated as:

$$Density = \frac{wt\ of\ biodiesel}{vol\ of\ biodiesel} \qquad (4)$$

Specific gravity was calculated as using:

$$SG = \frac{Density\ of\ biodiesel}{Density\ of\ equal\ vol\ of\ water} \qquad (5)$$

The API gravity was calculated as:

$$API = \frac{141.5}{S.G} - 131.5 \qquad (6)$$

4.5 Acid value, Iodine value, peroxide value, saponification value, Cetane number- The values of these properties were calculated using the appropriate formulae and the values obtained were compared with the standard.

The acid value of the biodiesel was calculated:

$$AV = \frac{5.61*T}{W} \qquad (7)$$

Where T is volume in ml of 0.5N NaOH required for titration in ml and W is weight in grams of sample taken.

Iodine value was calculated using:

$$IV = \frac{12.7\ (B-S)}{Weight\ of\ sample\ (g)} \qquad (8)$$

Where S is volume of thiosulphate used with oil sample and B is volume of thiosulphate without oil/ blank.

The peroxide value was calculated using:

$$PV = \frac{(S-B)*N*1000}{Weight\ of\ sample\ (g)} \qquad (9)$$

Where N is molarity of NaOH required for titration in ml

The saponification value was calculated using:

$$SV = \frac{28.05*(T_2-T_1)}{W} \qquad (10)$$

Where T_2 is volume in ml of 0.5N acid required for the blank, T_1 is volume in ml of 0.5N acid required for the sample. Cetane Number was calculated as

$$CN = \frac{46.3+5458}{SV - (0.225\ x\ IV)} \qquad (11)$$

4.6 Preparation of Plant Extract

Waste onion scales were sourced domestically. The scales were washed, cut into strips and sun dried for two days. The dried leaves were ground using an electric grinder. 50g of the ground onion scales was soaked in 400ml of ethanol and boiled in a soxhlet extractor for three (3) hours. The resulting solution was cooled and filtered using whatman No. 42 grade filter paper. After filtration, the amount of the ground leaves that was extracted into the solution was quantified as the difference between the initial weight of the ground leaves and the weight of the dried residue. 20ml of the stock (extract) solution was withdrawn for phytochemical analysis.

4.7 Qualitative Phytochemical Analysis- The qualitative tests were carried out using the standard methods of analysis for Flavonoids and Phenolics as described by Estherlydia and Praveena (2014). Test for Flavonoids: 1ml of 2 N NaOH was added to 2ml of the plant extract. The yellow colour observed showed that flavonoids were present.

Test for Phenolics 2ml of Iron (III) chloride was added to the extract. The dark violet colouration revealed the presence of phenolics in the sample. After the phytochemical analysis was carried out, the ethanolic extract was placed in a water bath set to $82^{O}C$ with continuous stirring in order to vapourize the ethanol. After vapourising most of the ethanol, the extract was placed in a hot air oven at $68^{O}C$ for fifteen minutes to ensure complete drying and removal of the extraction solvent.

4.8 Analysis to Determine Antioxidant Activity of the Obtained Extract

In order to determine the antioxidant activity of the extract in biodiesel, 0.5g of the extract was introduced into 200ml of the biodiesel produced. Another 200ml of biodiesel without the onion extract was set aside for comparison. These two samples were analyzed weekly by carrying out tests for Acid Value and Peroxide value on both of them. This process was repeated weekly for a period of seven weeks.

IV. RESULTS AND ANALYSIS

The results from the physicochemical characterization of biodiesel produced from spent cooking oil is presented in table 1 below and compared with ASTM and European biodiesel standards (EN14214).

The result of qualitative phytochemical analysis of the onion extractis is presented in table 2. These phytochemical compounds include quercetin, which is a flavanoid, and other compounds which are generally believed to be responsible for the oxidation inhibitive effects of plant extracts.

After successfully carrying out the peroxide value tests on the biodiesel sample without the onion extract (neat biodiesel), the results obtained are presented in table 3 alongside peroxide value tests for biodiesel with onion extract and the percentage reduction in oxidation achieved by the addition of onion extract for each week studied.

Table 1 Physicochemical Properties of Biodiesel from Spent cooking oil.

Properties	Biodiesel from Spent cooking oil	American Society of Testing and Materials (ASTM) diesel standard	EN14214 European Biodiesel Standard
Color	Amber Yellow	-	-
Moisture Content (%)	0.06	0.05 max	0.02
Specific Gravity	0.875	0.86-0.9	0.85
Viscosity (mm²/s @40°C)	2.34	1.9-6.0	3.5-5.0
Iodine Value	118.652	-	120 max
%FFA	1.26	-	-
Acid Value	2.52	<0.80	0.5 max
Saponification value	165.495	-	-
Peroxide Value	6.00	-	-
API gravity	30.214	150	-
Cetane number	52.58	47 min	51-60
Yield (%)	87.8	-	-

Table 2 Result of Qualitative Phytochemical Analysis.

S/N	Compound	Onion Extract
1.	Flavonoids	Present
2.	Phenolics	Present

Table 3 Change in peroxide value with time

Time (weeks)	Peroxide Value (meq.$O_{2\,kg}^{-1}$) (Biodiesel with Onion extract)	Peroxide Value (meq.$O_{2\,kg}^{-1}$) (Neat Biodiesel)	Percentage Reduction In Oxidation (Based On Peroxide Value)
0	6	6	0
1	6.15	6.53	5.8193
2	6.35	7.08	10.3107
3	7.56	8.2	7.8049
4	8.89	9.93	10.4733
5	9.26	10.4	10.9615
6	9.87	10.92	9.6154
7	10.14	11.56	12.2837

The average percentage reduction in oxidation achieved by the addition of onion extracts is 9.6098. After successfully carrying out the acid value tests on the biodiesel sample without the onion extract (neat biodiesel), the results obtained are presented in table 4 alongside peroxide value tests for biodiesel with onion extract and the percentage reduction in oxidation achieved by the addition of onion extract for each week studied. The average percentage reduction in oxidation achieved by the addition of onion extracts is 10.3505.

Table 4 Change in Acid Value with time.

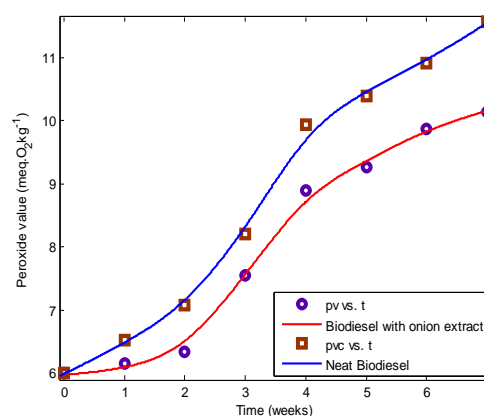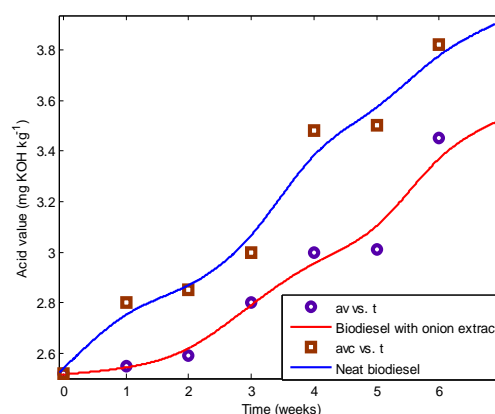| Time (weeks)	Acid Value (mg KOH_{kg}^{-1}) (Biodiesel with Onion extract)	Acid Value (mg KOH_{kg}^{-1}) (Neat biodiesel)	Percentage Reduction in Oxidation (Based on Acid Value)
0	2.52	2.52	0
1	2.55	2.8	8.9286
2	2.59	2.85	9.1228
3	2.8	3	6.6667
4	3	3.48	13.7931
5	3.01	3.5	14.0000
6	3.45	3.82	9.6859
7	3.5	3.9	10.2564

Fig. 1 Peroxide value versus time

Fig. 2 Acid value versus time.

V. DISCUSSION

The Moisture Content of Biodiesel from Spent Cooking oil was obtained to be 0.06%. Though this value is a bit high, it still closely approximates to the maximum requirement given by the American Society of Testing and Materials. The high moisture content could be as a result of improper handling of the biodiesel as well as

using apparatus that are not well dried before carrying out analyses. When moisture content value is too high, it could result in the growth and accumulation of micro organisms which could act on the biodiesel and hasten its degradation, thereby making it unfit for use in automobile engines.

The Specific Gravity was obtained to be 0.875 which is well within the specification given by the American Society for Testing and Materials; hence the specific gravity is acceptable. The Acid Values of the biodiesel from Spent Cooking Oil was measured to be 2.52mgKOH/g. Acid value is a measure of the content of free fatty acids in the biodiesel which could be as result of oxidation. From table 1, it may be observed that the standard specified by the American Society of Testing and Materials is way below the calculated value. This could be as a result of inadequate covering of the biodiesel which exposed it to atmospheric oxygen much more than was required. The Viscosity was obtained to be 2.34mm^2/s which falls within the standard range specified by the American Society of Testing and materials. The viscosity of biodiesel should not be too high; else the fuel won't run on an automobile engine. If it becomes slightly lower than the standard, then it could result in an increased fuel consumption which is not economically desirable. The Cetane number of the biodiesel was obtained to be 52.58. Since this value is within the specified standard range, it means that the biodiesel produced from spent cooking oil will ignite and combust properly with moderate exhaust gas emissions.

From the plot of fig. 1, it can be observed that there is an increase in peroxide value for both the neat biodiesel and the one containing the onion extract. However, the rate of increase in peroxide value for the second sample (containing onion extract) is observed to be slower. This can be attributed to the inhibitive action of the onion extract in slowing down the oxidation process, thereby minimizing the formation of peroxides. From the plot of fig. 2, it can be observed that there is a progressive increase in acid value for both the neat biodiesel sample and the one that is containing the onion extract.

However, it could also be noted that the acid value increases at a higher rate in the sample without the onion extract. Since Acid value is also a measure of the extent of oxidation in biodiesel whose value represents the further breakdown of peroxides to form acids, it can be concluded that the onion extract is fairly effective in inhibiting the decomposition of peroxides into acids in the biodiesel sample as it reduces oxidation by about 10%.

VI. CONCLUSION

Biodiesel was produced from spent cooking oil using an alkali catalyzed transesterification process with a product yield of 87.8% after carrying out an esterification reaction twice to reduce the free fatty acid level of the oil from 2.16% to 0.9%. The physicochemical characterization of the product closely approximate to the standards given by the American Society of Testing and Materials for biodiesel. It may be concluded that spent cooking oil is a viable feedstock for the production of biodiesel and that the final product can be used as an alternative fuel for diesel engines. Also, it has been confirmed that the extract from waste onion scales can be used as an antioxidant to improve the oxidative stability of biodiesel, seeing that it is rich in flavonoids and phenolics which are natural oxidation inhibiting compounds. The antioxidant activity of the onion extract moderately inhibits the increase in acid and peroxide values in the biodiesel and can therefore be used for improving the shelf life of biodiesel.

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