



EFFECT OF TRANSESTERIFICATION REACTION TEMPERATURE ON THE YIELD AND QUALITY OF BIOFUEL PRODUCED FROM RUBBER SEED (*Haveabransilenses*) OIL



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Abstract: In this study, the effect of transesterification reaction temperature on the yield and quality of biofuel produced from Rubber Seed Oil (RSO) was analyzed. A two-step transesterification procedure was carried out to convert RSO to its methyl ester. Temperature was varied during transesterification and biofuel produced was analyzed for selected properties and compared with ASTM standards. Experimental results showed that as the reaction temperature was increased from 40 to 60°C, the yield increased from 40.4 to 76.9%, the kinematic viscosity decreased, the density remained constant at 870 kg/m³; acid value increased from 0.35 to 0.48; calorific value was initially constant at 36.23 MJ/kg when the reaction temperature was increased from 40 to 45°C, and increased to 36.28 MJ/kg when the reaction temperature increased to 50°C and remained constant thereafter even when the reaction temperature increased from 50 to 60°C. The flash point of the biodiesel initially decreased as the reaction temperature was increased from 40 to 50°C. Thereafter, the value of flash point had a constant value as the reaction temperature increased from 50 to 60°C. These fuel properties were generally found to be within the standards specifications of ASTM.

Keywords: Biofuel, fuel properties, quality, rubber seed oil, temperature, yield

Introduction

Energy demand is increasing dramatically because of the fast industrial development, rising population, expanding urbanization and economic growth in the world. To fulfil this energy demand, a large amount of fuel is widely used from different fossil fuel, especially petroleum (Ashrafulet *al.*, 2014). The magnitude of fossil fuel consumption is inversely proportional to the petroleum reserves currently available. Fossil fuel reserves are few in numbers and they are already reaching their peak production (Ahmad *et al.*, 2013). Alternative sources of fuels have been exploited by researchers and biofuel is one of such promising alternatives.

Biofuel is a generic name of liquid, solid or gaseous fuel that is produced from biological source; it is a product produced from biomass (Imaekhaiet *al.*, 2014). Biofuel is considered cleaner than fossil fuel (Lawrence *et al.*, 2014). Biofuels are fuels derived directly from living matters and they are a renewable form of energy. The process of converting vegetable oil into methyl ester is called transesterification, where alcohol reacts with triglycerides of fatty acids (vegetable oil) in the presence of a catalyst (Iyayiet *al.*, 2007). Methyl (or ethyl) ester is obtained during the process of transesterification of plant oils or animal fats with the presence of methanol or ethanol and some basic catalyst.

The main species analyzed for the production of biofuel has been kernel oil, coconut oil, jatropha oil, waste oil etc (Owolabiet *al.*, 2011). Rubber has been regarded as a multipurpose crop over the years. Rubber is renewable, non-edible and readily available in Nigeria. Rubber belongs to Euphorbiaceae family and native to Nigeria. The tree, wood and latex from rubber can be used for numerous purposes including fuel and manufacture of rubber related materials. The seed contains viscous oil which can be used for the manufacture of candles and soap. The oil extracted from rubber seed is used for producing biofuels. The production of biofuel involves the following steps; transesterification process and washing process (Da Luz *et al.*, 2015).

The aim of this study was to produce biofuel from vegetable oil, specifically rubber oil. Transesterification of RSO was carried out at different temperatures, to determine the yield at different temperature range. Characterization of RSO and the produced Biofuel were also carried out.

Materials and Methods

Materials

Heveabrsilensis, the rubber tree or rubber plant, is a tree belonging to the family Euphorbiaceae. It is the most economically important member of the genus *Hevea* because the milky latex extracted from the tree is the primary source of natural rubber. RSO used in this work was obtained from Rubber Research Institute, Iyanomo, Edo State, Nigeria. The reagents used were Methanol, Sodium Hydroxide, Sulfuric acid, Phenolphthalein, Hydrochloric acid, 0.5M Alcoholic potassium hydroxide. All reagents used were of analytical grade and were procured from a local vendor. Distilled water was used for washing and dilution. The RSO was carefully stored in a glass bottle before taken for analysis and reaction.

Methods

RSO composition analysis

The saponification value of RSO was determined using the Association of Official Analytical Chemists (AOAC, 2000) methods. Standard ASTM methods were being used to find, acid value (ASTM D664), viscosity (using viscometer NDJ-9S) ASTM D2270, ester value (ASTM D1617), molecular weight (ASTM D2503), calorific value (ASTM D240), kinematic viscosity (ASTM D445), density (ASTM D4052), and cetane number (ASTM D613).

Biodiesel production

The process consisted of two steps namely, acid esterification and alkaline esterification.

(a) Acid esterification: One litre of crude RSO was poured into a round bottom flask and heated to 40°C. 200 mL of methanol was added and stirred to ensure homogeneity, and 0.5% of sulfuric acid was added to the mixture. The mixture was stirred while heating to ensure uniform distribution of heat. On completion of this reaction, the product was poured into a separating funnel for separating the excess alcohol (Da Luz *et al.*, 2015).

(b) Alkaline esterification: 200 mL of the acid esterified oil was poured into a round bottom flask after which 40 mL of methanol and 10 g of NaOH were added. The mixture was heated at 40°C and stirred for 30minutes, and the product was separated using separating funnel. The bottom layer having a brownish red colour and containing the impurities and crude glycerol was drawn off. The biodiesel formed at the upper layer was collected and washed 2-3 times with clean water to remove the unreacted methanol and traces of catalyst

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in the biodiesel phase. The biodiesel yield obtained was calculated using equation (1).

$$\text{Yield (\%)} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of RSO used}} * 100 \quad (1)$$

This procedure was repeated for equal volume of oil, methanol and catalyst, but at temperatures of 45, 50, 55 and 60°C.

Properties of biodiesel produced

The biodiesel produced was analyzed for its properties. The ASTM standard test procedures were used to determine the following properties: acid value (ASTM D 664); flash point (ASTM D93); cetane number (ASTMD613); calorific value (ASTM D240), density (ASTM D4052) and kinematic viscosity (ASTMD445).

Results and Discussion

Oil characterization

Table 1 gives a summary of the physicochemical properties of RSO used in this study. From Table 1, RSO has a dark brown colour but clear, with an unpleasant odour which was similar to that reported by Asuquo *et al.* (2012). This indicates that in its natural form, RSO is most appropriate in applications where bright colour is not the major consideration although the colour of the oil can be enhanced by bleaching in order to make it suitable for bright-colour applications.

Table 1: Physicochemical properties of RSO

| Parameter | Observation/values | Unit |
|----------------------|--------------------|----------------------|
| Colour | Dark Brown | |
| Clarity | Clear | |
| Odor | Unpleasant | |
| Density at 15°C | 916.4 | kg/m ³ |
| Viscosity | 0.3631 | mm ² /sec |
| Acid value | 66.895 | mg KOH/g |
| FFA | 33.445 | % |
| Saponification value | 193.59 | mg KOH/g |
| Ester value | 126.70 | mg KOH/g |
| Molecular weight | 873.00 | g/mole |

In this study, the acid value of RSO was found to be 66.895 mgKOH/g. This was higher than the acid value of RSO reported by Satyanarayana and Muraleedharan (2011) and Hussain *et al.* (2016), which were 48 and 35.140 mgKOH/g, respectively. This is, however, lower than RSO values obtained by Zamberi and Ani (2016) which was 78.9 mgKOH/g. The variations in acid values exhibited by RSO may be due to different climatic and geographical locations (Ibiyemi, *et al.*, 2002). The acid values of RSO shows that it is highly acidic when compared with ASTM standards acid value of 0.5 maximum, and cannot be used directly for transesterification reaction, therefore a two-step transesterification reaction was required. The FFA value of 33.44% in this study was higher than FFA value of 23.68 % reported by Bello and Otu (2015). Ramadhas *et al.* (2004) suggested that the type and percentage of fatty acids contained in vegetable oil depend on the plant species and on the growth conditions of the plant. Ester value of 126.7 mgKOH/g was obtained in this study while Asuquo *et al.* (2012) reported a higher ester value of 191.93 mgKOH/g.

From Table 1, density was 916.4 kg/m³ and this value seems to indicate that there is no heavy element in the RSO. The density of RSO in this study was slightly higher than 870 kg/m³ reported by Gimibun *et al.* (2013) but lower than 0.920 reported by Hussain *et al.* (2016). The density at 15°C reported in this study was slightly higher than the limits specified by ASTM standard which is 820 – 900 kg/m³. Saponification value helps to determine the amount of potassium hydroxide (in mg) needed to neutralize the acids and saponify the esters contained in 1 g of the lipid. The higher the saponification value of oil, the higher the lauric acid content of that oil. The

lauric acid content and the saponification value of oil serve as important parameters in determining the suitability of oil in soap making (Asuquo *et al.* 2012). The oil saponification value of 193.59 mgKOH/g found in this study was higher than the values of 183.32±0.29 mgKOH/g and 191.93 mgKOH/g, respectively reported by Yousif *et al.* (2013) and Asuquo *et al.* (2012); on the other hand, Hussain *et al.* (2016) and Oyekunle and Omode (2008) reported higher values of 202.7 and 203.4 mgKOH/g, respectively. According to Asuquo *et al.* (2012), the higher the saponification value of oil, the higher the lauric acid content of that oil.

Influence of temperature

The transesterification reaction was carried out at 40, 45, 50, 55 and 60°C. The yields of biodiesel produced from RSO at these temperatures are shown in Fig. 1.

Generally, as the reaction temperature increases, the rate of reaction increases. The yield increased from 40.4 to 76.9% as the temperature was raised from 40 to 60°C. Therefore, higher temperature improves the efficiency of transesterification, which in turn enhances the RSO conversion. This observation is in agreement with findings elsewhere (Hussain *et al.* 2016). It was, however, reported by Hussain *et al.* (2016) that increasing the temperature above 65 °C results in reduced yield. This is due to methanol evaporation at temperature higher than its boiling point of 64.7°C, oil to methanol ratio cannot be maintained to achieve a desirable reaction. In this study, the optimum temperature for RSO trans-esterification was found to be 60°C as the yield of biodiesel was at its highest value of 76.9%.

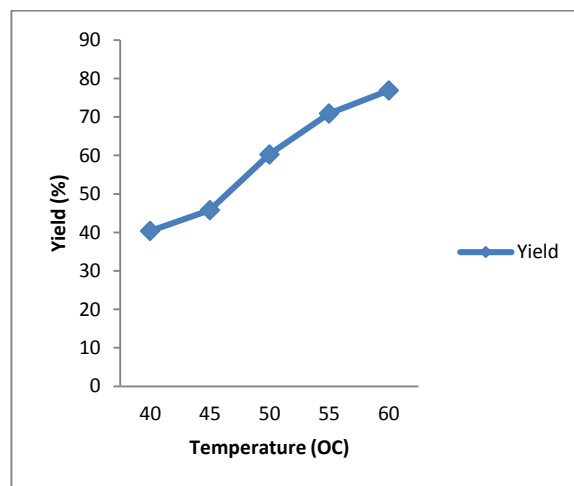


Fig. 1: Effect of temperature on the yield of biofuel produced from RSO

Table 2: Biodiesel properties at various temperatures

| Parameters | 40°C | 45°C | 50°C | 55°C | 60°C | Unit |
|---------------------------|-------|-------|-------|-------|-------|----------------------|
| Calorific value | 36.23 | 36.23 | 36.28 | 36.28 | 36.28 | (MJ/Kg) |
| Kinematic Viscosity, 40°C | 4.57 | 4.55 | 4.49 | 4.33 | 4.3 | (mm ² /s) |
| Flash point | 133.5 | 133.4 | 131.8 | 131.8 | 131.8 | °C |
| Density at 15°C | 870 | 870 | 870 | 870 | 870 | kg/m ³ |
| Acid value | 0.35 | 0.37 | 0.45 | 0.45 | 0.48 | mg KOH/g |
| Cetane number | 47 | 47 | 49 | 49.5 | 49 | |

Selected properties of the biodiesel produced RSO at 40, 45, 50, 55 and 60°C are given in Table 2.

Table 2 shows that as the reaction temperature did not significantly affect the calorific value of the biodiesel produced. The calorific value of biodiesel was constant at 36.23 MJ/kg even when the reaction temperature was increased from 40 to 45°C, and only increased slightly to 36.28 MJ/kg when the reaction temperature increased to 50°C. The calorific value of the biodiesel remained constant

thereafter even when the reaction temperature increased from 50 to 60°C. This may be due to the fact that the quality of biodiesel produced at the reaction temperatures was essentially the same even when the yields varied.

Flash point is a measure of flammability of fuels and thus an important safety criterion in transport and storage. The flash point of the biodiesel produced initially decreased from 133.5 to 131.8°C as the reaction temperature was increased from 40 to 50°C. Thereafter, the value of flash point had a constant value of 131.8°C as the reaction temperature increased from 50 to 60°C. It was noticed that the biodiesel produced at the various reaction temperature had flash points that are still within the ASTM acceptable minimum value of 130°C.

The acid value was found to increase from 0.35 to 0.48 as the reaction temperature was increased from 40 °C to 60 °C. The acid values are still within the ASTM acceptable limits of (<0.5) for biodiesel. The cetane value initially increased from 47 to 49.5 as the reaction temperature was increased from 40 to 55°C, but decreased from 49.5 to 49 as the reaction temperature increased from 55 to 60°C. The highest value of cetane number was 49.5, and this was obtained in the biodiesel produced at a reaction temperature of 55°C. It was noted however that the biodiesel produced at the various reaction temperature had cetane numbers that are still within the ASTM acceptable minimum value of 47 (ASTM D6751).

The densities of biodiesels are generally higher than those of fossil diesel fuel. The values depend on their fatty acid composition as well as on their purity. Density increases with decreasing chain length and increasing number of double bonds, or can be decreased by the presence of low-density contaminants such as methanol. In this study, the density of biodiesel produced at the various reaction temperatures (40 – 60°C) remained constant at 870 kg/m³. This constant value may be due to the small temperature range used in this study. This value of density is within the ASTM limits of 820 – 900 kg/m³. Kinematic viscosity is an important parameter when considering engine output. The kinematic viscosity of biodiesel is higher than that of fossil diesel, and in some cases at low temperatures becomes very viscous or even solid. High viscosity affects the volume flow and injection spray characteristics in the engine and at low temperatures may compromise the mechanical integrity of injection pump drive systems. In this study, it was observed that increase in reaction temperature from 40 to 60°C resulted in a decrease in kinematic viscosity from 4.57 to 4.30 mm²/s. These values were however found to be within the range specified by ASTM standard of 1.9 – 6.0 mm²/s.

Conclusion

This study led to the conclusion that transesterification temperature does not affect the density of biofuel produced. It was also found that as the reaction temperature increased the yield also increased. It was also concluded that reaction temperature affected the following fuel properties of the biofuel produced: kinematic viscosity, calorific value and flash point.

Conflict of Interest

There is no conflict of interest associated with this work.

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