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Production of biodiesel by transesterification of refined soybean oil

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ABSTRACT

This study focused on the production of biodiesel via transesterification of refined soybean oil obtained locally. Sodium hydroxide was used as the alkali catalyst and methanol (as alcohol) was used in the transesterification process due to its low cost. The methanol-to-oil molar ratio was maintained at 6:1. The effect of reaction temperature with time and the catalyst loading were studied. The reaction temperature and the catalyst loading were varied at 30, 40, 50, 60 and 70 ^{o}C; and at 0.5 and 1.0% weight of oil, respectively. After transesterification of the soybean oil, the fatty acid methyl esters [FAMEs (biodiesel)] conversion was found to rise with an increase in the catalyst loading and also with the reaction temperature but no significant difference ($P > 0.05$) was found between the temperatures of 60 ^{o}C and 70 ^{o}C. The optimum methyl esters conversion of 97.89% was achieved at 60 ^{o}C for 3 h with 1% (w/w) catalyst. The viscosity (at 40 ^{o}C), density, cloud point, pour point, flash point and acid number were 3.40 cSt, 0.86 g/ml, -1 ^{o}C, -7 ^{o}C, 175 ^{o}C and 0.19, respectively. This optimum methyl esters conversion obtained met ASTM standard of D-6751. Therefore, soybean oil has been shown in this study as a good candidate for biodiesel production and the data acquired can be scaled up for large scale production.
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Keywords: Renewable energy, fatty acid methyl esters, diesel, catalyst.

INTRODUCTION

The increasing energy demand in the world, the instability in the price of crude oil and pollution problems caused by the widespread use of fossil fuels request for a rapid measure to develop the renewable energy sources such as biodiesel. Biodiesel are fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs). Biodiesel, as an alternative fuel, has many merits that make it preferable to the conventional petroleum diesel. It is renewable, biodegradable, environmentally-friendly and non-toxic. Biodiesel can suitably substitute for petroleum diesel because of its properties; especially flash point, cetane number as well as volumetric heating value, which have been shown to be comparable to that of fossil fuel-based diesel (Ma and Hanna, 1999; Lang et al., 2001; Usta, 2005; Jeong et al., 2006).

Biodiesel is produced via conversion of vegetable oils or animal fats or waste oils.

Such fatty acids-based materials include soybeans, neem seed, jatropha seed, tallow, lard, and waste oil. Soybeans cultivation and utilization which originated in China more than 3000 years ago subsequently spread through the Orient (Hosken, 2003). There have been reports of successful cultivation of soybeans in Africa, Nigeria being the leading producer (Ade-Omowaye et al., 2004). The United States produced 75 million metric tons of soybeans in 2000, representing 50% of the global production. The World production increased to 219.8 million metric tons in 2007 (Soy Stats, 2008). Total soybean oil availability within this period was 38.4 million metric tons. Fatty acids composition of soybean oil is shown in Table 1.

Various techniques employed in biodiesel production include esterification, transesterification, and hydrotreatment. In the transesterification (Figure 1) of different types of oils or fats, triglycerides react with an alcohol, generally methanol or ethanol, to produce biodiesel and glycerol. Methanol is the most commonly used alcohol because of its low cost. The presence of a catalyst accelerates the conversion. Alkali, acid and enzyme (lipases) are the catalysts that have been reported in transesterification. Alkali catalyst is preferred to acid catalyst in the industries. This is because alkali process is more efficient and less corrosive than the acid process. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two catalysts (Nelson et al., 1996; Watanabe et al., 2001). Alkali-catalyzed transesterification studies have been reported (Freedman et al., 1984). Parameters that are relevant to transesterification reaction are the free fatty acid contents and water contents in feedstock, oil-to-methanol molar ratio, the catalyst type and amount, the reaction temperature, and the time (Lang et al., 2001; Jeong et al., 2006; Freedman et al., 1984). A 6:1 molar ratio of alcohol to soybean oil and a reaction temperature near the boiling point of the alcohol (e.g. 60 °C for methanol) were recommended (Noureddini and Zhu, 1997). After the transesterification reaction, different

separation techniques to purify the biodiesel product from the other products were investigated by Karaosmanoğlu et al. (1996). They concluded that the use of hot water at 50 °C in washing was the best way to obtain high purity and yield (86%) of the biodiesel product. Freedman et al. (1984) transesterified peanut, cotton-seed, sunflower and soybean oil under the condition of methanol–oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60 °C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93–98%).

In this work, transesterification studies of locally produced soybean oil were carried out by varying reaction temperature and catalyst concentration. This was with a view to establishing the optimum conditions for conversion of the oil to methyl esters and to measure the physical and chemical properties of the biodiesel produced, in order to determine its suitability as replacement for the conventional petroleum diesel.

MATERIALS AND METHODS
Materials

Refined soybean oil, a product of Jof Ideal Family Farms Limited, Vegetable Oil Division, Owo, Ondo State, was bought in Oja Ife Market in Ile-Ife, Osun State. Methanol, sodium hydroxide, anhydrous calcium chloride, n–pentadecane, chloroform, trimethyl sulphonium hydroxide and methyl oleate were all of analytical grade.

Equipment

Perking Elmer Autosystem gas chromatograph (GC), Brooke Auto viscometer (for determination of viscosity), Koehler Pensky-Martens Flash Cup tester, pour point tester, cloud point tester, Erlenmeyer rotary evaporator and incubator shaker.

Methodology
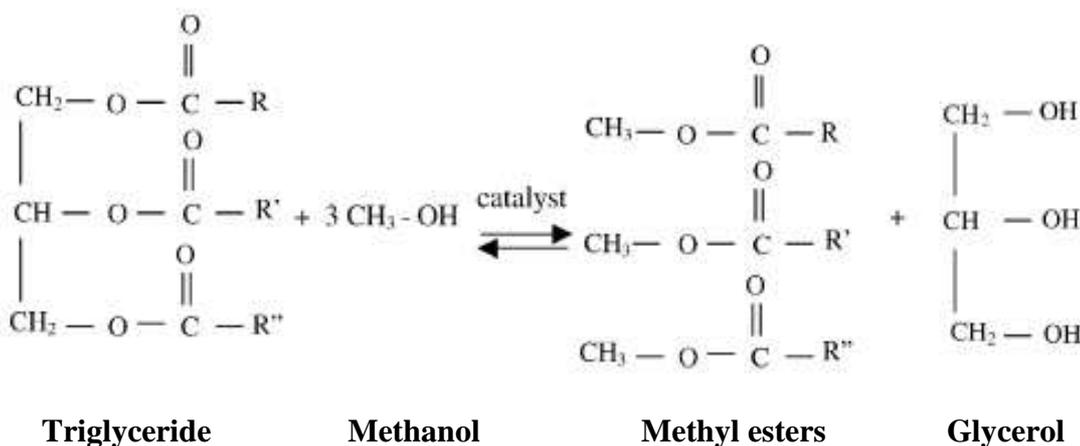#### Transesterification of the soybean oil

Batch reactions were carried out in a 250-ml Erlenmeyer flask containing 100 g of soybean oil. These were done on an incubator

Table 1: Fatty acid composition of soybean oil.

Fatty acid composition, % by weight						
Lauric $(C_{12:0})$	Myristic $(C_{14:0})$	Palmitic $(C_{16:1})$	Stearic $(C_{18:0})$	Oleic $(C_{18:1})$	Linoleic $(C_{18:2})$	Linolenic $(C_{18:3})$
0.10	0.10	10.20	3.70	22.80	53.70	8.60

Source: Marchetti et al., 2007

Triglyceride   **Methanol**   **Methyl esters**   **Glycerol**

Figure 1: The overall chemical reaction of the transesterification process.

shaker at different temperatures of 30, 40, 50, 60 and 70 ^{o}C, keeping the rate of agitation and oil to alcohol ratio constant at 200 rpm and 1:6, respectively. Catalysts of 0.5% (w/w) and 1% (w/w) of sodium hydroxide were used. The catalyst was dissolved into methanol according to the oil to alcohol ratio (1:6). The oil was heated up to reaction temperature in the Erlenmeyer flask and once the alkali got dissolved, the alcohol-alkali mixture was added to the oil, and the reaction was allowed to run for various periods of 0.25, 0.50, 1, 2 and 3 h. These samples were allowed to settle overnight in a separating funnel by gravity, settling into a clear, golden liquid biodiesel on the top with the light brown glycerol at the bottom. On the second day the glycerol was drained off from the bottom of the separating funnel. The raw biodiesel was washed with water three times to remove the unreacted catalyst and glycerol. To get a pure biodiesel, this was purified in a rotary evaporator to remove any excess methanol. Following this, the ester phase was dried over anhydrous calcium chloride. The methyl esters produced were analyzed for the following parameters: methyl esters, pour point, cloud point, flash point, density, kinematic viscosity at 40 ^{o}C and acid number.

Analysis of the soybean-based biodiesel
Determination of soybean-based biodiesel concentration

Analyses were performed on the Perking Elmer Autosystem Gas Chromatograph with flame ionization detector. Methyl esters concentration determination was done according to the modified methods of Freedman et al. (1984), Mariani et al. (1991) and Foidl et al. (1996). The Gas Chromatograph was equipped with a 30 m capillary column (ID 0.25mm/0.50μm) and reference standard used was methyl oleate (Sigma) while the internal standard and the solvent used were n–pentadecane (Merck, Germany) and Chloroform (analytical grade), respectively. The initial temperature (160 ^{o}C) was raised at a rate of 10 ^{o}C/min to 230 ^{o}C

and then at a rate of 20 ^{o}C/min to 300 ^{o}C. Sample was prepared by diluting 10 mg of the ester in 100 µl of 1.5% of internal standard solution (n–pentadecane in chloroform). To 50 µl of the solution, 50 µl of trimethyl sulphonium hydroxide were added.

Characterization of soybean-based biodiesel

For the characterization of the biodiesel produced, parameters determined with the standard methods used are presented in Table 2. Flash point was determined by the Flash cup closed tester.

Cloud and pour points were determined simultaneously using the Pour and Cloud Point tester. Density and the viscosity were measured at 40 ^{o}C using the density bottle and the Brooke Auto Viscometer, respectively. The acid value is defined as the amount of potassium hydroxide (mg) needed to neutralize fatty acids in 1 g of sample. It shows the amount of free fatty acid content in biodiesel produced. Here, indicator solution (1.0% phenolphthalein indicator in isopropyl alcohol) was added to the required amount of solvent (equal parts by volume of isopropyl alcohol and toluene) in ratio of 2 ml to 125 ml and neutralize with alkali to a faint but permanent pink colour. Five grams of the well mixed sample was weighed into an Erlenmeyer flask and 125 ml of the neutralized solvent mixture was added. It was ensured that the sample was completely dissolved before titration was carried out. The sample was shaken vigorously while titrating with the standard alkali (0.1N KOH) until the first permanent pink colour was reached. The acid value was calculated using Equation (1).

$$\text{Acid value (mg KOH/g of sample)} = \frac{(A-B)*N*56.1}{W} \quad \text{......(1)}$$

Where   A = volume of standard alkali used in the titration (ml),
B = volume of standard alkali used in titrating the blank (ml),
N = normality of standard alkali
W = mass of sample (g).

Statistical analysis

The One–way ANOVA was performed with Origin 7 statistical software.

RESULTS
Soybean-based biodiesel production

Transesterification method employed in this work for the soybean-based biodiesel production gave excellent results. The by-product, glycerol was separated under gravity with the aid of the separating funnel within a few hours. It was observed that glycerol settled at the bottom of the funnel, indicating that the by-product is denser than the crude biodiesel product. The process of purification adopted in this work proved to be effective in getting pure biodiesel.

Studies on variation of reaction temperature and catalyst loading

Figures 2 and 3 show results obtained in the investigation of varying reaction temperature and catalyst concentration for the transesterification of soybean oil into methyl esters. For all the studies carried out, as the transesterification time increased, the percentage conversion increased. Furthermore, the results showed that irrespective of the concentration of the catalyst used (0.5 or 1% w/w), as the temperature increased, the percentage conversion of soybean oil into methyl esters also increased. Conversion observed at 30 ^{o}C was lower than the results of other studies carried out at reaction temperatures of 40, 50, 60 and 70 ^{o}C. After 2 h of transesterification, there was about 10% increase in the percentage of conversion at reaction temperature of 60 ^{o}C compared to that of 30 ^{o}C (Figures 2 and 3). This observation is irrespective of the concentration of the catalyst used. It was noted also that results for both 60 ^{o}C and 70 ^{o}C reaction temperatures were similar. The data obtained showed that at the 0.05 significance level, the results were not significantly different.

Table 2: Standard methods for biodiesel characterization.

Property of Ester	Test Method
Viscosity	ASTMD – 445
Density	ASTMD – 287
Flash Point	ASTMD – 93
Pour Point	ASTMD – 97
Cloud Point	ASTMD – 2500
Moisture Content	ASTMD – 2709
Acid Number	AOCS Method Te la – 64

However, the data obtained when 1% (w/w) catalyst was employed were better than when 0.5% (w/w) catalyst was used. After 3 h of transesterification, the percentage conversions recorded were 97.89 and 97.55 for reaction temperatures 60 ^{o}C and 70 ^{o}C, respectively when catalyst loading of 1% (w/w) was used, while the percentage conversions were 93.36 and 93.45 for reaction temperatures 60 ^{o}C and 70 ^{o}C, respectively, when catalyst loading of 0.5% (w/w) was employed. In general, the optimum result was observed at a reaction temperature of 60 ^{o}C and catalyst concentration of 1% (w/w). Besides the higher percentage of conversion, working with reaction temperature of 60 ^{o}C is preferable to 70 ^{o}C, because the boiling point of methanol is 60 ^{o}C. The alcohol will be lost via evaporation at higher temperature than its boiling point. Methanolysis of soybean oil with 1% potassium hydroxide catalyst gave the best yields and viscosities of the esters (Tomasevic and Marinkovic, 2003). It has been reported that the amount of catalyst that should be added to the reactor should vary from 0.5% to 1% (w/w) (Srivastava and Prasad, 2000; Barnwal and Sharma, 2005).

Table 3 shows the effect of reaction temperature on the viscosity of the transesterified oil. The viscosity decreases slightly as the temperature increases. All the values observed fell within the limit set for diesel fuel (Table 4). The kinematic viscosity showed a reduction of about 90% after the soybean oil was converted to biodiesel via transmethylation process in all the reaction temperatures investigated (Table 3). Viscosity of vegetable oil at 35.39 cSt may trigger

severe problems in the fuel filter and the engine. Knothe (2005) reported that high viscosity of untransesterified oils and fats leads to operational problems in the diesel engine such as deposits on various engine parts.

Table 4 shows the properties of the biodiesel produced under optimum conditions, refined soybean oil, the Automotive Gas Oil (AGO) and fuel limit. The properties of the soybean-based biodiesel produced are in close agreement with the standard values (Table 4). Also, the characteristics of the biodiesel compared favourably well with that of petroleum diesel (AGO). The results suggest that the biodiesel produced from soybean can suitably substitute for AGO.

DISCUSSION

This research was undertaken with the aim of establishing the possibility of using locally produced soybean oil for the production of biodiesel. Results from this present study are comparable to those earlier reported. Ali et al. (1995) reported the following properties for biodiesel produced from soybean oil: kinematic viscosity, 4.5 mm^{2}/s; cloud point, 1 ^{o}C; pour point, -7 ^{o}C; flash point, 178 ^{o}C and density, 885 kg/m^{3}. Boocock et al. (1998) carried out transesterification of soybean oil with methanol at different concentrations of sodium hydroxide. The reported ester contents after 1 min for 1.1, 1.3, 1.4 and 2.0% sodium hydroxide were 82.5, 85, 87 and 96.2%, respectively. They suggested that hydroxide concentration could be increased up to 1.3
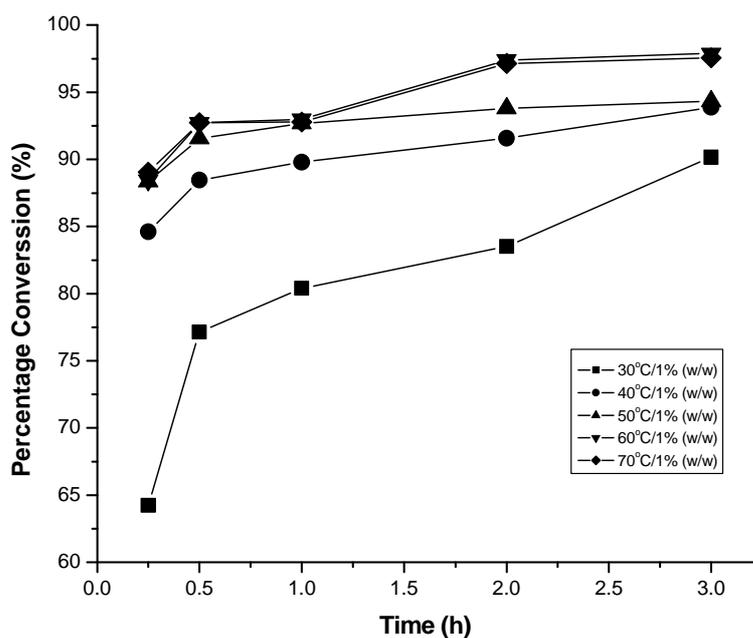
Figure 2: Plot of percentage conversion against time for the 1% (w/w) alkali catalyst during transesterification of soybean oil.
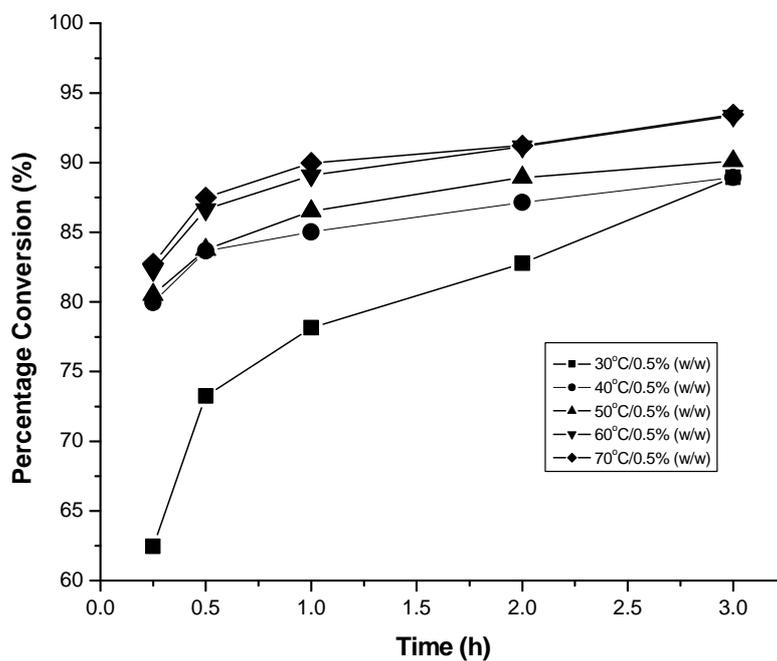
Figure 3: Plot of percentage conversion against time for the 0.5% (w/w) alkali catalyst during transesterification of soybean oil.

Table 3: Effect of varying temperature with time on kinematic viscosity of soybean-based biodiesel.

Time (h)	Kinematic Viscosity (cSt)				
	30 ^{o}C	40 ^{o}C	50 ^{o}C	60 ^{o}C	70 ^{o}C
0.25	3.75 ± 0.005	3.73 ± 0.000	3.65 ± 0.002	3.61 ± 0.001	3.62 ± 0.000
0.5	3.76 ± 0.028	3.62 ± 0.001	3.60 ± 0.000	3.55 ± 0.001	3.58 ± 0.000
1	3.74 ± 0.000	3.60 ± 0.004	3.57 ± 0.002	3.44 ± 0.000	3.44 ± 0.001
2	3.68 ± 0.007	3.57 ± 0.000	3.56 ± 0.001	3.40 ± 0.000	3.41 ± 0.001
3	3.62 ± 0.000	3.67± 0.007	3.56 ± 0.001	3.40 ± 0.000	3.39 ± 0.001

Measurements were in duplicates and data presented are the mean values.

Table 4: Properties of soybean-based biodiesel, soybean oil and automotive gas oil (AGO).

Properties	Soybean-based Biodiesel	Soybean oil	AGO	*Limit
Viscosity @ 40°C (cSt)	3.40	35.39	3.073	3.5-5.0
Flash Point (^{o}C)	175	-	71	Min 100
Pour Point (^{o}C)	-7	-	-16	-
Cloud point (^{o}C)	-1	-	-12	-1.0-4.0
Density @ RT (kg/m^3)	860	890	860	860-900
Acid number, mg KOH/g	0.19	0.38	-	Max 0.5

*Antolin et al., 2002.

wt%, resulting in 95% methyl ester after 15 min. Using 1% sodium hydroxide in this present study, ~98% methyl ester was produced in 3 h. Noureddini and Zhu (1997) recommended a 6:1 molar ratio of alcohol to soybean oil which was adopted in this work and a reaction temperature near the boiling point of the alcohol (60 ^{o}C for methanol). Optimal conversion of soybean oil to methyl ester was also established under these conditions in this work. Methanolysis of soybean oil with 1% potassium hydroxide catalyst has given the best yields and viscosities of the esters (Tomasevic and Marinkovic, 2003). It has been reported that the amount of catalyst that should be added to the reactor should vary from 0.5% to 1% (w/w) (Srivastava and Prasad, 2000; Barnwal and Sharma, 2005). Freedman et al. (1984) transesterified peanut, cotton-seed, sunflower and soybean oil under the condition of methanol–oil molar ratio of 6:1, 0.5% sodium methoxide catalyst and 60 ^{o}C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, they observed that the conversion was almost the same for all four oils (93–98%). At a reaction temperature of 65 ^{o}C, the conversion was completed in 20 h. Results on the kinematic viscosity obtained in this work showed a reduction of about 90% after the soybean oil was converted to biodiesel via transmethylation process at all the reaction temperatures investigated. Viscosity of vegetable oil at 35.39 cSt may trigger severe problems in the fuel filter and the engine. Knothe (2005) reported that high viscosity of untransesterified oils and fats leads to operational problems in the diesel engine such as deposits on various engine parts.

Conclusion

In this study, we determined the optimum conditions for transesterification of

soybean oil into methyl esters by varying the reaction temperature and catalyst loading. The conditions established were: 60 ^{o}C reaction temperature and 1% (w/w) alkali catalyst loading using soybean oil-to-methanol molar ratio of 6:1. The properties of soybean-based biodiesel produced satisfied ASTM standard of D-6751, hence, it can act as alternative fuels for the Internal Combustion Engines (ICE). Soybean oil has been shown in this study as a very good candidate for biodiesel production and the data acquired can be scaled up for large scale production.

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