



Conversion of Soybean Sludge and Palm Kernel Free Fatty Acid into Biodiesel via Two-step Catalysed Reaction

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ABSTRACT

Biodiesel production is expected to play critical role in climate protection due to its carbon neutrality and this can only be achieved when non-edible or waste vegetable oils are utilized. In this work, a two-step catalyzed process was used to convert Soybean Sludge (SBS) and Palm Kernel Free Fatty Acid (PK FFA) into biodiesel. The feedstock were initially subjected to esterification reaction in the presence of HCl catalyst under a prescribed reaction condition and free fatty acids conversion of 85.96% and 97.19% was obtained for SBS and PK FFA, respectively. The product obtained after esterification was subjected to trans-esterification in the presence of KOH catalyst with vegetable oil/methanol molar ratio 1:5, temperature of 65°C and reaction time of 1 h and biodiesel yields of 91.54% and 92.04% were obtained for SBS and PK FFA, respectively. The fuel properties such as kinematic viscosity 4.23 - 4.56 mm²/s, flash point 58 - 62°C, density 0.83 - 0.91 g/cm³ were within the recommended limit as prescribed by America Standard for Testing and Materials (ASTM). The result obtained showed that the feedstock used were of good source in biodiesel production.

Keywords: Biodiesel, Catalyst, Esterification, Trans-esterification

Introduction

According to the United States Department of Energy (USDE), the price of oil was \$10.82 per barrel on July 1, 1998 and on July 1, 2008 it reached \$140.97 per barrel, a 13-fold increase in ten years is expected (Bransby, 2008). More importantly, the price was \$69.91 on July 1, 2007 and \$88.71 on February 1, 2008, indicating that over half of the increase in the past ten years occurred within just twelve months (Bransby, 2008). These statistics reveal that a huge energy crisis is underway. The temporary decline in oil prices may be connected to the present economic recession. Another problem with energy supply is the source, the major part of all energy consumed world-wide comes from fossil sources (petroleum, coal and



natural gas) and however, these sources are limited and will be exhausted in the nearest future (Anitha and Dawn, 2010). One of the pathways to reduce our dependence on fossil fuels is the production and utilisation of renewable energies especially bio-fuels. Bio-fuels are fuels derived from oil producing plants of various kinds. The primary products of bio-fuels are bio-ethanol and bio-diesel which can be used as substitutes for gasoline and diesel. They can also be proportionally blended for automobiles' consumption. Renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution to global warming (MacLeana and Laveb, 2003). In order to control carbon dioxide emissions from transportation system, introduction of biomass-derived fuels has been proposed and used for both gasoline (mainly ethanol, or a derivative of ethanol: ethyl-tertiobutyl-ether) and diesel (methyl ester from vegetable oils) (Ayodele *et al.*, 2016). The increasing demand but declining supply of fossil fuel and associated severe environmental problems with the exploitation of fossil fuel are drawing attention towards utilisation of alternative renewable energies like bio-energy. Bio-energies which include bio-ethanol, biodiesel, and bio-oils are fuels that are derived from biomaterials. Presently, bio-ethanol is mainly produced from starchy food such as corn while biodiesel is produced from vegetable oils and waste oils. For bio-oils, wide varieties of feed-stocks are being used. Some of the advantages associated with biological products include: renewability and sustainability, environmentally benign (reduce air pollution and global climate change), and economic stimulation. Bio-oils have been regarded as promising products that can partially substitute petroleum fuels used for heat and power generation (Chiaromonti *et al.*, 2007). In the past one decade, several studies and campaigns have been geared towards the production of biodiesel from woody plants but the problem associated with it is that of low yield, which is a great concern affecting its commercialisation and forest sustainability. Therefore, consideration for the use of non-timber forest products from agroforestry plantation is an alternative raw material for bio-energy production. The use of soybean sludge and palm kernel free fatty acid as biofuel could be another bio-energy source, they are non-edible by-products obtained from soybean and palm kernel in form of residue. Converting the waste to bioenergy will help to reduce expenditure due to the huge amount of money spent on the importation of refined fossil fuel and at the same time increase optimization of industrial waste thus leading to reduction in environmental hazards. The study thus investigated the use of soybean sludge and palm kernel free fatty acid for the production of biodiesel.

MATERIALS AND METHODS

Sample preparation

The collected SBS and PK FFA were processed into biodiesel following a two-step catalysed techniques namely esterification and trans-esterification reactions in the presence of acid



(HCl) and base (KOH) catalysts, respectively. The PK FFA and SBS were first pre-heated at a temperature of 120 °C and 100 °C, respectively in order to dry up the residual moisture and to convert them from semi-solid to liquid phase.

Esterification reaction

The esterification reaction was conducted using HCl as catalyst via the following steps:

Step 1: The PKO and SBS were measured to the required quantity with the aid of measuring cylinder after pre-heating them (Table 1).

Step 2: HCl was added to methanol at first, after which the mixture was added to the required quantity of SBS and PK FFA and stirred vigorously for 1hr at room temperature with the aid of magnetic stirrer.

Step 3: The mixture was left overnight in order for it to settle down, and then the esterified FAME was collected at the top fraction through decantation method while the glycerol was left at the bottom fraction of the mixture.

Table 1: Mixing ratio of methanol and catalyst (HCl) to SBS for esterification process.

Treatments	SBS and PK FFA ratio	Methanol ratio	HCl (ml)
A	1	5	3.33
B	1	5	1.67
C	1	15	1.25
D	1	15	0.63

Trans-esterification reaction process

The trans-esterification reaction process was conducted using KOH as catalyst through the following steps:

Step 1: The FAME was measured to the required quantity with the aid of measuring cylinder.

Step 2: KOH was added to methanol at first and stirred for 5 min., after which the mixture was added to the required quantity of FAME and stirred vigorously for 1hr at room temperature.

Step 3: The mixture was allowed to settle down overnight leaving the biodiesel at the top fraction and the glycerol at the bottom fraction of the mixture after which the biodiesel was decanted. The mixing ratio is presented in Table 2.



Table 2: Mixing ratio of methanol and catalyst (KOH) to both SBS and PK FFA for trans-esterification process.

Treatments	SBS and PK FFA ratio	Methanol ratio	KOH (wt)
A	1	1	1.00
B	1	2	0.67
C	1	4	0.40
D	5	1	1.67

Sample separation and purification

Step 1: The decanted biodiesel after trans-esterification was purified in the ratio of 5:1 of biodiesel to distilled water after which the mixture was agitated for 15 minutes with the aid of centrifuge and was left to settle for 1hr. The biodiesel was collected at the top fraction of the mixture by decantation while the impurities settled at the bottom fraction. The procedure was repeated 3 times for all the samples produced at different ratios.

Step 2: The decanted biodiesel after distilled water purification was again purified by adding ratio 1 (w/w) of Mg₂SO₄ to 20 (w/w) of biodiesel after which the mixture was agitated for 15minutes using centrifuge. The mixture was left to settle for 4hrs and the biodiesel was collected at the top fraction of the mixture by decantation while the impurities settled at the bottom fraction. The procedure was only done once for all the products obtained at different ratios.

The biodiesel product obtained was characterised by determining the pH using a calibrated pH meter and this was done at the end of each production step. The density was also calculated using the following equation.

$$\text{Density (g/cm}^3\text{)} = \frac{\text{Mass}}{\text{Volume}} \dots\dots\dots (i)$$

Where: M = Mass of the biodiesel obtained (g)

V = Volume of biodiesel obtained (cm³)

The viscosity of the biodiesel was determined using glass viscometer. The sample was thoroughly shaken to allow easy flow inside the viscometer. A syringe was used to introduce the sample into the viscometer until it was filled to the required point. Air was allowed in the viscometer so that the sample could start flowing, the rate of flow was determined with the aid of stopwatch to know the time taken for the sample to flow through a specified distance in the viscometer. The mathematical formula used to calculate the viscosity is shown in the following equation:



$$\text{Viscosity} = \frac{2r^2(\rho)g}{9 \times V_t} \dots\dots\dots (ii)$$

Where: r = Radius

ρ = Density (g/cm³)

g = Acceleration due to gravity (m/s²)

$$\text{Terminal Velocity (V}_t\text{)} = \frac{\text{Distance}}{\text{Time}} \text{ (m/s)} \dots\dots\dots (iii)$$

Flash point was determined in accordance with ASTM D 93 (2010). This was done by pouring 2g of the produced biodiesel inside an evaporating dish (crucible), placed on a stove and then heated. Thermometer was placed very close to the dish to obtain the temperature changes that occurred. Heating continued until ignition occurred, this was recorded as the flash point of the biodiesel.

RESULTS

Percentage FAME and biodiesel yield

The yields for both PK FFA and SBS are presented in Figures 1 to 4. Figures 1 and 2 shows that the yield of esterified (FAME) SBS ranged from 72.40% to 85.96%, 1.43% to 12.00% and 12.15% to 15.46% for FAME, glycerol and loss (unrecovered) respectively. The biodiesel, glycerol and loss for trans-esterified SBS ranged from 80.33% to 91.54%, 0.00% to 5.48% and 7.80% to 16.20%, respectively. In the same vain, Figures 3 and 4 shows that the yield of esterified PK FFA for FAME ranged from 83.24% to 97.19%, the loss ranged from 2.81% to 16.76% while there was no trace of glycerol in all the samples. The biodiesel yield for trans-esterified PK FFA ranged from 88.72% to 92.04%, the glycerol ranged from 0.00% to 1.49% and loss ranged from 7.77% to 14.17% for all the samples.

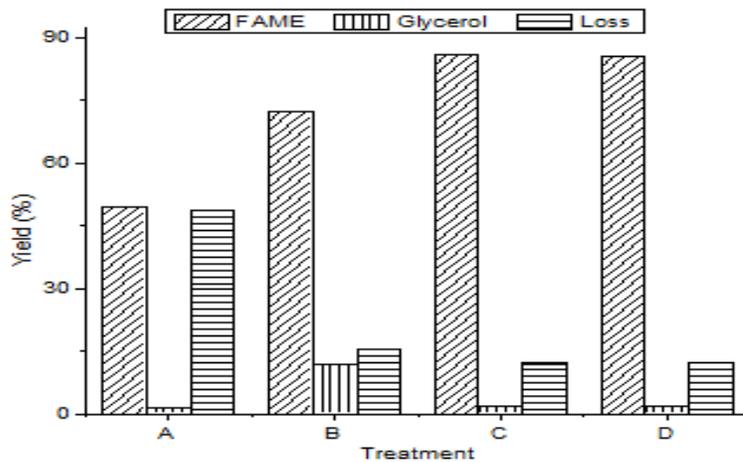


Figure 1: The yield of fatty acid methyl ester produced from esterified soybean sludge

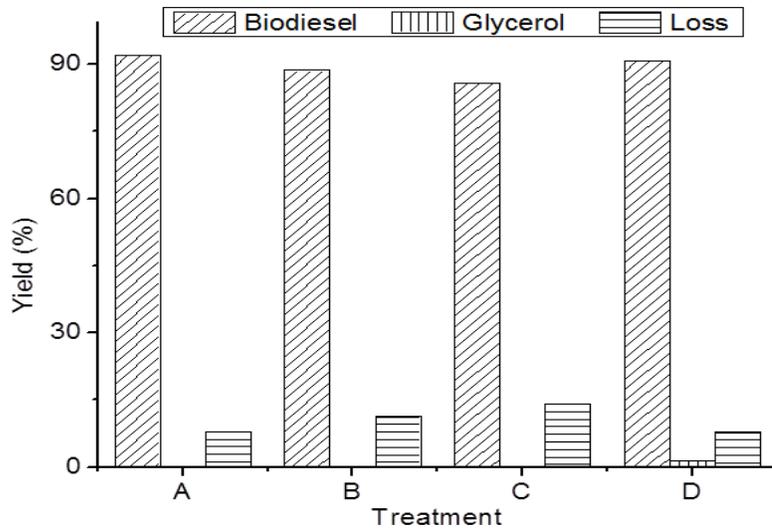


Figure 2: The yield of biodiesel produced from trans-esterified soybean sludge

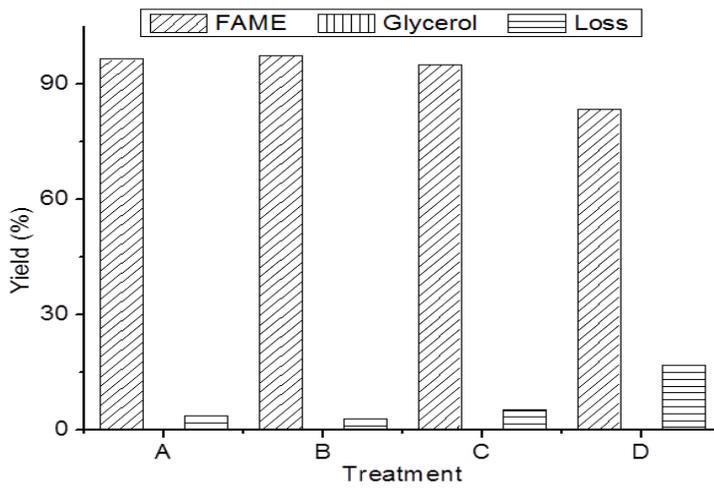


Figure 3: The yield of fatty acid methyl ester produced from esterified Palm Kernel free fatty acid

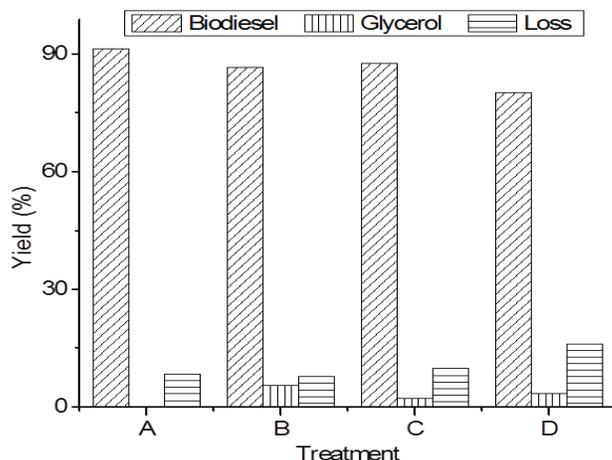


Figure 4: The yield of biodiesel produced from trans-esterified palm kernel free fatty acid.

Visual Observation of the Purified Biodiesel Water (H₂O) purification

The visual observation of biodiesel produced from PK FFA and SBS after water purification is presented in Table 3. It was observed that all the samples formed layers of impurities with variations in their colours. Treatments B and D for SBS formed yellowish colour while treatments A and C formed whitish brown and light yellowish colour, respectively. In addition, treatments A and D formed yellowish colour while A and C formed whitish yellow and yellowish colour, respectively.

Magnesium sulphate (Mg₂SO₄) purification

The visual observation of biodiesel from SBS and PK FFA for Mg₂SO₄ purification is presented in Table 4. It was observed that all the samples formed layers of impurities with variations in their colours. Treatments B and D for PK FFA formed whitish yellow colour while A and C formed whitish and transparent yellowish colour, respectively. Treatments B and D for SBS formed light yellowish colour but treatments A and B formed whitish brown and light yellowish colour, respectively.



Table 3: Visual observation of the treatments purified with water

	Treatments	Observations
SBS	A	Light yellow in colour, layers of impurities formed, oily surface.
	B	Yellowish in colour, layers of impurities formed.
	C	Whitish brown in colour, layers of impurities formed.
	D	Light yellow in colour, layers of impurities formed, oily surface.
PKO	A	Yellowish in colour, layers of impurities formed.
	B	Yellowish in colour, layers of impurities formed.
	C	Whitish yellow in colour, layers of impurities formed.
	D	Yellowish in colour, layers of impurities formed

Table 4: Visual observation of the treatments purified with Mg₂SO₄

	Treatments	Observations
SBS	A	Light yellowish in colour, layers of impurities formed.
	B	Yellowish in colour, layers of impurities formed.
	C	Whitish brown in colour, layers of impurities formed.
	D	Yellowish in colour, layers of impurities formed.
PKO	A	Transparent yellowish colour, layers of impurities formed, oily surface.
	B	Whitish yellow colour, layers of impurities formed.
	C	Whitish in colour, layers of impurities formed.
	D	Whitish yellow colour, layer of impurities formed.

Physical characterization of biodiesel

Density of biodiesel

The results presented in Figure 5 indicated that the density of the biodiesel for all the treatments ranged from 0.78 to 0.91(g/cm³) and 0.78 to 0.83 (g/cm³) for both SBS and PK FFA, respectively. The lowest value of biodiesel for SBS was recorded for treatment B and the highest value for treatment D while biodiesel produced from PK FFA had the lowest value for treatment B and the highest for treatment D.



Flash point of biodiesel

The results presented in Figure 6 show that the flash point of the biodiesel for all the treatments A, B, C, and D ranged from 42 to 62 and 42 to 58°C for both SBS and PK FFA, respectively. The lowest value was recorded for treatment B in SBS and the highest was for treatment A. The lowest and highest flash point observed for biodiesel produced from PK FFA were recorded for treatment D and C, respectively.

Viscosity of biodiesel

The viscosity for SBS and PK FFA are presented in Figure 7. The values ranged from 4.23 to 7.75 mm²/s and 4.56 to 6.38 mm²/s for biodiesel produced from SBS and PK FFA, respectively. The value is high for PK FFA in all the treatment except for A while the viscosity of the biodiesel produced from SBS is slightly higher than PK FFA.

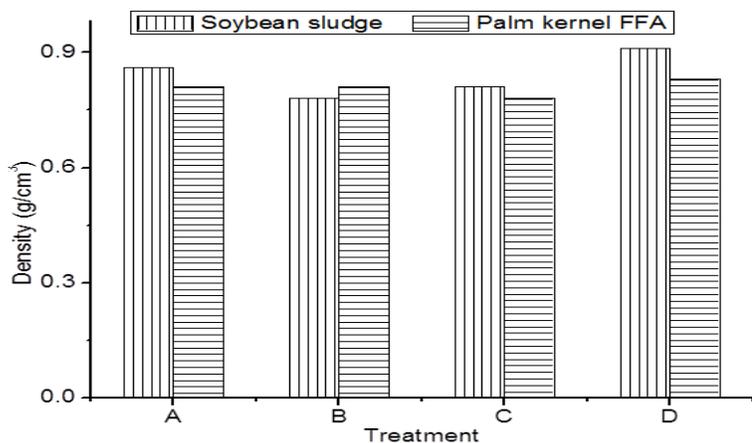


Figure 5: Density of biodiesel produced from soybean sludge and palm kernel free fatty acid. Treatments A, B, C and D are the different concentration levels of SBS and FFA to acid and base catalyst.

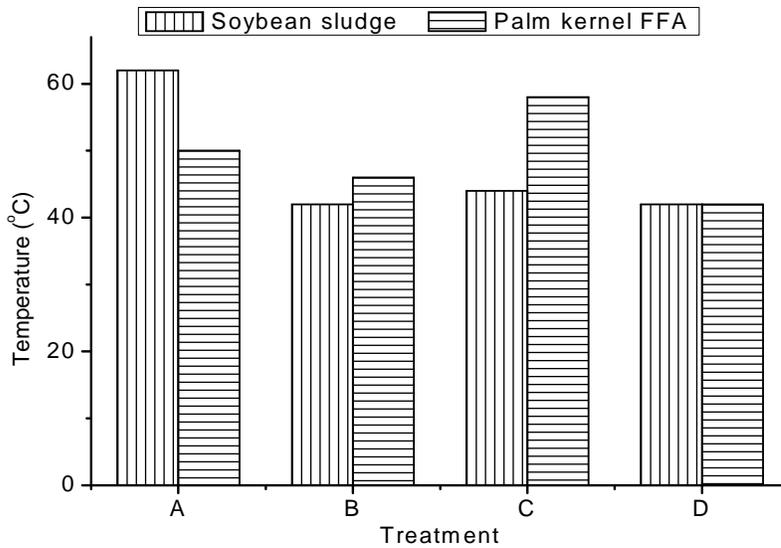


Figure 6: Flash point of biodiesel produced from soybean sludge and palm kernel free fatty acid. Treatments A, B, C and D are the different concentration levels of SBS and PK FFA to acid and base catalyst.

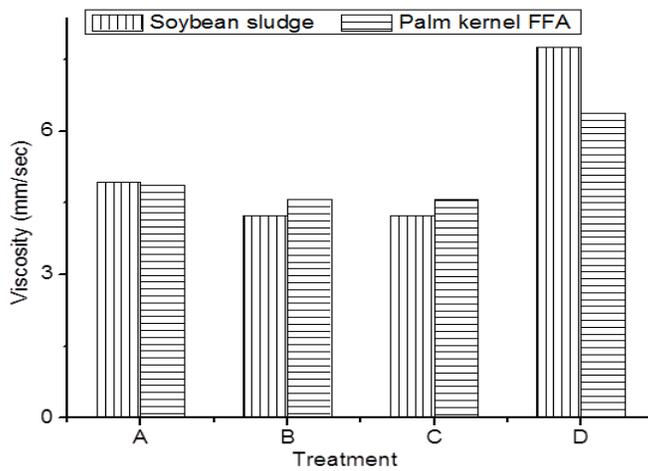


Figure 7: Viscosity of biodiesel produced from soybean sludge and palm kernel free fatty acid. Treatments A, B, C and D are the different concentration levels of SBS and FFA to acid and base catalyst.



pH determination

Table 5 presents the pH values for all the biodiesel production process. The pH values of FAME for both the SBS and PK FFA ranged from 0.27 to 1.92 while that of biodiesel produced from SBS and PK FFA ranged from 3.4 to 7.86. The values for the purified biodiesel (water and Mg₂SO₄ purification) ranged from 1.17 to 11.33 and 1.40 to 8.78, respectively.

Table 5: pH determination for SBS and PK FFA

	Treatments	FAME	Biodiesel	H ₂ O purification	Mg ₂ SO ₄ purification
SBS	A	0.27	6.59	8.79	1.40
	B	0.12	7.34	8.32	6.98
	C	1.22	3.4	1.17	6.60
	D	1.52	7.56	6.23	5.92
	Treatments	FAME	Biodiesel	H ₂ O purification	Mg ₂ SO ₄ purification
PK FFA	A	1.27	7.43	11.35	2.19
	B	1.12	5.32	7.01	6.98
	C	1.62	1.52	1.47	7.14
	D	1.92	7.86	8.32	8.78

Discussion

Percentage FAME and biodiesel yield

As indicated in Figures 1- 4, the yield of FAME for SBS increased with high concentration of acid. This is in agreement with the observation of Santos *et al.*, (2009). This increment revealed that the conversion of FFA to FAME is strongly affected by the quantity of acid catalyst which shifts the reaction towards formation of FAME. The loss recorded during the reaction was due to the splashes during stirring, un-reacted methanol and residual catalyst which is found to be in agreement with the results reported by Alamu *et al.*, (2007, 2008). However, the FAME produced from PK FFA decreased with increase in quantity of acid catalyst. A notable observation revealed that there was no glycerol produced at the end of the esterification process of PK FFA which could be because of its total conversion to FAME.

Generally, the biodiesel yield from FAME reduced with increase in the quantity of methanol. This reduction is due to high amount of methanol interference which might increase the solubility, leading to separation of glycerol (Maceiras *et al.*, 2009). The glycerol in the solution drives the reaction equilibrium back thereby resulting in lower yield of biodiesel as



reported by (Kotwal *et al.*, 2009). In addition, the amount of catalyst can affect the transesterification resulting in different free fatty acid conversion and biodiesel yield (Santos *et al.*, 2009).

Density of biodiesel

The biodiesel density is presented in Figure 5. The densities which varied from 0.78 to 0.91 g/cm³ and 0.78 to 0.83 g/cm³ for biodiesel produced from SBS and PK FFA are similar to 0.89 g/cm³ reported for raw waste oil, 0.85 for diesel and 0.89 for biodiesel produced from waste cooking oil (Anitha and Dawin, 2010). It was also observed that the result falls within the European standard for biodiesel which is 0.88 g/cm³ as reported by Dawodu *et al.*, (2014). The slight difference revealed from one treatment to the other in this study could be attributed to the different concentration of production mixture. This implies that the density could possibly be affected by the mixing ratio of catalyst, methanol and SBS and PK FFA used.

Flash point of biodiesel

The flash point for biodiesel produced is presented in Figure 6. The flash point varied from 42 to 68°C for both SBS and PK FFA. This was observed to be less than 167°C reported for biodiesel from PKO (Peterson *et al.*, 1990). However, it is close to ASTM standard which is 74°C for diesel (Alamu *et al.*, 2007). This variation in flash point could be as a result of the mixing ratio used for the biodiesel produced. This low flash point is a good indicator that the biodiesel produced from PK FFA and SBS would be very suitable fuel for internal combustion engine because this may boost atomization and combustion efficiency.

Viscosity of biodiesel

Viscosity is a measure of internal friction or resistance of oil to flow. The viscosity values for this study are presented in Figure 7. This shows that the highest value is recorded for treatment D for both SBS and PK FFA. This could be attributed to the mixing ratio used in producing the biodiesel. The values recorded in this study falls within the range reported by different authors and organisation such as 5.58 mm²/sec for sludge palm oil (Adeeb *et al.*, 2010), 7.1 to 8.8 mm²/sec (AFDC, 2009), 4.84 mm²/sec for palm kernel oil (Alamu *et al.*, 2007 and 2008). The values recorded for viscosity in this study are appropriate for the biodiesel fluidity in diesel engine.

pH of biodiesel

The pH values recorded in this study at the final purification stage of biodiesel shows that treatment B for both SBS and PK FFA fall within the neutral pH value 7 which could justify its use as fuel.



Conclusion

A two-step catalysed esterification and trans-esterification reaction in the presences of acid (HCl) and base (KOH) for both SBS and PK FFA to produce biodiesel were carried out in this study. The operating parameters such as methanol and catalyst quantity were found to affect the reaction process. The conformity of viscosity, density, and all other tested parameters proved positive for the use of SBS and PK FFA for biodiesel production especially treatment B. Thus, the results from this study show that SBS and PK FFA are considerable alternatives for petro-diesel.

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