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Utilization of Bagasse based Activated Carbon as Catalyst for Production of Glycerol-aceticacid esters and their Application for Diesel blends

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ABSTRACT

The increasing agitations for alternative fuels especially transportation fuel creates large surplus of glycerol from biodiesel production. In view of this, the current work investigates the conversion of glycerol into petro-diesel fuel blend. The glycerol was esterified using acetic acid over activated carbon derived from sugarcane bagasse as catalyst to produce acetins. The carbon was prepared from bagasse through controlled pyrolysis and activated with sulphuric acid. The generated activated carbon was characterized using FT-IR. The acetins (glycerol esters) were produced via acetylation of glycerol with acetic acid under reflux at different reaction conditions and characterized using FT-IR and GC-MS. Optimization of process parameters for acetylation of glycerol was determined by Response surface based on Box-Beinkhen design. The optimum yield of acetin (80.60%) was achieved at the temperature, catalyst dose, time and glycerol to acetic acid ratio of 110°C, 2.5%wt, 3 hours and 1:4.5 respectively. The physicochemical properties of petrol-diesel and its blends with the produced acetins were analyzed using ASTM methods. Parameters like kinematic viscosity, cloud point, pour point and cetane number of petro-diesel and its blends were in conformity with the ASTM specifications for diesel fuel. The produced glycerol-acetic ester significantly improve the kinematic viscosity, cold flow properties and cetane number of petro-diesel fuel.

1.0 Introduction

Over the past few years there has been increasing concern about global warming, resulting in a growing demand for renewable energy sources, which have significant lower contribution to CO_2 emissions. In particular, biodiesel became a world-recognized renewable substitute for fossil fuels. It is generally produced from the transesterification of vegetable oils with alcohols in the presence of catalyst. This process yields glycerol to biodiesel ratio of 1:10 by weight; with a sharp rise in biodiesel production, an oversupply of glycerol is created, causing its cost to decline substantially. As consequence, new applications for glycerol are being investigated because it can be considered a promising building block for biorefineries[1]. One of the several ways of converting glycerol to value added chemicals is as fuel additives for petro-diesel, biodiesel and or gasoline.

Fuel additives are substances added or blended with fuel especially gasoline, diesel and or biodiesel to improve their properties leading to excellence performance [2, 3]. Additive when added to fuels it can reduce harmful emissions such as hydrocarbons particulate, CO_2 and NOx emissions. It improves viscosity, anti-knock, octane number, cetane number and cold flow properties of the fuels as well as improves the thermal stability, cleanliness and prevents corrosion of engine parts [3]. Utilization of waste resources for generation of valuable sustainable products has remained the focus of many researchers across the globe. Thus, the current study investigates the conversion of glycerol into petro-diesel fuel blend and the use of activated carbon derived from sugarcane bagasse as catalyst for glycerol acetylation.

2.0 Materials and Methods

Glycerol with percentage purity of 95.5% was purchased from Sigma-Aldrich (Merck), Acetic acid (99.0%), Potassium hydroxide (85.0%), Dichloromethane (99.0%), Sulphuric acid (98.6%), Potassium Iodide (98.0%), Sodium bicarbonate (95.0%), Bromine (97%), Hydrochloric acid (36.0%), Pyridine (99.9%) and Sodium thiosulphate (94.8%) were of analytical grades are obtained from British Drug house and Sigma-Aldrich (Merck). A petroldiesel fuel used for blending with glycerol-acetic acid esters was purchased at A.A. Rano filling station along Birninkebbi road, Wamakko local government area of Sokoto State, Nigeria

2.1 Catalyst Preparation

The synthesis of activated carbon was performed by adopting the method of Gonclaves*et al.,*[4] with slight modification. The collected sugarcane bagasse sample was washed and then dried in an oven at 100°C for 3 hours. The dried sample was grinded and then sieved through a mesh (>60 mesh). Ten grams (10g) of the sieved bagasse sample was accurately weighed and placed in a stainless steel reactor. The reactor was inserted into a tubular furnace and then subjected to a controlled pyrolysis

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at a heating rate of 10°C per minute from ambient temperature to a temperature of 400°C and then held for four hours. Before each run, the stainless steel tubular furnace was washed thoroughly with detergent and distilled water and allowed to dry and the reactor was purged three times with nitrogen gas in order to provide inert atmosphere.

Activation of the carbon prepared from bagasse was done by adoption the method of Gomez *et al.,* [5] with slight modifications. Exactly, 20.0 g of the carbon obtained from pyrolysis was accurately weighed and placed in 25cm^3 round bottom flask. Two hundred cubic meters (20cm^3) of 5M H_2SO_4 was added to it and the mixture was heated under reflux at 80°C for 3 hours. After reaction, the mixture was allowed to cool and was then filtered. The residue was washed repeatedly with warm distilled water (50°C) until neutrality and then dried in an oven at 120°C for three hours. After the drying, the activated carbon was then sieved through a mesh (>60 mesh).

2.2 FT-IR Analysis of the activated Carbon

The surface functional groups of both activated and un-activated carbon was determined by using Fourier transform infrared (FT-IR) spectroscopic analysis (Carry 630 Model Spectrophotometer). The analysis was performed by mixing dry carbon samples with potassium bromide (KBr) in a 1:20 weight ratio and ground into fine powder. The mixture was dried at 100°C for 3hours, and thin pellets were made in manual equipment. The spectra were acquired at this temperature by accumulating 100 scans at 4-400cm^{-1}.

2.3 Glycerol acetylation with Acetic acid

Acetylation is an esterification reaction with acetic acid; it introduces an acetyl functional group into a chemical compound. In this study glycerol acetylation with acetic acid was performed by adopting the method of Okoye *et al.,*[6] albeit with slight modification. In typical run, 9.2g of glycerol, 18.0g of acetic acid and 0.1g of the activated carbon catalyst was accurately weighed and placed in a 250cm^3 round bottom flask and heated under reflux on a hot plate equipped with magnetic stirrer at a temperature of 100°C for one (1) hour. The experiment was repeated under different experimental conditions; glycerol/acetic acid molar ratio of 1:3 to 1:6, 100 to 120°C reaction temperature, 1-3 hours reaction time and 1-4 wt% of the catalyst dosage (relative to glycerol weight). After the reaction the catalyst was recovered by filtration method.

2.4 Purification of the acetylated products

The products obtained from the acetylation reaction may contain excess un-reacted acetic acid and *in situ* water formed during the reaction. In order to neutralize the excess acid, a solution of sodium bicarbonate (10%) was slowly added to the products with constant stirring until disappearance of effervescence. Then 50cm^3 of dichloromethane was added to the products in order to remove the organic layer from the aqueous layer. The mixture was then quantitatively transferred into a 25cm^3 separating funnel and shaken vigorously and then allowed to settle for five minutes. The mixture forms two layers, the aqueous on the top as it is less dense than the organic layer. The organic layer was then collected in beaker, then subjected to rotary evaporation in order to separate the solvent (DCM) from the products.

2.5 Data Analysis

The acetylated product yield obtained from the experiments conducted were analyzed on MINITAB 17 Statistical Software base on Box Beikhen design to estimate the main interaction effects on the reaction variables (i.e.; temperature, time, glycerol/AcOH Concentrations and catalyst dosage), on the acetylated products yield. The percentage products yield was fitted with a full quadratic polynomial model using regression analysis. The fitness of the model was evaluated by the coefficient of determination (R^2) and the effects of terms were evaluated using analysis of variance (ANOVA) at 95% confidence level. Contour plots were developed using the fitted quadratic polynomial equation. Optimizer on the MINITAB 17 was used to optimize the factors and the optimal level obtained was experimentally validated.

2.6 Characterization of Acetylated products

The Fourier transforms infrared (FT-IR) spectroscopic analysis and GC-MS analysis was carried out to determine the functional groups and chemical compositions of the acetylated products. The GC-MS analysis of the acetylated product was carried out using Agilent Technologies GC 7890B, MSD 5977A. The injection volume was 2il and the inlet temperature was maintained at 250°C. The oven temperature was programmed initially at 90°C for 1 min and then programmed to 280°C at the rate of 25°C per minute and holding the temperature for 5 minutes and the total run time was 26 minutes. The MS transfer line was maintained at 250°C, the source temperature was 230°C and maintained at maximum temperature of 250°C and the MS Quad at 150°C and maintained at maximum temperature of 200°C. The spectrum of the separated compounds was compared with the database of the spectrum of known compounds saved in the NIST02 Reference Spectral Library.

2.7 Preparation of blends of Acetylated product with conventional Diesel fuel

Petrol diesel was blended with different proportions of glycerol-acetic acid esters (10%, 20% and 50%). The blend (F_{10}) was prepared by heating 9cm^3 of diesel at 50°C on a hotplate magnetic stirrer agitated at 600 rpm and 1cm^3 of the glycerol-acetic acid esters was added and allowed stand for 15 minutes to ensure uniformity [7]. The same procedure was adopted in preparation of F_{20} and $F_{50.}$ (F_{20} = 20% additives and 80% diesel and F_{50} = 50% additives and 50% conventional diesel) F_{100} is 100% diesel fuel.

2.8 Determination of physicochemical properties of Blended Diesel fuel

The physicochemical properties of diesel fuel and its blends were determined using standard methods reported in various literatures. The cloud and pour points of conventional diesel fuel and its blends was determined using ASTM methods [8]. Kinematic viscosity of the conventional diesel fuel and its blend was determined using the method of Cannon manual [9]. The iodine and saponification values of both conventional diesel and its blends were determined following the methods of Akpan *et al.*[9] and Kyari[10].Mohibbe*et al.,*[12] procedure was adopted for calculation of cetane number from saponification and iodine values as related by equation 1

$$Cetanenumber = 46.3 + \frac{5458}{Saponificationvalue} - 0.225\ xIodinevalue \quad \ldots\ldots\ldots 1$$

3.0 Results and Discussion

3.1 Absorption bands of FT-IR Spectrum of the activated Carbon

The FT-IR spectra of the neat carbon and activated carbon portrayed different function groups. The FTIR spectra show a broad band at 1230cm^{-1} which can be attributed to esters, ethers, or phenol groups. The absorption band at around 2920 cm^{-1} indicates the presence of C-H bonds. The appearance of C-H absorption indicates the presence of methyl and methylene groups. The peak at 1450 cm^{-1} was attributed to CH_3 group similar peak was also observed by Bachrun*et al.*[13]. A band at 1610cm^{-1} indicates the presence of C=C vibrations possibly in aromatics compounds. The band at 1710cm^{-1} can be assigned to carboxylic groups[14]while a broad and strong vibration at 3390cm^{-1} corresponding to O-H stretching and H bending indicating the presence of alcohols and phenols. The broad vibration observed is in consistency with the aromatics and carboxylic groups observed in literature [14]. A sulphonic group was seen at 1030cm^{-1} in addition to a shoulder peak at 1750cm^{-1}, similar peaks and absorptionsband werealso reported in literatures [3]. However, the spectrum of activated carbon showed sulphonic group which is no present in the neat carbon, but nearly same peaks were observed with different intensities. The peak of phenolic group of activated carbon was seen at 3200cm^{-1} became less broader when compared with that of the un-activated carbon and the peak intensities of C-H seen at2920cm^{-1} for activated carbon comparatively reduced. Similar observations were also reported [14]. The absorption band and possible functional groups observed were presented in Table 1.

Table 1: Absorption bands and possible functional groups

Absorption band (cm^{-1})	Bond Type
3390	O-H
2920	C-H
1710	C=C
1610	C=C
1450	CH_3
1230	C-O-H
1030	SO_3H

3.2 Effect of the Process Variables on the Yield of Acetylation Reaction

The percentage yield of acetins obtained from glycerol acetylation with acetic ranged from 34.93% to 80.60%. Highest yield of 80.60% was obtained at a temperature of 110°C, 3 hours reaction time, 2.5 wt% catalyst dose and glycerol/acetic acid molar ratio of 1:4.5. The analysis of variance (ANOVA) and Regression analysis shows that the model F-value for acetins yield is significant. The significant of the model is confirmed by relatively higher Fischer's 'F-statistics' value and lower value of probability ('P' value)[15]. The "lack of fit" (*F*-value = 22.04) and (*p*-value = 0.004) implies that the lack of fit of the data is statistically significant ($p < 0.05$, at $\alpha = 0.05$). The high coefficient variation (R^2 = 94.67%) shows that the model adequately accounts for the empirical relationship between the acetins yield and the process variables.

3.3 Effect of glycerol/acetic acid ratio and reaction temperature on the yield of acetins

The contour plot as shown in Figure 1, indicates that glycerol to acetic acid ratio has significant impact on the yield of acetins. Glycerol acetylation with acetic acid is a consecutive three-step stoichiometric reaction, where, three moles of acetic acid is required to react with one molar glycerol in the stoichiometric reaction to effectively convert MAG to TAG [6]. A yield of 80.60% was obtained at 1:4.5 glycerol to acetic acid molar ratio at a temperature of 110°C, while the catalyst dosage and time were maintained at 2.5% wt and 3 hours respectively. The yield slightly decreases to 76.47% as the glycerol/acetic acid ratio decreases from 1:4.5 to 1:3, however, the lowest yield 34.93% was obtained as glycerol/acetic acid molar ratio increases to 1:6, this may be attributed to fact that high concentration of acetic Acid beyond optimal value reduces the rate of forward reaction[16]. Acetylation reaction of glycerol with acetic acid to produce acetins is an equilibrium reaction. Therefore, reaction variables such as temperature, time, catalyst dosage, and glycerol/acetic acid ratio can shift the equilibrium towards the formation of the products.

As shown in Figure1, temperature has significant effect on the yield of acetins. The maximum yield of 80.60% was achieved at a temperature of 110°C, glycerol/acetic acid ratio of 1:4.5, while the catalyst dose and time were held at 2.5% wt and 3 hours respectively. As the temperature decreases to 100°C, the yield obtained also decreases to 69.25%; this implies that, as the temperature increases from 100 to 110°C the yield obtained also increases. However, as the temperature increases further to 120°C, the acetins yield decreases abruptly to 34.93% which is the lowest yield obtained in this study. Decrease in the yield as the temperature increases to 120°C is attributed to the fact that, the boiling point of acetic acid is 118°C, therefore, increasing the temperature to 120°C beyond the boiling point of acetic acid causes it to start boiling which will limit its contact with glycerol, as a result of which also limits the conversion of glycerol and acetic acid to acetins. However, the high temperatures are not preferred, as the temperature increase and reached the boiling point of acetic acid (118°C), the acetic acid immediately vaporize and form a large number of bubbles, which inhibits the reaction on the two-phase interface and thus decreases the acetins yield. Similar observation was reported by Okoye *et al.,* [6]

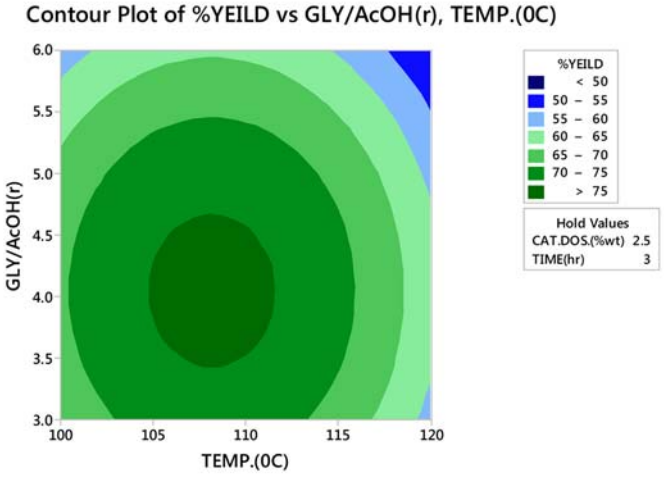

Figure 1: *Effects of glycerol/acetic acid ratio and reaction temperature on the yield of acetins*

3.4 Effect of reaction time and catalyst dose on the yield of acetins

Figure 2, shows the acetins yield from acetylisation of glycerol and acetic acid in different reaction time from 1 to 3 hours. As shown in the figure 2, time has significant effect on the yield of acetins, the conversion of glycerol increased with the increase in reaction time from 1 to 3 h. Yields of less than 50% were achieved when the reaction time is 1 hour. However, as the time increases from 1 to 3 hours, the acetins yield also increases; the optimum yield of 80.60% was achieved at a reaction time of 3 hours when the values of temperature, catalyst dose and glycerol/acetic acid ratio are 110°C, 2.5% wt and 1:4.5 respectively. In a similar experiment [6], glycerol conversion to MAG, DAG and TAG of (88.2%) after 3 hours reaction time was reported.

In their separate reports[17, 18], it was observed that DAG and TAG selectivity increased at the expense of decreasing MAG as the time increases from 1 to 3 hours. Hence, a linear relationship between increasing DAG and TAG formation and reaction time suggests consecutive reaction steps from glycerol esterification to MAG and subsequent acetylation to form DAG and then from DAG to TAG. However, the acetylation of DAG to TAG appears to be very much progressing with reaction time.

The effect of catalyst loading on glycerol esterification was determined by ranging the catalyst load from 1-4 wt% (i.e. 0.1-0.4g). From Figure 2, it is observed that the acetins yield increase with increase in catalyst dose with respect to time. The optimal yield was determined to be 0.25g with acetins yield of 80.60%. However, the minimum acetins yield of 34.93% was observed at catalyst dose of 0.1g (1 wt %). The glycerol conversion was found to increase as the catalyst increases from 1 to 2.5% wt. The yield remained constant as the catalyst dosage increase to 4% wt. It is therefore, evident to note that the active sites saturation of the catalyst was observed above 2% wt catalyst dose since no changes in glycerol conversion was observed as catalyst dose increased to 4% wt. Similar observation was also reported in literature [6]. Glycerol acetylation has also reported to proceed without catalyst but at very slower rate and the selectivity to the acetylated products are predominantly towards MAG (70%) rather than the DAG and TAG [19]. In the presence study, catalyst promotes enhanced glycerol conversion (> 80%). The catalyst achieves this by promoting acylium ion moiety that attacks the hydroxyl group of glycerol. The active centers of the catalysts are usually anionic radicals of the so-called "super acid" groups (e.g., sulfuric or sulphonic acids). The activity of these radicals is also directly related to their textural characteristics, acid site density and nature of the acid group [6].

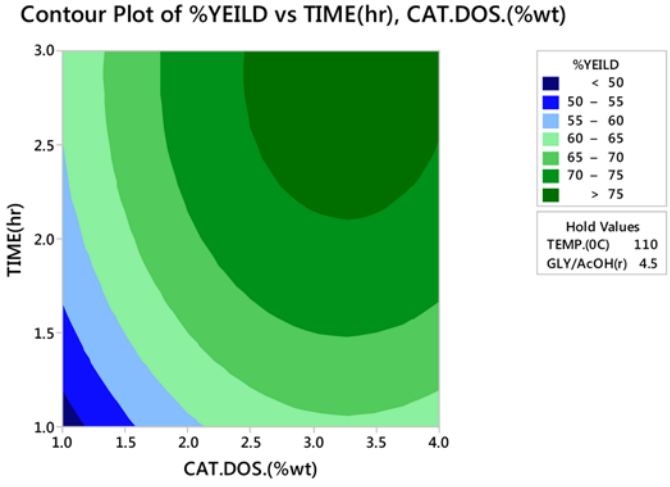

Figure 2: *Effects of catalyst dosage and reaction time on the yield of acetins*

3.5 Response Optimization and Validation

Table 2 shows the predicted results for optimal solutions obtained from the optimization. The solutions predicted maximum acetins yield of 85.63 and 80.60% and desirability of one (1) for each of the two solutions with optimal process conditions of temperature (108.3°C and 115.1°C), time (2.9 and 3 hours), catalyst dose (4 wt%) and glycerol/acetic acid (1:3 for each solution) respectively.

Acetins yield of 85.74 and 80.43% was obtained from validation of experiment carried out at the levels of the process variables predicted in solutions 1 and 2. It was observed that the optimized predicted and experimental validated results for the two solutions were 85.63%, 80.60%

Table 2: Predicted Result of Optimization and Validation of Acetins obtained from glycerol acetylization

Solutions	Temp. (^{0}C)	Catalyst(%wt)	Gly/AcOH ratio	Time(h)	Yield (%)	Desirability
1	108.30	4.00	3.00	2.90	85.63	1
2	115.10	4.00	3.00	3.00	80.60	1

and 85.74%, 80.43% respectively. Thus, with predicted yields of 85.63% and 80.60% which is similarly closer to the experimental yields of 85.74% and 80.43%, it can be concluded that the optimization model is reliable and may therefore be more attractive for larger scale acetins production from glycerol acetylization catalyzed by activated carbon obtained from sugarcane bagasse.

3.6 Characterization of Acetylated products obtained

3.6.1. FT-IR characterization of the Acetins produced

The FT-IR spectrum of the acetinsobtained has main absorption band at 3400cm^{-1} which illustrates the O-H bond for alcohols. The stretching absorption C=O was observed at 1720cm^{-1} which indicates a characteristic absorption of carbonyl group, and a sharp stretching absorbance band at 1250cm^{-1} probably indicates C-O stretching for C-O-C linkage in ester. However, from the spectrum obtained in the analysis of the acetins produced, it shows the presence of major peaks corresponding to O-H for alcohols, C=O absorption for carbonyls, and probably a C- O absorption band for esters. From the above observations, it is safe to say the spectrum obtained is for an alcohol compound attached with an ester group. Therefore, the spectrum of the compound obtained may be a monoacatin or a diacetin glycerol ester. The absorption band and possible functional groups observed were presented in Table 3.

Table 3: Absorption bands and possible functional groups

Absorption band (cm^{-1})	Bond Type
3400	O-H
1720	C=O
1250	C-O
2900	C-H

3.6.2. GC-MS profile of the Acetylated (Acetins) Product obtained

The mixture of glycerol and acetic acid was subjected to esterification reaction over an activated carbon derived from sugarcane bagasse as a catalyst was analyzed using GC-MS. The products obtained from the analysis are: 1,2,3-propanetriol-1-acetate, glycerol-1,2-diacetate and triacetin. Other compounds identified from the GC-MS data include, dichloro acetic acid and methylene dichloride. Dichloro acetic acid is formed as a result of reaction between the un-reacted acetic acid left in the reaction container and the solvent used which is methylene dichloride. Other organic products detected by GC-MS are most likely by-products.

3.7. Physicochemical parameters of Diesel fuel and the Blends

Fuel additives are usually added to conventional diesel in order to improve its fuel properties such as cetane number, kinematic viscosity, pour point, cloud point etc. The physicochemical properties of fuel blends (F_{10}, F_{20} and F_{50}) is presented in Table 4 .

Table 4: Properties of diesel blends with fuel additive

Parameter	Unit	F_{100}	F_{10}	F_{20}	F_{50}
Kinematic viscosty@40°C	mm^2/s	2.70	2.90	3.20	3.90
Cloud point	$^\circ$C	2.00	1.60	1.20	-2.10
Pour point	$^\circ$C	-16.20	-17.10	-18.30	-20.00
Cetane number	-	46.30	46.80	47.20	48.40

Key: F_{100}= 100% conventional diesel, F_{10}= 10% additives + 90% diesel, F_{20}= 20% additives + 80% diesel and F_{50}= 50% additives + 50% diesel fuel.

The blends show significant improvements in qualities of petroleum diesel such as cetane number i.e. Conventional diesel (F_{100}) 46.30 to 48.40 of blend (F_{50}) e.t.c

4.1 kinematic Viscosity

Kinematic viscosity is an important property of fuel, it affects the fluidity, lubricity and atomization of the fuel[20]. Fuels with low viscosity may not provide sufficient lubrication resulting in wear and high viscosity causes poor combustion and increases exhaust emission.

The acceptable range of kinematic viscosity for diesel fuel at 40°C was determined to be 1.3 to 4.1 mm^2/s as specified by ASTM standards. The conventional diesel (F_{100}) analyzed was found to have kinematic viscosity of 2.70 mm^2/s, which is similar to the value (2.80 mm^2/s) for petro-diesel obtained by Muhammad *et al.*[20]. The viscosity of F_{10}, F_{20} and F_{50} blends of fuel additive with diesel fuel are 2.9, 3.2 and 3.9mm^2/s respectively. The viscosity of diesel blends with additives increases slightly from 2.7 to 3.9mm^2/s. Even though additives increases the viscosity of diesel the values obtained for both blends F_{10}, F_{20} and F_{50} are within the specified limits (1.3 to 4.1 mm^2/s) of ASTM standards. The results obtained from these blends are highly favorable as per the proper ignition due to lower values of viscosity which is capable of improving the diesel fuel and effectively used for better performance of diesel engine. The blends show significant improvements in qualities of petroleum diesel.

4.2 Cloud point

The cloud point is the temperature at which the dissolved materials are no longer soluble in the fuel and precipitated, which will give the fuel cloudy appearance. The ASTM Specification for maximum allowed values of cloud pointis within the range of -15 to 5 °C. The cloud point of market purchased diesel fuel was found to be 2°C which is lower than the values of 5.2°C obtained byMuhammad *et al.,*[21]. From Table 3, blends F_{10}, F_{20} and F_{50} were found to have cloud point of 1.6, 1.2 and –2.1°C respectively. From these values, it is evident that theglycerol-acetic acid esters added to the diesel fuel decreases its cloud point slightly. Thus, all the values obtained were within the ASTM standard range of required values of cloud point of petro diesel.

4.3 Pour point

The pour point of liquid is the temperature below which the liquid loses its flow characteristics. It is defined as the minimum temperature in which the oil has the ability to pour down from a container. The pour point is carried out to determine the freezing point of the sample. The ASTM Specification for maximum allowed values of pourpoint is within the range of -15 to -25°C. The pour point obtained for purchased diesel fuel was found to be -16.2°C which corroborated with the result of -15.9°C obtained by Muhammad *et al.,* [21]. From Table 3, blends F_{10}, F_{20} and F_{50} were found to have pour point of -17.1, -18.3 and -20°C respectively. All the values obtained from (Table 3) are within the range of ASTM standards of pour point for diesel. Similar to cloud point, blending the diesel with glycerol-acetic acid ester reduce its pour point but stillwithin the limit of ASTM for diesel fuel. The produced ester positively improves the cold-flow properties of diesel by reduction of 2.1°C and 3.8°C for cloud and pour point respectively.

4.4 Cetane number

Cetane number (CN) measures the ignition performance of a fuel. It is a fuel quality parameter that is related to the ignition delay time and combustion quality of a fuel, it measures the readiness of a diesel fuel to auto ignites when injected into the diesel engine. Generally, the higher the cetane number, the shorter the ignition delay and the higher the propensity of the fuel to ignite[22]. A fuel of higher cetane number gives lower delay period and provides smoother engine. Diesel blended with glycerol-acetic acid ester has higher CN than petro-diesel because of its higher oxygen content[23].The cetane number of conventional diesel calculated was 46.30, this corroborated the result obtained (46.22) for diesel fuel by Metin*et al.*[24], and the cetane number of 46.80, 47.20 and 48.40 was achieved for F_{10}, F_{20} and F_{50} respectively as diesel fuel was blended with additives accordingly (Table 3). Similar result was also reported[24], on the effectiveness of Mn, Mg, Cu and Ca solutions as additives to diesel fuel. Also with the result reported by Punam and Rajat[23], which indicates the increase in cetane number from 45.60 to 48.30 when diesel fuel is blended with 1,3-dioxolan-4-yl) methanol, 2-ethyl-2-methyl-1,3-dioxolan-4-yl)

methanol and (2-ethyl-2-methyl-1,3-dioxolan-4-yl) methyl hexanoate in different proportion. From the result obtained in Table 3 it indicates that the blends have high cetane number compared to the conventional diesel and therefore, will have superior ignition quality compared to conventional diesel which is attributed to the higher oxygen content present in the additives synthesized.

5. Conclusion

This study demonstrated the production of glycerol-acetic acid esters via acetylation reaction over activated carbon prepared from sugarcane bagasse. The prepared activated carbon has successfully and effectively catalyzed the glycerol esterification to produced MAG, DAG and TAG of 80.60%). An optimum yield of acetins was achieved at 3 hours reaction time, 110^0C temperature, 2.5 wt% catalyst load and glycerol to AcOH ratio of 1:4.5. The prepared blends of petro-diesel fuel with the produced glycerol-acetic acid esters significantly improved he kinematic viscosity, cold flow properties and cetane number of conventional diesel fuel.

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