

OPTIMIZED REDUCTION OF FREE FATTY ACID CONTENT ON NEEM SEED OIL, FOR BIODIESEL PRODUCTION

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ABSTRACT

Neem seed oil has been used in the production of biodiesel but with a two step free fatty acid content reduction. This study looks at the effect of various methanol quantities on acid concentration on reduction of free fatty acid content in neem seed oil having acid value of 29.87mgKOH/g and optimization of methanol and acid concentration during its pre-treatment for making biodiesel. With reaction and separation time of 1hr, temperature of 60^oc, variation of the two parameters significantly affected the acid value, with methanol being most effective. Using 100ml of the oil, the optimum combination for reducing the free fatty acid level of neem seed oil to less than 0.5% after pre-treatment was 0.58:1 methanol-to-oil ratio, 0.75% v/v sulphuric acid to-oil volume, at set conditions. After pre-treatment of neem seed oil, trans-esterification reaction was carried out with 20% methanol-to-oil volume and 1% w/v NaOH as an alkaline catalyst to produce the fatty acid methyl ester. Physicochemical analysis was carried out to ascertain its biodiesel status which conformed to ASTM specification, i.e Acid value of 0.42mgKOH/g, Viscosity of 3.58cst at 30^oC, Density of 0.8732 with an ester conversion of 98%.

Keywords; Biodiesel; Neem seed oil; Esterification; High free fatty acids.

INTRODUCTION

The demand for energy supply in the world have increase tremendously due to increase in consumption rate. Report cited that the world non-renewable energy resources such as petroleum, gas, coal etc will soon be exhausted, hence there is need to act fast in other to start generating an alternative source of fuel that are renewable to replace the fossil fuel. The alternative fuel that is to replace the fossil fuel must be readily available , environmentally acceptable, economically competitive and technically feasible. Fatty acid methyl ester derived from renewable source such as vegetable oil, which could either be fresh or waste vegetable oil are find useful in Europe, America and Asia as a feedstock in production of biodiesel, as a consequence, biodiesel derived from a wide variety of sources can be used as a direct substitute for petro-diesel fuels[9] . However the use of edible oil as a feedstock in engine fuel is not economical, hence a non-edible oil is best suited for this, for effective economic purpose. They are several non-edible oilseed species such as thevetia(thevetia peruviana), karanja(pongomia pinnate), jatropha(jatropha curca), neem(azadirachta indica) etc, that could be utilized as a feedstock oil in biodiesel production. Among these, azadirachta indica seed which contain about 25%-45% oil on dry matter basis is a non-edible oil that can be use in biodiesel production. Azadirachta indica is an evergreen tree natural to southeast Asia, growing in tropical and semi tropical regions. It belong to the mahogany family (meliaceae) and also one of the two species in the genus Azadirachta, the fruit is smooth olive-like drupe which varies in shape from elongated to oval to nearly roundish, its exocarp is thin and the bitter sweet pulp (mesocarp) is yellow-white and very fibrous having thickness between 0.3-0.5cm, the white hard inner shell endocarp enclose one, rarely two or three elongated seed(kernels) having a brown seed coat that contain between 25%-45% neem oil. The oil contain three bitter compound that can be extracted from it which are nimbin, nimbinin and nimbidin which are mostly responsible for it medicinal value[1], it can also be use in cosmetics preparation and act as an effective mosquito repellent. Neem oil is known for high free fatty acid value which is accompanied with moisture content, this two have significant effect on the trans-esterification of glycerides with alcohol using catalyst[2], to reduce the cost of biodiesel production it is required that a less expensive feedstock containing fatty acids such as non-edible oil, waste food oil, animal fats and by-products of refining vegetable oil be use[11]. However most non-edible oil have high free fatty acid content which will add cost to it production via trans- esterification, an FFA content more than 2% will form soap and the separation of the product will be very difficult as a result, it produces low yield fatty acids methyl esters.

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MATERIALS AND METHODS

Materials

The extracted Neem seed oil was obtained from National research institute for chemical technology (NARICT) Zaria, Nigeria. The average composition of neem oil fatty acids composition is given in table 1, commercial grades of sodium hydroxide, methanol and sulphuric acid were used in this study, a round bottom flask was used as laboratory scale reactor, a hot plate with magnetic stirrer arrangement was used for heating the mixture in the flask while stirring at the speed of 150rpm at controlled temperature of 60⁰c.

Table 1 Average fatty acid composition in crude Neem seed oil[5]

| FATTY ACID | SYSTEMATIC NAME | FORMULA | COMPOSITION RANGE |
|-------------|-------------------------------------|--|-------------------|
| Linoleic | Cis-9, cis-12- Octadecedianoic | C ₁₈ H ₃₂ O ₂ | 6-16% |
| Oleic | Cis -9-octadecenoic | C ₁₈ H ₃₄ O ₂ | 25-54% |
| Palmitoleic | Cis-9-hexadecenoic | C ₁₆ H ₃₀ O ₂ | ?% |
| Palmitic | Hexadecanoic | C ₁₆ H ₃₂ O ₂ | 16-33% |
| Stearic | Octadecanoic | C ₁₈ H ₃₆ O ₂ | 9-24% |
| Linolenic | Cis-6,cis-9,cis-12-octadecatrienoic | C ₁₈ H ₃₀ O ₂ | ?% |

Experimental procedure

Biodiesel production from vegetable oil depend on several basic variables such as catalyst-to-oil ratio, alcohol-to-oil ratio, catalyst type, alcohol type, reaction time, agitation rate, reaction temperature, FFA and water content of oils[8]. This experiment looks at the effects of various methanol and sulphuric acid concentrations on acid value in neem seed oil during esterification, indicating the most effective combinations at a fixed reaction time of 1hr, temperature of 60⁰c, agitation rate of 150rpm and separation time of 1hr. The esterified oil was subjected to trans-esterification process to ascertain the yield of it methyl ester.

Acid pre-treatment

100ml of Neem seed oil was introduce in the reactor flask and heated to 60⁰c while stirring, this was repeated severally while keeping the oil volume constant and changing the variables. Step One; 0.50, 0.75, 1.00, 1.25 and 1.50%v/v of sulphuric acid-to-oil volume and 45ml,50ml, 55ml, 58ml,60ml,63ml,65ml and 70ml of methanol was mixed with concentrated sulphuric acid in each of the experiment to obtain the optimum combination where the FFA value is lowest.

Step two, 0.75%v/v of sulphuric acid volume-to-oil and 58ml of methanol in 100ml of oil representing 0.58:1 methanol- to-oil ratio, was used in the esterification process to obtain the optimum combination. In this study, sulphuric acid was mixed with the oil and allow to stir for 5min before adding methanol, the reaction time was kept at 1hr in all the experiments. The stirrer was stopped when the reaction time was complete and the esterified oil transferred into a separating funnel, which is allow to stand for 1hr, the methanol-water layer was formed at the top which was subsequently removed before analysing the FFA value. The optimum combination of methanol and acid that produced the lowest FFA value in the oil was obtained, this was then used in trans-esterification process to produce the methyl ester.

Analytical method

Acid value

The acid value of the reaction mixture in all the experiments was determined with acid/base titration technique using AOCS 2001 method. A standard solution of 0.1M KOH solution was used and result was calculated with the following formula.

$$AV = (TV) \cdot (56.1) \cdot (0.1) / \text{oil wgt}$$

$$FFA = AV / 2$$

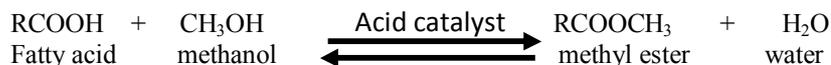
Table 2. Physicochemical properties of the methyl ester of Neem seed oil was carried out to ascertain it biodiesel status, the result are seen in the table above.

| PARAMETER | RESULT |
|--------------------------------------|-------------------------|
| Acid value | 0.42mgKOH/g |
| Viscosity @ 30 ⁰ C | 3.58cst |
| Specific gravity @ 30 ⁰ C | 0.8732gcm ⁻³ |
| Ester conversion | 98% |
| Cloud point | 13 ⁰ C |
| Pour point | 10 ⁰ C |
| Flash point | 175 ⁰ C |
| Carbon residue | <0.2%wt |

Chemistry of reaction

Biodiesel synthesized from vegetable oil with high FFA content using the two-steps process involving acid catalysis which is quite effective in converting FFAs to methyl ester producing water as one of it by-product and

the reaction is practicable[4]&[3], findings pointed out that some have adopted this method in their research work[10],[6] &[7]. It is very necessary to reduce the FFA content of oil before trans-esterification because of the formation of soaps which promote stable emulsion formation, this is as a result of hydrolysis reaction that is catalysed by the present of water. The overall reaction can be represented as follow,



The amount of water content generated from the reaction depend on the concentration of free fatty acid in the oil and the volume ratio of methanol and acid to the oil. However, a perfect combination of the variables could be achieve were the FFA content can actually be reduce to near zero by adding the exert methanol concentration and catalyst, as excess in any of the variables will affect the equilibrium.

Based catalyzed trans-esterification

The esterified oil that has been pre-treated from the optimum combination of methanol and acid was poured into a reaction vessel while maintaining the temperature at 60⁰c, a solution of 1%w/v of sodium hydroxide- to-volume of oil and 20% methanol to volume of oil was mixed and heated to 60⁰c in an air-tight vessel which dissolve to form sodium methoxide prior to addition to the heated oil. The mixture was stir at 150rpm at a controlled temperature of 60⁰c for 45min, this was transferred to the separating funnel and allow to stand for 2hr before decanting to obtain the methyl ester having 96% yield.

Washing

The technique used was bubble washing were 10% water to biodiesel volume was used for the process, washing was carried out in three stages. The biodiesel was poured into a separation funnel and water is gently bubbled with the aid of syringe to minimize soap formation and emulsification, gentle agitation was applied to enhance the dispersion of water throughout the biodiesel, water being denser absorbs excess alcohol, sodium hydroxide and suspended soap in the biodiesel before settling at the bottom were it was drained off. The first water drained off the bottom was milky while the final washed water drained off was cleared. The biodiesel was finally subjected to heating at 110⁰c for 20min to eliminate the remaining water present.

AV against CH₃OH

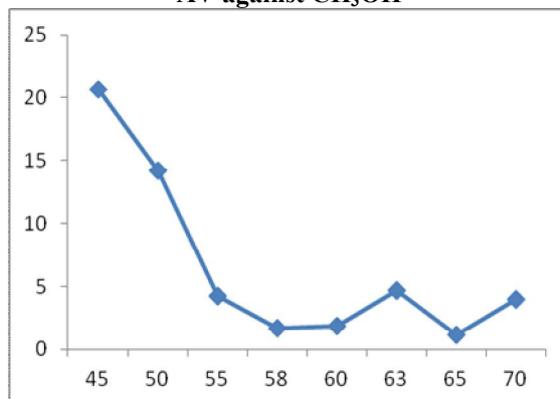


Figure 1. Variation of acid value and methanol concentration during acid esterification process by using 0.5% by volume of sulphuric acid-to-oil volume

AV against CH₃OH

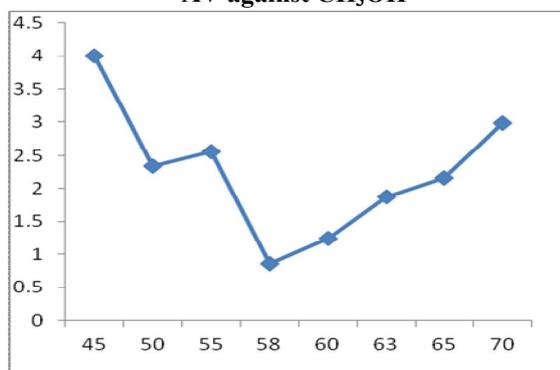


Figure 2. Variation of acid value and methanol concentration during acid esterification process by using 0.75% by volume of sulphuric acid-to-oil volume

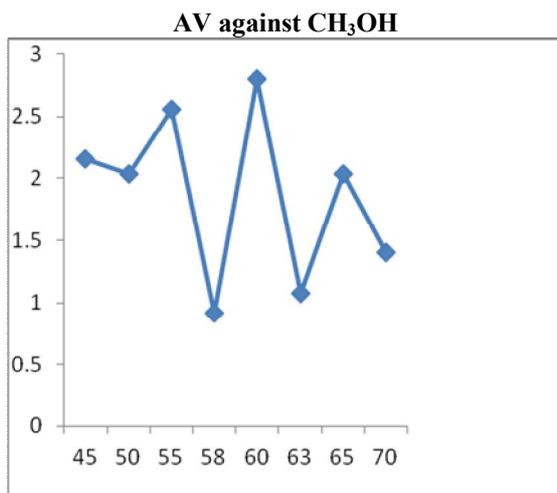


Figure 3. Variation of acid value and methanol concentration during acid esterification process by using 1.00% by volume of sulphuric acid-to-oil volume.

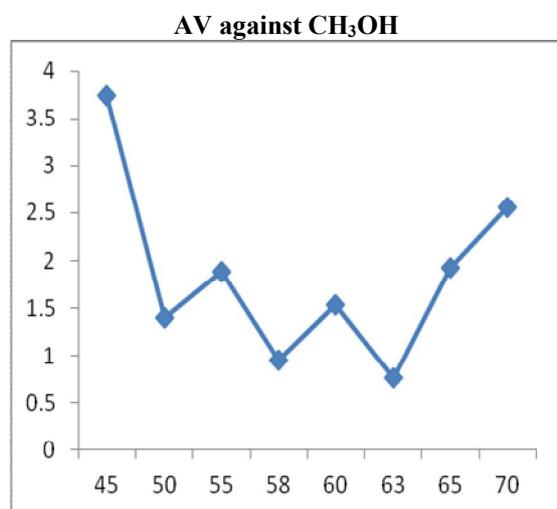


Figure 4. Variation of acid value and methanol concentration during acid esterification process by using 1.25% by volume of sulphuric acid-to-oil volume.

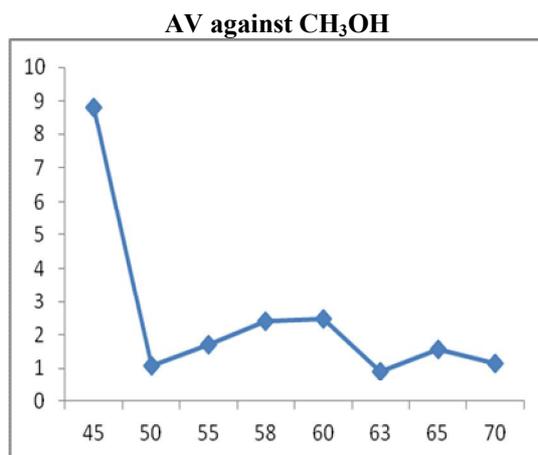


Figure 5. Variation of acid value and methanol concentration during esterification process by using 1.5% by volume of sulphuric acid-to-oil.

RESULTS AND DISCUSSION

Figure 1-5 shows the various effects of methanol concentration on acid value in neem seed oil during acid esterification process by using 0.5, 0.75, 1.00, 1.25, 1.5%v/v of sulphuric acid-to-oil volume and 45ml, 50ml,

55ml, 58ml, 60ml, 63ml, 65ml, 70ml of methanol. The optimum combination was achieved at 0.75%v/v sulphuric acid and 58ml of methanol, this produced an acid value <math><1.0\text{mgKOH/g-oil}</math>, which is equivalent to an FFA <math><0.5\%</math>.

Figure 2, keeping sulphuric acid concentration constant at 0.75%v/v to- oil, the graph depicts that the acid value gradually reduces from 45-58ml methanol, with 58ml and 45ml being the lowest and highest level of acid value point, representing 0.863 and 4.03mgKOH/g-oil, while above 58ml methanol concentration, the graph shows increasing acid value in this other 1.24< 1.88< 2.16 and 2.98mgKOH/g with respective increasing methanol concentration in this other 0.60< 0.63< 0.65< 0.70 to-oil ratio. This significant increasing effect of acid value just above 58ml methanol concentration shows that above this point the methanol concentration becomes excess and offsets the equilibrium reaction in the acid-catalysed esterification process.

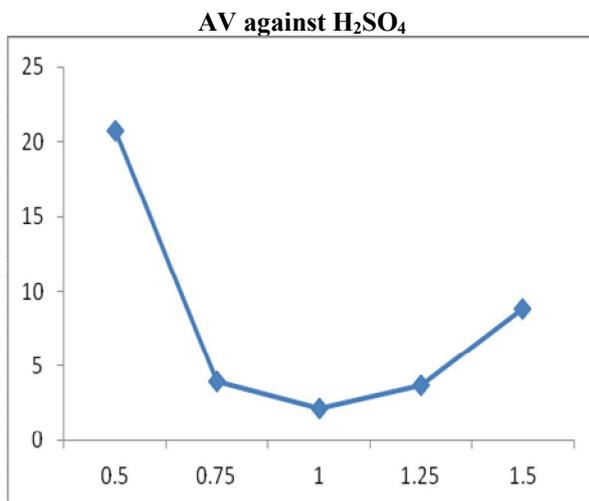


Figure 6. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.45:1 methanol-to-oil ratio.

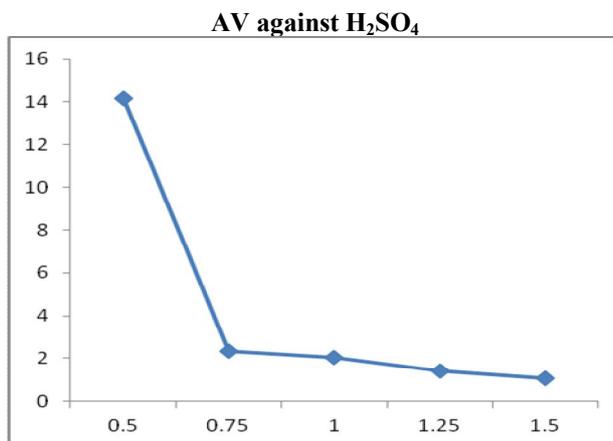


Figure 7. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.50:1 methanol-to-oil ratio.

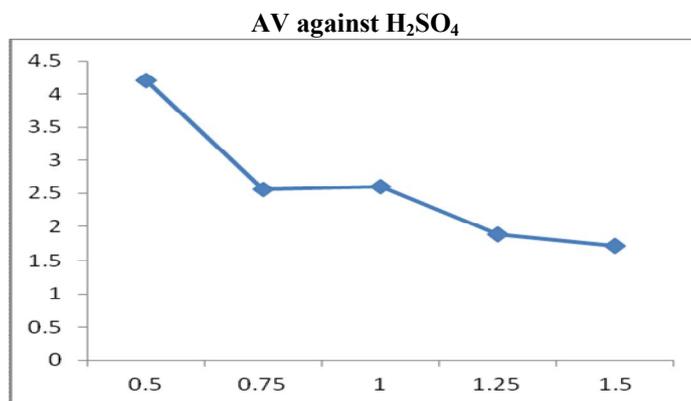


Figure 8. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.55:1 methanol-to-oil ratio.

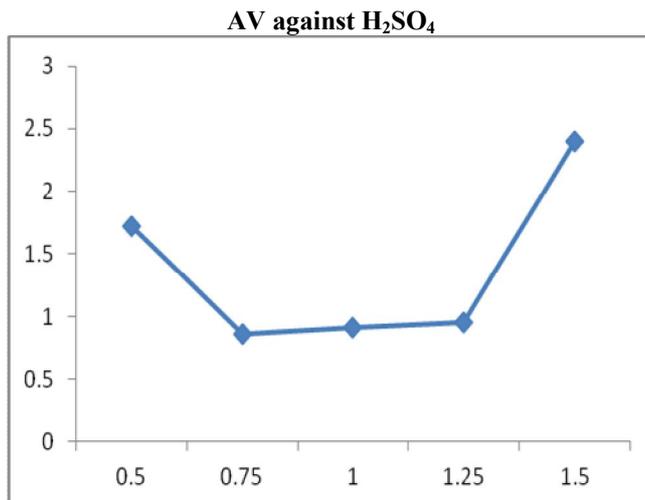


Figure9. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.58:1 methanol-to-oil ratio.

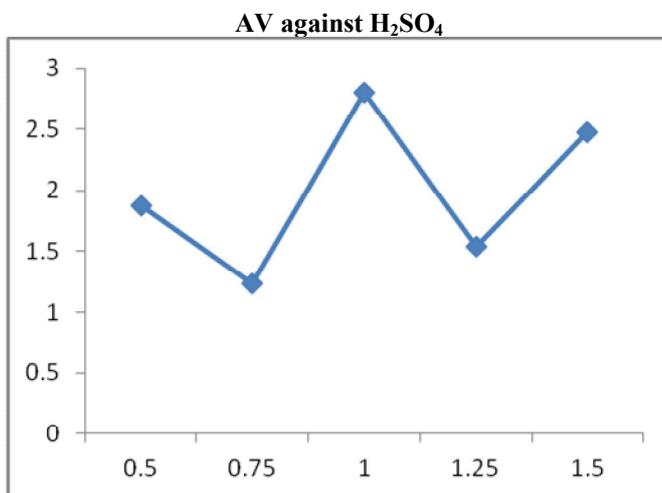


Figure10. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.60:1 methanol-to-oil ratio.

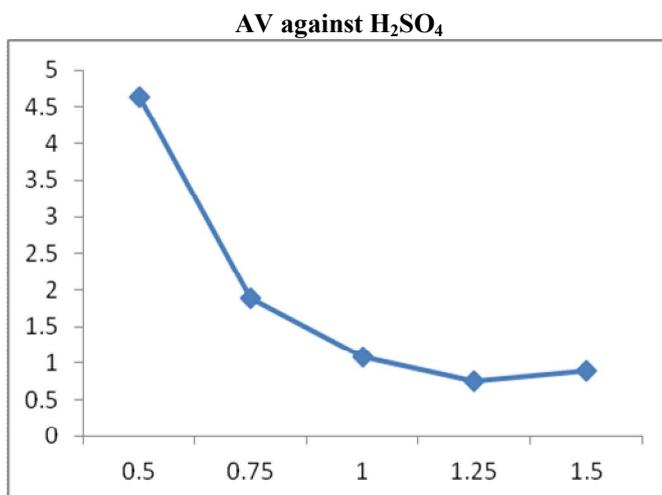


Figure 11. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.63:1 methanol-to-oil ratio.

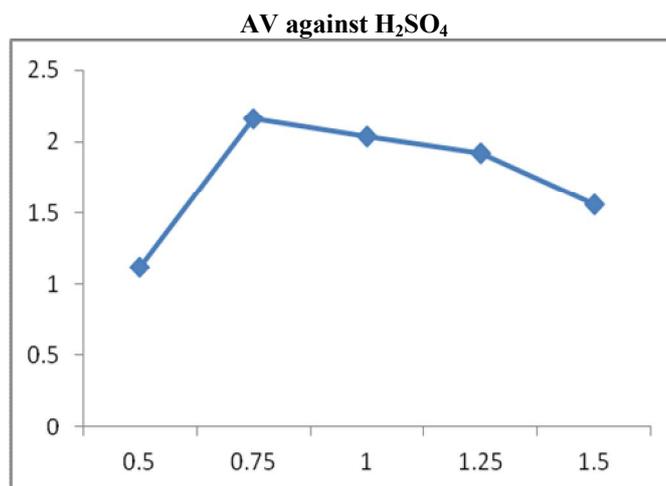


Figure 12. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.65:1 methanol-to-oil ratio.

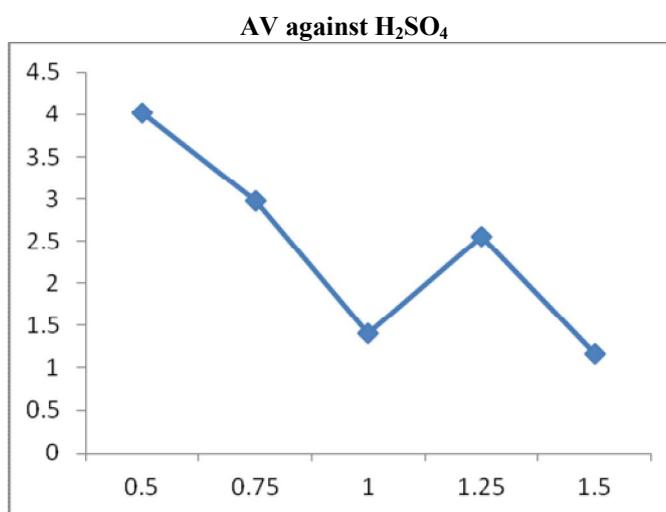


Figure13. Variation of acid value (AV) and sulphuric acid concentration during esterification process by using 0.70:1 methanol-to-oil ratio.

DISCUSSION

Keeping the oil volume and methanol concentration constant, while varying sulphuric acid concentration, a combination of 1.25%v/v sulphuric acid to-oil volume and 63ml of methanol in figure(11) gives acid value of 0.81mgKOH/g-oil, while the combination of 0.5%v/v sulphuric acid to- oil volume and 45ml of methanol in figure(6) gives acid value of 20.74mgKOH/g-oil, representing the lowest and highest acid values in all the experiments. In figure 9, the acid value shows sharp decrease from 1.72mgKOH/g to 0.86mgKOH/g and start increasing as the concentration of sulphuric acid is just above 0.75%v/v to-oil volume indicating that > 0.75%, the sulphuric acid concentration becomes excess and aid in acid value increment. The research shows that the acid value obtained in figure(6) at a combination of 0.5%v/v sulphuric acid to-oil volume and 45ml of methanol represent a reduction level of acid value with just 30.57%, while in figure(11) at a combination of 1.25%v/v sulphuric acid to-oil volume and 63ml of methanol represents reduction level of acid value with 97.29% in one step process.

CONCLUSION

The objective of this study was to investigate the effect of various methanol and acid concentration on free fatty acid(FFA) content and optimize the combination of the two variables to obtain an FFA value of <0.5% from neem seed oil. It has been determined that vegetable oil with high FFA content can not be trans-esterified with alkaline catalyst in one-step process, this is owing to the reaction between the catalyst and the FFA which forms soap, promoting emulsion formation that hinders the separation of the biodiesel from the glycerine. The effect of various methanol volume, acid amount while keeping other variables constant on reduction of FFA were studied with neem seed oil having acid value of 29.87%.This study showed that the FFA level of the

feedstock could be reduced to less than 0.5% with a one-step process that involves the pre-treatment of the feedstock by acid-catalysis. The optimum combination for the two variables was 0.75%v/v sulphuric acid to-oil volume and 0.58 of methanol-to-oil ratio and 1.25%v/v sulphuric acid to-oil volume and 0.63 of methanol-to-oil ratio, which produces FFA < 0.5%. This study further shows that at set condition of 0.75%v/v sulphuric acid, while varying the methanol concentration, the FFA gradually reduces from 0.45-0.58 methanol concentration with 0.58 being the lowest point where optimum combination is achieved. However it was discovered in figure (2), that in all variations of methanol concentration and while keeping acid concentration constant at 0.75%v/v sulphuric acid to-oil, the FFA produced is less than or equal to 1%, while with <45ml of methanol concentration, the FFA achieved was >2%. It is recommended that the optimum combination achieved in this work be applied during acid pre-treatment in order to reduce cost and maximize the yield of the methyl ester during biodiesel production.

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