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EFFECTS OF TEMPERATURE, CONCENTRATION OF CATALYST AND REACTION TIME ON BIODIESEL PRODUCTION FROM *GOSSIPIUM HIRSUTUM* SEED OIL

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ABSTRACT*:* *Gossipium hirsutum (cotton) seeds were collected and processed. 500.00 g of the processed cotton seeds were subjected to soxhlet extraction for 5 hours at 85°C using absolute methanol (as extracting solvent). The extract (cotton seed oil) was recovered from extracting solvent by rotary evaporation and conce°ntrated to a constant weight at 37°C. A solution mixture of volume ratio, 1: 9 of cotton seed oil to methanol was prepared and subjected to transesterification reaction under different operational conditions of temperature, concentration of catalyst (KOH) and reaction time for biodiesel production. The biodiesel produced was separated from the associated product (glycerol). The excess methanol containing biodiesel produced was removed by distillation. The saponification value of the glycerol component of the transesterification product was determined. The work showed that the optimum operational conditions for maximum biodiesel production were 65°C, 1.00 M of KOH (as catalyst) and 65 minute. The work also showed that: temperature above 65°C led to decomposition of biodiesel; catalyst concentrations above 1.00 M led to formation of soap as by-product and; prolonging of reaction time beyond 65 minute led to hydrolysis of the biodiesel formed.*

KEYWORDS*:* *Gossipium hirsutum seed oil; transesterification reaction; biodiesel; glycerol; saponification value.*

INTRODUCTION

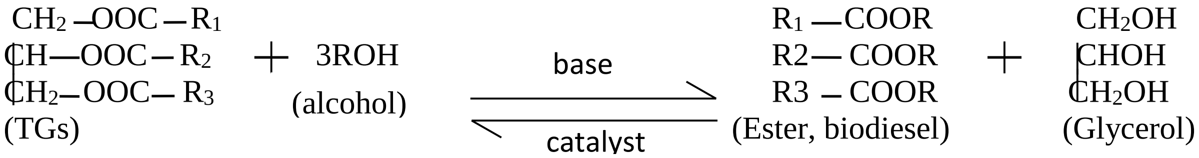
Presently, Nigeria is in the grip of an unprecedented energy crises caused by the political influence on fuel supply and distribution by the major and independent petroleum products marketers. There is also the problem of face-up between the oil-rich communities and the Federal Government of Nigeria due to long time neglect of the region in terms of infrastructural development and environmental pollution (Ndana and Manko, 2010). In addition, the hike price of fossil fuels (petrol, diesel, kerosene, liquefied natural gas, e.t.c.), which are difficult to get by the majority of common people also contributes nuisance in using these fuels (Ekwenchi and Yaro, 2010).

The interest in adopting the use of renewable energy came to the fore during the worldwide energy crisis of the 1970s when high fuels (oil and gas) demand highlighted the world's dependence on fossil fuels in which the rate of consumption was much faster than it was drilled from the earth crust, which may result in the depletion of fossil fuels supply all over the world (Ndana and Manko, 2010). Population growth worldwide, which led to high energy demand, environmental problem and health hazards associated with the use of fossil fuels also fronted the search for renewable energy sources as alternative to popular conventional fossil fuels (Sani, *et al*, 2014).

In order to overcome or minimize the aforementioned problems associated with the drilling, refining and combustion of fossil fuels, as well, as to succeed in achieving alternative renewable energy sources (biodiesel inclusive), there is the need to embark on research and exploitation of seed oils from renewable biomass resources in our natural environment. This can be achieved by domesticating and growing viable plants as energy crops on our endowed vast land (Garba *et al*, 2012). Some common raw material for biodiesel production include : soya beans, palm oil, shear butter oil, poultry oil, fish oil, groundnut oil, algae, *Jatropha curcas* seed oil, *Gossipium hirsutum* seed oil, seseme oil and sorghum (Pinto *et al*, 2005).

Biofuels are generally alternative renewable energy sources, which are environmentally-friendly due to their biodegrability and low emission of carbon (ii) 0xide, sulphur-free quality and non toxic nature (Sani *et al*, 2014). Biodiesel was found to be promising alternative to popular fossils fuels, as it possesses all the properties of the conventional diesel, such as high flash point and improved cetane number (Shajaratun *et al*, 2014). Biodiesel is a clean burning fuel produces through transesterification reaction between triglycerides (TGs) and short chain alcohol (methanol or ethanol) in the presence of catalyst. The process of biodiesel production (i.e. transesterification reaction) is achieved through various methods such as base catalyed transesterification, direct acid catalysed transesterification or conversion of oil to fatty acid and subsequently to biodiesel (Ndana and Manko, 2010).

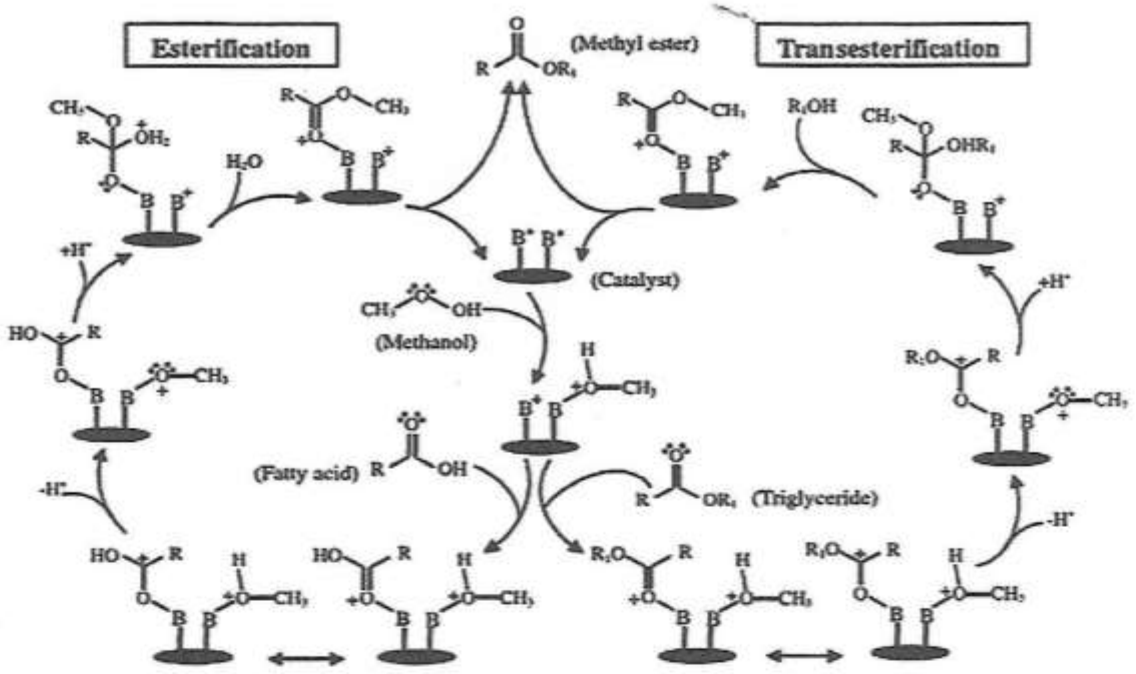
The chemistry of biodiesel production through transesterification reaction involves deprotonation of alcohol with a base and become a very strong electrophide. The base serves as a catalyst, which helps the transesterification reaction between TGs and short chain alcohol (usually methanol) to quickly occur and form ester of fatty acid (biodiesel) and glycerol (trihydric alcohol) according to the equation below as reported by Nasar *et al* (2016).



$$\begin{array}{l} CH_2-OOC-R_1 \\ CH-OOC-R_2 \\ CH_2-OOC-R_3 \\ \text{(TGs)} \end{array} + \begin{array}{c} 3ROH \\ \text{(alcohol)} \end{array} \underset{\text{catalyst}}{\overset{\text{base}}{\rightleftharpoons}} \begin{array}{l} R_1-COOR \\ R2-COOR \\ R3-COOR \\ \text{(Ester, biodiesel)} \end{array} + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \\ \text{(Glycerol)} \end{array}$$

During transesterification of TGs into biodiesel, some of the biodiesel formed decomposed into glycerol at temperature above 65°C ; more TGs participate in saponification reaction with the catalyst at high concentration of base catalyst and; extension of reaction time leads to hydrolysis of ester into TGs, which subsequently produces soap (Garba *et al*, 2012).

The major focus of recent advancement is the development of recyclable heterogeneous solid acid catalyst (SACs) for easier production of biodiesel. These catalysts have been established as favourable alternative to commercially used catalyst for biodiesel production (Nasar *et al*, 2016). SACs both the Bronsted–type (such as sulphonic acid containing materials) and Lewis-type (such as mixed sulphated oxides) combined the advantages of heterogeneous base catalysts and mineral acids (Choundan and Sarma, 2011). The exceptional advantages to this particular class of catalyst (SACs) are insensitivity to moisture and simultaneous esterification and transesterification reactions as can be seen in the following schematic reaction diagram as reported by Nasar *et al* (2016):



B^+ = Bronsted acid site on the catalyst surface

R = alkyl group of fatty acid

R_1 = alkyl esters of triglyceride

Elimination of the final biodiesel washing step, minimizing of corrosion problem even in the presence of acid species, selectivity, recyclability and easy regeneration of catalyst after use are also advantages of SACs (Guo *et al*, 2012). Another advantage of SACs is its ability to sterically hinder salvation of the catalytic active sites from the action of water, which helps in minimizing catalyst deactivation, minimizing of product (biodiesel) contamination as a result of easy separation from the reaction medium (Nusterer *et al*, 1996). In addition, the applicability and hydrophobic surface of SACs, which prevents the polar by-products (water and glycerol) from deactivating the active sites, which in return enhances selectivity adsorption of oily hydrophobic molecules to the surface of the catalyst as reported by Choundan and Sarma, (2011). These advantages among many others attracted attention in considering solid acid catalysed biodiesel production much over base catalysed process on low grade feedstock (Nasar *et al*, 2016).

However, very little has been done on the mechanism and reaction pathways of TGs on SACs during the production of biodiesel. These short comings together with some other technological challenges necessitated the adoption of predominantly conventional method of biodiesel production. (i.e. base catalysed transesterification method) in the present work. This work reports studies on the effects of temperature, reaction time and concentration of catalyst on the production of biodiesel and glycerol from *Gossipium hirsutum* seed oil and The work also reports studies on the quantitative determination of soap generated under these operational conditions.

MATERIALS AND METHODS

Collection and Processing of Experimental Sample

Dried cotton (*Gossipium hirsutum*) seeds were collected from a cotton processing factory in Malumfashi Local Government Area, Katsina State, Nigeria. The seeds were ground using grinding machine and sieved to a particle size of less than 250 x 10^{-6} m using mesh according to the method described by Ekwenchi *et al* (1998) with few adjustments.

Extraction of Cotton Seed Oil.

A mass (500.00 g) of ground *Gossipium hirsutum* seeds were subjected to soxhlet extraction for 5 hours at 85^{o}C using absolute methanol. The extract (cotton seed oil) was recovered from the extracting solvent (methanol) by rotary evaporation and concentrated to a constant weight at 37^{o}C on hot plate in fume cupboard.

Preparation of Solution Mixture

A solution mixture was prepared by mixing of methanol with cotton seed oil in the volume ratio (1:9) of cotton seed oil to methanol according to the method described by Garba *et al* (2012) with few adjustments.

Effect of Temperature on Biodiesel Production

A volume of solution mixture (400.00 cm^3) containing 10.00 cm^3 of 1M KOH (as catalyst) was place in a reactor (500.00 cm^3 round bottomed flask). The mixture was heated on a hot plate at 35^{o}C along with stirring using magnetic stirrer at the rate of 450 rpm. The heating and stirring were stopped when 2 distinct liquid phases were formed, which were allowed to cool and settle. The top phase containing the ester of fatty acid (biodiesel) was separated from the bottom phase (glycerol) using separating funnel. The excess methanol in the top phase was removed by distillation leaving behind the biodiesel according to the method described by Ndana and Manko (2010). The volume of the biodiesel and glycerol collected were measured and recorded. The process was repeated at 45 ^{o}C, 55 ^{o}C, 65 ^{o}C and 75 ^{o}C using equal volume of catalysed solution mixture (i.e. 400.00 cm^3 containing 10.00 cm^3 of 1M KOH.

Effect of Concentration of Catalyst (KOH) on Biodiesel Production

In order to investigate the effect of concentration of KOH (as a catalyst) on biodiesel production, 10.00 cm^3 each of 0.50 M, 1.00 M, 1.50 M, 2. 00 M and 2.50 M of KOH was added into 5 different reactors of equal capacity (i.e. 500.00 cm^3 round bottomed flasks) each containing 400.00 cm^3 of the solution mixture earlier prepared, which were labeled A,B,C,D and E, respectively.

The catalysed solution mixtures in the reactors were heated at 65 ^{o}C along with stirring at the rate of 450 rpm using magnetic stirrer. The heating temperature, 65 ^{o}C was from the findings of the effect of temperature carried out earlier in the present work). The process of biodiesel collection was carried out as earlier described in the effect of temperature of the present work.

Effect of Reaction Time on Biodiesel Production.

In this experiment, 10.00 cm^3 each of 1.00 M KOH was added into 5 different reactors of equal capacities (i.e. 500.00 cm^3 round bottomed flasks) each containing 400.00 cm^3 of solution mixture, which were labeled A, B, C, D and E.(The concentration of KOH used was from the findings of the effect of catalyst concentration in the preceding investigation in this work).
The catalysed solution mixtures were heated each at 65 °C along with stirring using magnetic stirrer at the rate of 450 rpm. The reaction times (minutes) used for transesterification reaction in A, B, C, D, and E were 35, 45, 55, 65, and 75, respectively. The process of biodiesel collection was carried out as previously described in the effect of temperature in this work.

Determination of Saponication Value

In order to determine the amount of soap generated as by-product due to side reactions of glycerol during transesterification of TGs into biodiesel, 25.00 cm^3 of glycerol obtained in each of the investigations (ie effects of temperature, concentration of catalyst and reaction time) carried out in the proceedings experiments was placed in a 250 ml conical flask containing 40.00 cm^3 of freshly prepared 0.10 M ethanolic potassium hydroxide solution. The conical flask was attached to a reflux condenser and heated at 65 °C on a water-bath for 30 minutes with frequent shaking to ensure the homogeneity of the solution mixture (i.e. glycerol and ethanolic potassium hydroxide solution). 1.00 cm^3 of 1% phenolphthalein indicator was added into the hot excess ethanolic potassium hydroxide solution and titrated with 0.10 M HCl. A blank titration was also carried out using distilled water. The process was repeated 3 times and the average titre volume of 0.10 M HCl used was computed. The saponification value was evaluated (in mol/dm^3) using the modified form of equation adopted by Alabi (2014) below.

$$SV=\left(\frac{(S-B) \text{ x } C \text{ x mass of 0.1 M KOH}}{\text{Volume of glycerol used}}\right)$$

where SV= Saponifacation Value
S= Sample titre Value
B= Blank titre value
C= Molar concentration of HCl

Results and Discussion

The results of all the experiments carried out in this work are shown in Tables 1-3 below. Table 1 shows the effect of temperature on transesterification of TGs into biodiesel and glycerol. Table 2 gives the results obtained under the effect of concentration of base catalyst (KOH) during the transeterification of TGs into biodiesel at 65 °C. Table 3 shows the effect of reaction time on transeterification of TGs into biodiesel and glycerol at 65 °C.

Table 1: Effect of Temperature on Transesterification of 400.00 cm^3 of Solution Mixture Containing 10.00 cm^3 of 1.00 M KOH

Temperature (°C)	35	45	55	65	75
Volume of biodiesel (cm^3)	116.50	131.00	148.00	200.00	172.00
Volume of glycerol (cm^3)	52.50	56.00	80.00	96.50	126.00
Saponification Value (mol/dm^3)	0.00	0.00	0.00	0.00	0.25

Table 2: Effect of Concentration of Catalyst (KOH) on Transesterificationof 400.00 cm^3 of Solution Mixture at 65°C

Concentration of KOH (mol/dm^3)	0.50	1.00	1.50	2.00	2.50
Volume of biodiesel (cm^3)	122.00	198.00	188.50	185.00	180.00
Volume of glycerol (cm^3)	68.00	92.80	96.80	97.00	97.50
Saponification Value (mol/dm^3)	0.00	0.00	0.09	0.18	0.27

Table 3: Effect of Reaction Time on Transesterification of 400.00 $cm^3$of Solution Mixture Containing 10.00 cm^3 of 1.00 M KOH at 65°C

Reaction time (minute)	35	45	55	65	75
Volume of biodiesel (cm^3)	167.00	182.00	190.50	197.00	186.00
Volume of glycerol (cm^3)	66.50	74.00	86.00	93.00	99.50
Saponification Value (mol/dm^3)	0.00	0.00	0.09	0.00	0.20

DISCUSSION

The result of the effect of temperature on transesterification reaction between *Gossipium hirsutum* oil and methanol is shown in Table 1. The result (Table 1) showed that transesterification reaction occured within temperature range (35°C-75 °C), which significantly varied with temperature. The low yield of biodiesel and glycerol observed at temperatures below 65°C (i.e. 35°C, 45°C, 55°C) and the high yield of biodiesel and glycerol achieved at 65°C could be attributed to incomplete and complete transesterification reactions, respectively. This findings are in accordance with the findings of Garba *et al* (2012). The decrease in the amount of biodiesel and the corresponding increase in the amount of glycerol observed at 75°C may be attributed to the decomposition of biodiesel into glycerol as reported by Sensoz *et al* (2000). The little saponification value observed at 75°C could possibly be connected to side saponification reactions of TGs, which led to formation of soap (as by-product). This is also in accordance with the findings of Garba *et al* (2012).

Table 2. shows the influence of catalyst concentration on the amount of allied products (biodiesel and glycerol) and by-product (soap) generated through transesterification reaction between *Gossipium hirsutum* seed oil and methanol at 65°C. The result showed that 1.00 M was the optimum concentration of catalyst. The low yield observed at concentration (0.50 M) of catalyst and high yield recorded at concentration (1.00 M) of catalyst could be possibly be associated with the incomplete and complete conversions of TGs respectively as reported by Enciner *et al* (2005). The decrease in the amount of biodiesel and the corresponding increase in the amounts of glycerol and saponification values observed at concentrations above 1.00 M (ie 1.50 M, 2.00 M, and 2.50 M) of KOH may be associated with the over participation of more TGs in the saponification reaction with the KOH in the affecteds solution mixture as reported by Mohibbe and Waris Nahar (2005); Garba *et al* (2012).

Table 3 presents the result of the effect of reaction time on biodiesel and glycerol yield, as well, as the saponifiaction value recorded at 65°C. From the result (Table 3), it could be said that 65 minutes was the optimum reaction time for biodiesel production because it was the time at which highest collection of biodiesel was achieved. The increase in the volumes of biodiesel and glycerol at reaction times from 35 minutes to 65 minutes observed may be connected to progressive increase in transesterification reaction as reaction time increases to a maximum product yield at 65 minutes. This is because during tranesterification, biodiesel production continues with the reaction time up to completion provided that there are enough reactants (oil and alcohol) in the reactor as reported by Sani *et al* (2014). The decrease in biodiesel and increase in glycerol noted at reaction time (75 minutes) may be associated with the hydrolysis of ester (the biodiesel formed). This is because after complete transesterification of TGs into biodiesel, extension of reaction time leads to hydrolysis of biodiesel formed into fatty acid, which causes the formation of more soap (by-product) as reported by Garba *et al* (2012). The relative high saponification value obtained at reaction time (75 minute) could be connected to the formation of more soap from the hydrolysis of the ester formed into fatty acid. This is because fats and oils undergo hydrolysis with caustic alkali to form propane 1,2,3- triol and the corresponding sodium or potassium salts(soap) of the component fatty as reported by Ababio,(1985).

CONCLUSION

Optimum operational conditions of temperature, reaction time and concentration of catalyst for maximum production of biodiesel from *Gossipium hirsutum* seed oil and methanol by base catalysed tranestrification reaction were established. Therefore, the experimental findings of the present work could serve as basis for maximum production of environmentally–friendly biodiesel on large scale from renewable feedstocks (seed oils) as alternative to popular conventional environmentally-aggressive petrodiesel.

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