OPTIMIZATION OF BIODIESEL PRODUCTION PROCESS PARAMETERS OF JATROPHA CURCAS OIL USING CALCINED EGGSHELL CATALYST

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ABSTRACT

The search for alternative sources for petroleum-based diesel fuels as led to search on a new perspective which utilizes vegetable oils and animal fats to produce biodiesel fuels as substitution to the current petroleum-based fuel. **This research was aimed to study the process parameters of biodiesel production from jatropha curcas and solid base catalyst*(calcium oxide from waste egg shells)* for the *transesterification of triglycerides with methanol.* The objectives were to study the *effect of catalyst dosage, methanol to oil ratio, reaction time and reaction temperature on jatropha methyl ester yield. The jatropha methyl ester known as biodiesel produced was characterized as an alternative diesel fuel. The density, flash point, viscosity, Acid number and heating value of the biodiesel were 0.8412 g/ml, 165 ℃ ,4.97 mm^2/s, 4.18 mgKOH/g and 40.41 MJ/kg respectively. Comparisons were drawn in line with ASTM D6751 literature. Jatropha methyl ester optimum yield of 93.58% was obtained at a methanol to oil ratio 13:1, catalyst dosage 8 wt%,reaction time 60 min and reaction temperature 70 ^{o}C. Hence, biodiesel produced from jatropha oil, methanol and calcined eggshell ash can be used as renewable yet cost-effective alternative to petroleum diesel.***

Keywords: Biodiesel, transesterification, waste eggshells, jatropha methyl ester,

INTRODUCTION

The development of alternative energy sources becomes increasingly relevant with the intensifying search for a sufficient substitute to fossil fuel. Biodiesel is considered to be an alternative fuel having numerous environmental, economic, and social benefits. Biodiesel is a non-petroleum fuel produced through chemical reaction which breaks down the triglyceride present in fatty acids. The benefits of biodiesel include its bio-degradable nature, non-toxic, free from sulphur (< 0.001 %) and 60% less net carbon dioxide emissions, high flash point (greater than 160 ^{o}C) which makes transportation and storage safe (Al Zuhair, 2007; Mauel, 2007; Prabu and Anand, 2012; Ngoya *et al.,* 2017).

Romano *et al.,* 2006 had earlier discussed that the cost is of main concern in biodiesel production and trading (mainly due to oil prices) which led to the use of non-edible vegetable oils that has been studied for several years with good results (Tint and Mya, 2009; Bello and Makanju, 2011; Kumar and Kant, 2013; Venkateswara, 2015; Narwal *et.al.,* 2015; Solima *et al.,* 2014; Reddy *et.al.,* 2016). The production of biodiesel could be cheap as it could be extracted from non-edible oil sources such as Jatropha curcas owning to the fact that it is readily available at low cost which has made it more popular as an alternative fuel, it is also significant to point out that, the non-edible vegetable oil of jatropha curcas has the vital potential providing a promising and commercially viable alternative to diesel oil since it has desirable physical chemical and performance characteristics comparable to diesel (Raja *et al.,* 2011). Some other undeniable advantage of non-edible oils for biodiesel production lies in the fact that it is not in competition with foodstuffs. It is produced by transesterification reaction.

Transesterification reaction is a chemical process that involves the reaction of a vegetable oil /animal fat with short chain alcohol such as ethanol/ methanol in the presence of either an acidic, basic or emzymatic catalyst to produce fatty acid ethyl/methyl esters. Biodiesel is produced mostly by homogeneous catalysis. Recently, however, heterogeneous catalysis is being considered as a cheaper alternative to the homogeneous catalysis due to its availability and ease processability (Kilonzi *et.al.,* 2015). Heterogeneous transesterification is considered as a green process, the process requires neither catalyst recovery nor aqueous treatment steps and very high yields of ethyl/methyl esters can be obtained, close to the theoretical value without the need for expensive purification processes that separates the catalyst from reaction products typical in the use of homogeneous catalysts (Kilonzi *et.al.,* 2015). Waste eggshell contains high content of calcium oxide, a strong alkali that is suitable as a basic catalyst in the production of biodiesel (Ngoya *et.al.,* 2017), many researchers have studied the characterization of eggshell using different analytical methods such as: Brunauer, Emmett and Teller (BET) used to determine the pore size and pore diameter, catalyst surface area; X-Ray Diffraction (XRD) used to estimate structure

properties e.g. deflects, grain size and phase composition; Scanning electron microscope (SEM) used to determine the morphology structure of the elements present in the calcined egg shell, FTIR is used for the study of physical and chemical properties of the calcined eggshell (Yogesh *et.al.,* 2010; Romero *et.al.,* 2011; Taufiq *et.al.,* 2012; Reddy *et.al.,* 2016; Yelda, 2016; Ngoya *et.al.,* 2017; Andherson *et.al.,* 2018). All the results indicates that eggshells have the potential of being used as a heterogeneous catalyst for the production of biodiesel, its use as catalyst reduces cost, serves as a source of income if used on a large scale. It also promotes a clean environment.

Almost all biodiesel produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield provided the starting oil is low in moisture and free fatty acids(Reddy *et.al.*, 2006; Dossin et al. 2006a; Sarin *et.al.,* 2009; Veljkovick et al. 2009; Kamila *et.al.,* 2017). In this paper, non-edible oil of Jatropha curcas crude oil is selected for optimizing the process of biodiesel production using waste eggshells as the heterogeneous catalyst. The physico-chemical properties such as density, flash point, Kinematic viscosity, Free fatty acid and heating value were found out for Jatropha methyl ester (JME).

MATERIALS AND METHODS

The optimum production of biodiesel could be a subject of careful selection of materials and equipment for the purpose.

Materials and Equipments

In this study, the major raw materials used during the experiment was jatropha curcas oil purchased from Agro-energy Limited Company at Kano, analytical grade methanol and eggshells as a heterogeneous catalyst that was collected from petty traders that sell fried eggs along the street in Benin city, Edo state. The waste eggshells were washed and dried at a temperature of 105 ^{o}C in an oven before they were calcined in a furnace (Muffle Furnace Model SXL) at 900 ^{o}C. The catalyst was thus stored in a plastic bottle and kept in a desiccator to prevent the poisoning of the catalyst.

The following equipments were used during the experiment: UV-Vis spectrophotometer, calorimeter and viscometer. The magnetic stirrer with hotplate, conical flasks, three necks round bottom flask, measuring cylinder, beaker, separating funnel, burette, density bottle, pipette, Watman No.1 filter paper funnels.

Experimental Method

The experimental procedure includes the calcinations of the eggshells,the esterification and transesterification reaction process.

Calcination of eggshells

The eggshells were collected domestically from market, it was washed and dried at 105-110 ^{o}C for 2 ½ hr to remove some moisture and was pulverized using stone crusher to reduce it into smaller particle sizes. The pulverized eggshells was placed in a muffle furnace for calcination at a temperature range between 900-950 ^{o}C to obtain calcium oxide used as the heterogeneous catalyst which was stored in an air tight container ready to be used for the biodiesel production.

Esterification Reaction

Jatropha oil was esterified by weighing 100 g of the oil into in a reaction vessel with the addition of 1 g of concentrated sulphuric acid (H_2SO_4) as catalyst; also 1g methanol was added to the mixture for neutralization reaction to take place. The magnetic stirrer with hot plate was used to heat up the mixture to a temperature of 60 ^{o}C for 40 mins. After the reaction time was reached, the product was cooled and separated using a separating funnel. The esterified oil was collected and its acid value and percentage fatty acid value were calculated.

Alkali Transesterification Reaction

A constant mass of 100 g esterified jatropha oil was reacted with methanol in different ratio in the presence of calcined waste egg shell 2 g, 4 g , 6 g, 8 g, 10 g and 12 g as a solid catalyst at different working temperatures of 40 ^{o}C, 50 ^{o}C, 60 ^{o}C, 70 ^{o}C, 80 ^{o}C and 90 ^{o}C at a reaction time of 30, 60, 90, 120 and 150 minutes. After the completion of the reaction, the mixture is allowed to settle under gravity for 24 hours in a separating funnel.Three layers were formed which consists of the jatropha methyl ester (JME) known as the biodiesel, glycerol and catalyst. The catalyst solidified at the bottom, therefore biodiesel and glycerol was decanted through the top of the funnel. The decanted mixture was then transferred to another separating funnel for further separation into biodiesel and glycerol which forms two layers, the glycerol was removed from the bottom while the biodiesel was collected into a beaker. The produced biodiesel was washed with warm water to remove impurities such as residual catalyst, unreacted methanol and glycerol while the washed biodiesel was further treated by drying on the hot plate to remove any trace of water. The washed and dried biodiesel physicochemical properties such as acid value, density, viscosity, heating value and flash point were analysed. The percentage yield of jatropha methyl ester was determined using equation (1).

$$\% \text{ Yield} = \frac{\text{Weight of jatropha methyl ester}}{\text{Weight of jatropha oil}} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

The physical and chemical properties of biodiesel from jatropha methyl ester were studied. American Society for Testing and Materials (ASTM D 6751) for biodiesel was used as the standard to verify if the jatropha methyl ester produced fulfill meet up with the specifications for the consumers. Table 1 shows the properties of jatropha methyl ester and its comparison with ASTM D6751.It was observed that all the properties are within the range of American Society of Testing and Materials values. This implies that the biodiesel produced can be safe for storage and it has a high energy output when used in the engine.

Table 1. Physicochemical Properties of Jatropha Methyl Ester Compared with ASTM D6751

Properties	Jatropha methyl ester	ASTM D6751
Acid number (mgKOH/g)	0.28	< 0.8
Density (g/ml)	0.84	0.88
Viscosity at 40^{o}C	4.18	1.9-6.0
Flash point(^{o}C)	165	100-170
Heating value (MJ/kg)	40.41	> 45

Effect of Catalyst on Biodiesel Production

Types of catalyst and amount used could play a crucial role in the yield of biodiesel. Fig. 1 shows JME yield with varying amount of calcined waste egg shell catalyst ranging of 2 g, 4 g, 6 g, 8 g, 10 g and 12 g percentage weight dosage. The reactions were carried out at constant methanol to oil ratio of 6: 1 for 60 minutes at a reaction temperature of 70 ^{o}C. The yield of ester improved as the catalyst quantity increase, owning to the fact that more catalyst load signifies more active sites and surface area available for reaction to take place as shown in figure 1. JME rises gradually with the catalyst dosage of 2 g to 8 g. A slight increment was observed at a catalyst dosage between 8g and 10g having a JME yield of 76.82% and 76.83% respectively. The rate of JME yield however reduces with increasing catalyst dosage as observed for catalyst dosage between 8 g and 12 g. this could implied that optimum yield is eminent within the range of the catalyst dosage. It could therefore be inferred that the JME yield improves with increasing catalyst dosage but limited within the range 8 g – 12 g.

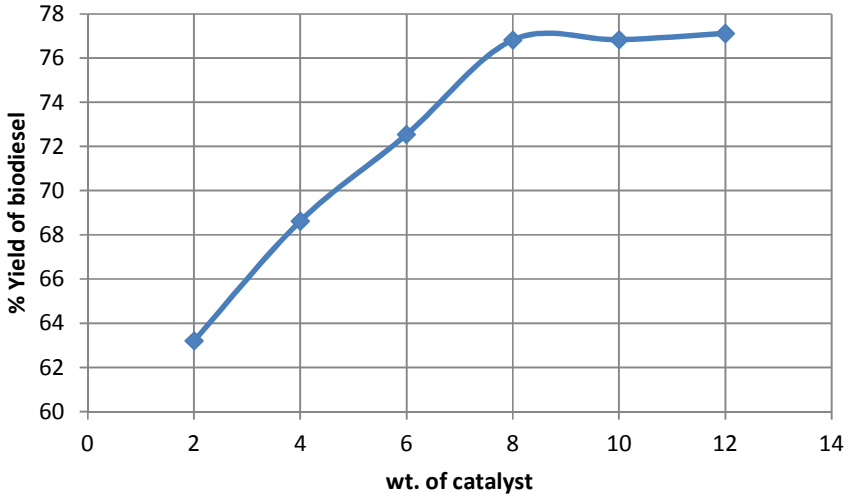

Figure 1: Effect of %wt Catalyst Dosage on JME Yield

Effect of Temperature on Biodiesel Production

Temperature is a crucial parameter as it influences the reaction rate and yield of biodiesel. Variation in reaction temperature increases reaction rate and decreases the time required to complete the process due to the reduction in viscosity of oils. Fig.2 depicts the effect of temperature on JME. In this study, the temperature was varied from 40oC to 90^{o}c at constant reaction time of 60 minutes, methanol to oil ratio of 6:1 and 8wt% catalyst dosage. It was observed that the conversion of JME was low during reaction at 40^{o}c but rises gradually till an optimum yield of 84.58% at 70oc was observed, further increase in temperature resulted in lower yield of JME, and this is as a result of the limiting reactant i.e methanol because of its lower boiling point of approximately 68^{o}C. Reduction in JME was noticed at temperature of 70^{o}C, 80^{o}C and

90°C with a yield of 84.58%, 76.53% and 68.47% respectively. At higher temperature, more methanol must have be evaporated thus, production of JME was reduced.

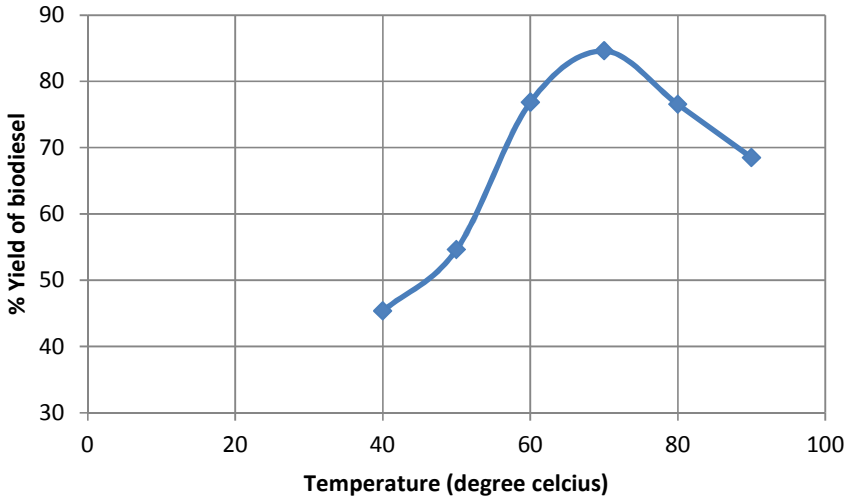

Figure 2: Effect of Temperature on Jatropha Methyl Ester Yield

Effect of Reaction Time on Biodiesel Production

Triglycerides conversion into esters increases with reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol with oil, but as the reaction time increases the yield also increase which enhances the contact between methanol and jatropha oil with basic catalyst. The reaction time is varied from 30min to 90min at constant methanol to oil ratio of 6:1, catalyst weight of 8% and at a temperature of 70°C. Figure 3 shows the effect of reaction time on the transesterification activity of egg shell obtained as catalyst with jatropha curcas oil, the yield of biodiesel increases with reaction time, but remains constant at 120min. This implies that the optimum time period or suitable reaction time required for the complete reaction to yield highest amount of JME (87.42%) is at 120min .Any further increase in the reaction time had no significant effect on yield.

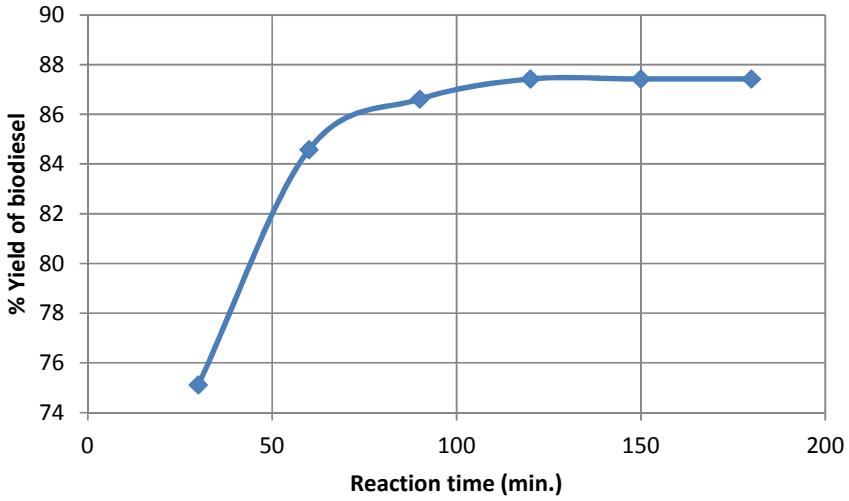

Figure 3: Effect of Reaction time on Jatropha Methyl Ester Yield

Effect of Methanol to oil ratio on Biodiesel Production

Effect of methanol to-oil molar ratio is investigated as it is shown in Fig.4 with varying different molar ratio of 3:1,5:1,7:1,9:1,11:1,12:1 and 13:1 during 60min reaction time at constant temperature 70°C and catalyst dosage of 8wt%. The yield of JME at 3:1 methanol/oil was low at the beginning of the reaction but it was elevated by introducing excess methanol to shift the equilibrium to the product side as refer to the LeChatelier's principle. The JME increased considerably from 55.31% to

93.58% when the methanol /oil ratio was increased from 3:1 to 13:1. The maximum yield of 93.58% was achieved at 13 : 1 molar ratio this is due to the presence of sufficient methanol that was able to disperse oil and catalyst phases and the mixture becomes more miscible for the reaction to proceed faster. Further increase of methanol oil ratio above 13:1 may result in slight increase of JME yield which when compared with the cost of production during purification process does not worth it because excessive methanol impedes separation of biodiesel and glycerol and large amount of energy is consumed to recover non-reacted methanol. Also, higher amount of glycerol drives the equilibrium back to the left and lowering the yield of biodiesel.

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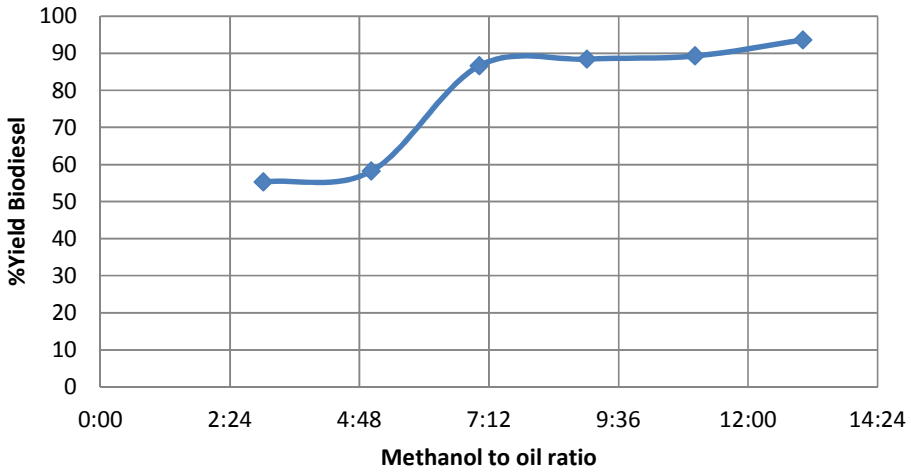

Figure 4: Effect of Methanol to Oil Ratio on Jatropha Methyl Ester Yield

CONCLUSION

Studies have been on biodiesel recently because of its environmental benefits and the fact that it is made from renewable resources. The cost of biodiesel, however, is the major obstacle to commercialization of the product. Biodiesel synthesis that employs waste shells and non-edible oil will definitely reduce waste disposal problem and reduce the price of biodiesel, making biodiesel a viable fuel alternative compared to petroleum-derived biodiesel. In this study, waste calcined eggshell catalysts was effectively employed for biodiesel synthesis from Jatropha oil and methanol. The result obtained shows that the physicochemical properties of jatropha methyl ester such as density, viscosity, heating value, acid number and flash point value were found to be within the range of the ASTM D6751 standards. The effects of different operating parameters such as, catalyst dosage, reaction time, reaction temperature and methanol to oil ratio on the yield of jatropha methyl ester were analyzed. The optimum condition of the parameters that yields 93.58% of jatropha methyl ester was attained at methanol to oil molar ratio 13: 1 with 8 wt. % calcined eggshells catalyst in 60min at 70°C. In conclusion, the use of eggshells as a catalyst, jatropha oil with methanol is a considerable potential in biodiesel production process due to the simplification of separation process of the products and cost of production.

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