Optimization of Transesterification of Sunflower Oil with Ethanol using Eggshell as Heterogeneous Catalyst

F.M Kilonzi[1]*   A. Kumar[1]   S. S. Namango[1]   H.K Kiriamiti[1]   D.K Some[2]

1.Department of Chemical & Process Engineering, Moi University, P.O BOX 3900- 30100, Eldoret Kenya

2.Department of Agricultural and Biosystems Engineering, University of Eldoret, P.O Box 1125-30100, Eldoret Kenya

Abstract

Biodiesel is currently mostly produced by homogeneous catalysis. Recently, however, heterogeneous catalysis is being considered as a cheaper alternative to the homogeneous process. Heterogeneous transesterification is considered a green process. The process requires neither catalyst recovery nor aqueous treatment steps and very high yields of ethyl esters can be obtained, close to the theoretical value. However, heterogeneously catalyzed transesterification generally requires more severe operating conditions, and the performance of heterogeneous catalysts is generally lower than that of the commonly used homogeneous catalysts. This study seeks to address this problem by studying the production of biodiesel using eggshells as heterogeneous catalysts. Heterogeneous catalysts can make biodiesel production more energy efficient, and therefore less expensive, by eliminating the need for expensive purification processes that separates the catalyst from reaction products typical in the use of homogeneous catalysts. Matlab was employed for the experimental design, statistical analysis and process modeling. Fatty acid ethyl ester was produced by transesterification of sunflower oil and ethanol using calcined eggshells as a heterogeneous catalyst. To optimize the process, some important variables such as reaction temperature, molar ratio of ethanol to oil and mass weight of catalyst were selected and studied. At the following conditions: 343K of reaction temperature, ethanol to sunflower oil ratio of 9:1 and 1 mass wt% of catalyst, an optimum fatty acid ethyl ester yield of 92% was obtained, indicating that eggshells have the potential of being used as a heterogeneous catalyst for the production of fatty acid ethyl ester from sunflower oil. Physico-chemical characterization of the fatty acid ethyl ester was performed and compared with the US Standard biodiesel properties, and it was observed that the biodiesel compared well with the standards.

Keywords: Transesterification, eggshell catalyst, process optimization, sunflower oil, ethanol

1.0 INTRODUCTION

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by carbon dioxide emission.

Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. The process of transesterification is affected by the mode of reaction, molar ratio of alcohol to oil, type of alcohol, nature and amount of catalysts, reaction time, and temperature.

Various studies have been carried out using different oils as the raw material and different alcohols (methanol, ethanol, butanol), as well as different catalysts, notably homogeneous ones such as sodium hydroxide, potassium hydroxide, sulfuric acid, and supercritical fluids or enzymes such as lipases. Recent research has focused on the application of heterogeneous catalysts to produce biodiesel, because of their environmental and economic advantages. This paper focuses on the optimization of transesterification of sunflower oil with ethanol using eggshells as heterogeneous catalyst.

1.1 Objectives of the research

1.1.1 General objective

Investigation of biodiesel production using transesterification reaction with eggshells as heterogeneous catalyst at laboratory scale and to compare the physical properties with the USA standard biodiesel properties.

1.1.2 Specific objectives

In the heterogeneously catalyzed transesterification reaction, a number of operating parameters such as temperature, extent of catalyst loading, mode of mixing, alcohol/oil molar ratio and the time of reaction are important in the transesterification reaction.

This paper covers the effect of alcohol to oil molar ratio and effect of catalyst weight on the yield of biodiesel in its scope. Hence, effects of the following parameters on the yield of biodiesel production: mass ratio of catalyst to mixture, molar ratio of ethanol to oil on biodiesel yield were the specific objectives.

2.0 MATERIALS AND METHODS
2.1 Materials and Equipments
The major raw materials used during the experiment was sunflower oil, analytical grade (AG) ethanol and eggshells as a heterogeneous catalyst. The sunflower oil was purchased from Bidco Kenya in Thika. The eggshells were collected from Down Bridge Restaurant in Nairobi. They were washed and dried at a temperature of 105^oC In an oven before they were calcined at KIRDI at 900^oC to be used as catalysts in the transesterification process.

The equipments used during the experimentations are glass reactor equipped with mechanical stirrer, thermometer, sand bath, conical flasks, measuring cylinder, separating funnel, hydrometer, Vibro viscometer, and thermostat.

2.2 Experimental Method
2.2.1 Calcination of eggshells
The eggshells were dried at 105^OC for 3hr to remove some moisture afterward all they
were crushed by using mortar and pestle into small particles and stored in the oven until the next process. Finally, the eggshells were calcined at 900^0C to convert them to calcium oxide.
2.2.2 Characterization of the catalyst
After calcination, the porosity of the eggshells was determined experimentally by performing the following experiment.
Procedure.
The calcined eggshells were transferred to a 100 cm^3 measuring cylinder and it was well shaken up to 50cm^3 mark.50 cm^3 of distilled water was mixed with the eggshells and the experiment left for 1 hour for water to percolate and fill the pores between the eggshells.

The porosity of the catalyst was calculated as the difference between the theoretical volume expected and the actual volume observed. The final volume of the mixture was then read.
2.2.3 Biodiesel Production Procedure
Initially, a known volume of sunflower oil was poured into a 250ml glass reactor. The reactor assembly was then heated to the desired temperature by using water bath. A measured amount of ethanol and heterogeneous catalyst was added to the reactor. The reaction was timed as soon as mechanical stirrer was turned on for 2 hours.

The transesterification was carried out at optimum reaction time and rotation speed to achieve maximum conversion with temperature being maintained at 70^0C. The reaction parameters were chosen as follows: Molar ratio of ethanol to oil from 1:10 to 1:2.5, mass ratio of catalyst to oil from 4% to 0.25%.

Finally, after transesterification was carried out, catalyst and glycerol part was separated from the biodiesel mixture by separating funnel for 20 hours. Then, rotary evaporator at 100 torr /mm Hg removed unreacted ethanol and trace moisture. The product, biodiesel was obtained as a clear amber-yellow liquid. These procedures are used for each experiments executed at different parameters using the experimental design matrix
2.2.4 Determination of optimum amount of catalyst
To determine the optimum amount of catalyst required, the mole ratio of oil to alcohol was kept constant at 1: 3 and then the amount of catalyst was varied from 4% to 0.25% and the amount of biodiesel produced measured. From the different experiments performed the yield of biodiesel obtained was recorded to determine the optimum amount.
2.2.5 Determination of optimum mole ratio of oil: alcohol
To determine the optimum mole ratio of the oil: alcohol, the amount of catalyst was kept constant at 1%.The mole ratios of the oil: alcohol was varied with the moles of the oil being kept constant at 1.The mole ratios were varied from 1:2.5 to 1:10 and for each mole ratio, the amount of the biodiesel produced was recorded so as to determine the optimum mole ratio.

The following experiments were then done so as to come up with the production yield model of the reaction Y_{11} , $Y_{10,}Y_{01,}Y_{00}$. A table of the average yield of biodiesel was developed every all the three runs did for each specific experiment.

The yields of the biodiesel were determined using the formula mass of biodiesel/mass of oil used. The masses for different yields were calculated by multiplying the volumes of the biodiesel x the density.

2.3 Methods for Biodiesel Characterization (Physico-Chemical Properties of Biodiesel)
ASTM method was used to characterize the Physico-chemical properties of biodiesel. The procedures for various tests done are described below.
2.3.1 Determination of Kinematic Viscosity, ASTM D 445
The kinematic viscosity: "the resistance to flow of a fluid under gravity". The kinematic viscosity is equal to the dynamic viscosity divided to the density and is a basic design specification for the fuel injectors used in diesel engines. If the viscosity is too high, the injectors do not perform properly. The viscosity has to be in a range of

1.9-6.0mm^2/s.

The viscosity of the biodiesel oil was measured using Cannon viscometer tube. The sample was heated in water bath and temperature monitored up to 40 ^{o}C.It was then put in the tube and allowed to flow in the tube freely and the time taken to reach the mark recorded. The kinematic viscosity is then equal to ratio of dynamic viscosity to the density of the biodiesel observed. The viscometer tube used was for size 150.

It will read the dynamic viscosity, which is resistance to flow.

Dynamic viscosity in cP /Sec = time in sec × constant (0.035)

Kinematic viscosity = Dynamic Viscosity/Density (mm^2/s)

2.3.2 Determination of Acid Value or Acid Number, ASTM D 664

The acid number is "the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point''. The acid number is a direct measure of free fatty acids. The free fatty acids can lead to corrosion and may be a symptom of water in the fuel. Usually, for a base catalyzed process, the acid value after production will be low since the base catalyst will strip the available free fatty acids. However, the acid value may increase with time as the fuel degrades due to contact with air or water. This test should be performed regularly as a part of the producer QC program. The requirement is a maximum of 0.8 mg of KOH/g.

The acid value of an oil or fat is defined as the number of potassium hydroxide required to neutralize the free fatty acid in 1g of the sample. The result is often expressed as the percentage of free acidity.

To determine the Acid value, Standard alcoholic NaOH solution (0.1 N) was prepared by dissolving NaOH (pellet) with ethanol. The solution was filtered and stored in brown bottle for five days. Furthermore, a mixture of 95% ethanol and diethyl ether in a ratio of 1 to 1 by v/v was prepared by mixing 500 ml diethyl ether and 500 ml of ethanol.

A weighed quantity of the oil sample was dissolved in 25 ml of 1 to 1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic NaOH solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic NaOH (V) for the sample titration was noted. The total acidity (acid number) in mg NaOH/ g was calculated using the following equation 3.5.

The acid value was determined to know the amount of free fatty acid composition in the oil.

$$Acid\ Value = \frac{Titration\ Volume\ (ml\ 0.1N) \times 5.61}{Weight\ of\ Sample} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.1$$

$$Acid\ Number = \frac{v \times 5.61}{m}$$

2.3.3 Determination of Heating Value (Calorific Value)

Heating value or heat of combustion is the amount of heating energy released by combustion of a unit value of fuel. The most important determinants of the heating value are moisture content.the moisture content of biodiesel is low and this increases the heating value of the fuel.

Calorific value (energy content or heat of combustion) of a fuel was determined by bomb calorimeter. Benzoic acid was used to standardize the calorimeter. A known amount of sample was taken in a crucible and made into a pellet and the initial weight was noted. It was placed in the bomb, which is pressurized to 18atm of oxygen.

The bomb was placed in a vessel containing a measured quantity of water. The ignition circuit was connected and the water temperature noted. After ignition, the temperature rise was noted after 10 minutes.

The pressure was released and the length of unburned fuse wire was measured. And the determination of the biodiesel's calorific value was conducted following the same procedure for standardization, except for the sample preparation, which was Biodiesel.

Including the corrections for heat transfer between the surrounding and the apparatus, heat liberated by the glowing wire etc, the heat value of the air- dried sample of the fuel is expressed according to the following formula.

Mass of Sample = a g

Final temperature reading ^{o}C = b

Initial temperature reading ^{o}C = c

Rise in Temperature ^{o}C = (b-c)

Gross cal value [cal] =2036.8 x (b-c)

Determination of Correction Value;

Heat of combustion, 1cm = 2.3 calories and the total length of the wire = 7cm

Therefore for the wire the heat of combustion = 2.3 x 7 = 16.1 calories

 For the thread, 1cm = 6.5 calories and the total length of thread = 10cm

Thus the total correction value = 16.1+ 65 =81.1 calories

$$Net\ calorific\ value = \frac{Gross\ Calorific\ Value - Correction\ Value}{weight\ of\ sample \times 10^3} \quad \dots\dots 2.2$$

but 1 gram calorie = 4.185 joules
Thus HHV = Net calorific value X 4.185 (MJ/Kg)

2.3.4 Determination of Iodine Value (IV)

The iodine value of an oil or fat is defined as the weight of iodine absorbed by 100 parts by weight of the sample. The glycerides of unsaturated fatty acids present (particularly of the oleic acid series) unite with a definite amount of halogen and the iodine value is therefore a measure of the degree of unsaturation.The iodine value is usually determined by Wijis' method.Wijis' solution. Dissolve 8g iodine trichloride in 200ml glacial acetic acid. Dissolve 9g iodine in300ml carbon tetrachloride. Mix the two solutions and dilute to 1000ml with glacial acetic acid.

Procedure.

Pour the oil into small beaker, add a small rod and weigh out a suitable quantity of the sample by difference into a dry glass-stoppered bottle of about 250ml capacity. The approximate weight in g of the oil too be taken can be calculated by dividing by 20 the highest expected iodine value. Add 10ml of carbon tetrachloride to the oil or melted fat and dissolve. Add 20ml of Wijis' solution, insert the stopper (previously moistened with potassium iodide solution) and allow to stand in the dark for 30 min. Add 15ml of potassium iodine solution(10%) and 100ml water, mix and titrate with 0.1N thiosulphate solution using starch as indicator just before endpoint(titration = a ml).Carry out a blank at the same time commencing with 10ml of carbon tetrachloride(titration =b ml)

$$Iodine\ value = \frac{(b - a) \times 1.269}{wt\ (in\ grams)\ of\ sample} \quad \dots\dots\dots\dots\dots\dots 2.3$$

If (b-a) is greater than b/2 the test must be repeated using smaller amount of sample.

2.3.5 Determination of Flash Point, ASTM D 93

The flash point is defined as the "lowest temperature, at which the application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test''. This test, in part, is a measure of residual alcohol. However, during production and purification of biodiesel, not all the ethanol may be removed, making the fuel flammable and more dangerous to handle and store if the flash point falls below 130ºC The requirement is a minimum of 130°C.

The flash point of the biodiesel was determined using closed cup method. The cup was filled with the biodiesel up to the mark (about 75 ml) and the cup was heated by a Bunsen burner. Small open flame was maintained from an external supply of natural gas.

Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached the surface of the oil catch flame, the temperature at the moment was noted and reported as flash point temperature.

2.3.6 Determination of Sulphated Ash for Biodiesel.

Ash is a measure of the amount of metals contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. It is important for heating value, as heating value decreases with increasing ash content.

Sulphated ash is the ash that remains after the sample has been carbonized, and ash residue subsequently treated with sulphuric acid and heated to constant weight. The crucible was heated in an electric Muffle Furnace at 700 ^{o}C for 10 minutes. Cool to room temperature in suitable container and weigh to the nearest 0.1 mg. A mass of the sample was measured into the crucible. The crucible and the sample were then heated carefully until the contents were ignited with a flame. The contents were maintained at that temperature so that the sample burned at a uniform and moderate rate, leaving only ash and carbon when burning ceased.

The residue was cooled and completely moistened by addition drop by drop of H_2SO_4. The contents were then carefully heated without spattering and continued until fumes were no longer evolved.

3.0 RESULT AND SUMMARY

3.1 Characterization of the catalyst

The characterization of the catalyst was done to determine the porosity as well as the amount of Cao present in the calcined eggshells.

As described above, the readings below were observed for the determination of porosity of the calcined eggshells.

Experiment no	Initial volume of Eggshells (cm^3)	Volume of distilled water added (cm^3)	Final volume of the mixture(cm^3)
1	50	50	68
2	50	50	67

$$\text{Change in the volume after percolation} = \frac{(100-68)+(100-67)}{2} = 32.5\text{cm}^3$$

$$\% \text{ porosity} = \frac{32.5}{50} \times 100 = 65\%$$

3.1.1 Determination of Calcium in the catalyst.

	A	B
Weight of catalyst(g)	1.0013	1.0013
Volume made to (ml)	250	250
Dilution factor	X 100	X 100
Concentration in ppm Ca^{2+}	22.719	21.084

Calculation of CaO

$$A \text{ percentage } \%\left(\frac{\text{w}}{\text{w}}\right) = \frac{22.719 \times 250 \times 100 \times 100 \times 1.3992 \times 10^{-6}}{1.0013} = 79.37\% \text{ CaO}$$

$$B \text{ percentage } \%\left(\frac{\text{w}}{\text{w}}\right) = \frac{21.084 \times 250 \times 100 \times 100 \times 1.3992 \times 10^{-6}}{1.0013} = 73.66\% \text{ CaO}$$

$$\text{Average amount of CaO}\%\left(\frac{\text{w}}{\text{w}}\right) = \frac{79.37\% + 73.66\%}{2} = 76.52\% \text{ CaO}$$

The amount of CaO present in the eggshells was found to be 76.52% .In any chemical reaction, when the molecules get adsorbed onto the surface of a catalyst, they do so in a particular orientation and this determines the rate of reaction. If in a reaction there are more than two reactants, then the third reactant molecule could act as a barrier to the reaction and what the catalyst may do in this case is to lock away these inhibitors away and thus promote the reaction.

Alternatively, the catalyst could be adsorbed the active molecules in a reaction in a given direction and hence promote the reaction. In either way this means that the higher porous the catalyst is the higher the reaction rate.

3.2 Optimization of catalyst, mole ratio of oil: alcohol and the determination of the coefficients of the production yield model for the reaction
3.2.1 Optimization of catalyst amount
Table 3.1 Determination of Optimum % weight of catalyst

| % Weight of catalyst	Assigned no	Yield of Biodiesel (ml)
4	1	16
2	0.75	16
1	0.5	16
0.75	0.25	13.5
0.5	0.125	7.5
0.25	0.0	5.4

Optimization Of the catalyst amount
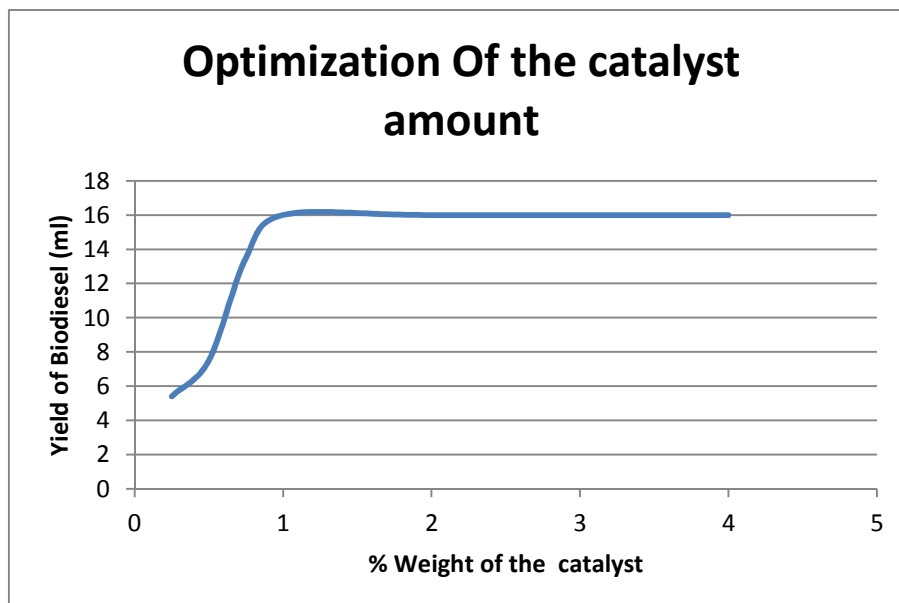
It is evident from the above results that the optimum amount of catalyst for the transesterification reaction using sunflower oil and ethanol is 1%.

From literature review,the optimum amount of catalyst used for transesterification of rapeseed oil catalysed by MgO, CaO, SrO and BaO at 64.5^0C,18:1 methanol/Oil ratio was 10%.Another researcher used 1.5% catalyst weight using CaO as catalyst in the transesterification of Jatropha Curcas Oil at 70^0C and obtained a yield of 93% for 2.5 hr reaction. Another one using Sunflower oil and molar ratio of 12:1 methanol/oil found that the optimum amount of catalyst was 1%.From the above literature review, the obtained optimum value of 1% is in within the values obtained by other researchers.

3.2.2 Determination of optimum mole ratio of oil: alcohol

The following table was developed from the experiments performed on the optimization of mole ratio of oil: alcohol.

Mole ratio of Oil: Alcohol	weight of catalyst %	Yield of biodiesel(ml)
1:10	1	316.5
1:9	1	316.5
1:7.5	1	226
1:5	1	145
1:2.5	1	16

Optimization of mole ratio
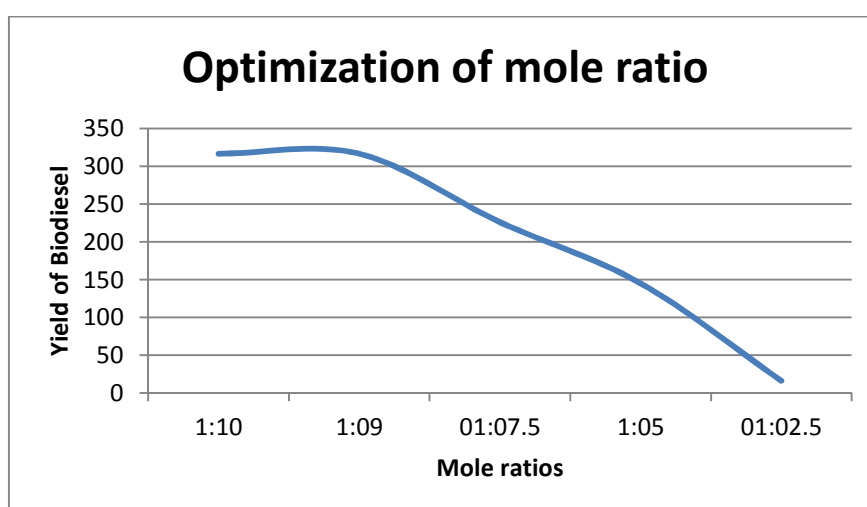
From the Graph above, the yield of the biodiesel kept on increasing as the mole ratio of oil: alcohol was increased from 1:2.5 up to when the mole ratio was 1:9 and then it was constant. Thus the optimum mole ratio of the oil: alcohol is 1:9.

From the table of optimization of the mole ratio, it is clear that the optimal mole ratio of oil: alcohol was 1:9.This is because beyond this figure, the yield of biodiesel remained constant as obtained from a series of

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experiments that were carried out at different concentrations of alcohol and the quantities of oil. This was done at constant temperatures of 75°C and at atmospheric pressure. This is because the one mole of oil maintained for the series of experiments, which were done, had a given maximum number of molecules to take part in a chemical reaction. These molecules were all used at the mole ratio of 1:9 and thus the yield could no longer increase beyond this figure. The possible type of solid catalyst and their uses plus potential yield with concentration done by other researcher is discussed below .

Veljikovick et al.(2009) studied CaO catalysts for the transesterification of sunflower oil at 6:1 molar ratio of methanol to oil,1% weight catalyst based on oil weight and CaO calcinations temperature was 550^{0}C.Yoosuk et al.,(2010),attempted to increase the CaO activity by producing it from CaCO$_3$ calcination ,using a calcination temperature of 800^{0}C for 3h.This treatment is likely associated with crystallites fracture and basic sites. Di serio et al.,(2006) tested MgO in the industrial production of biodiesel from soybean oil transesterification at 180^{0}C and 12:1 methanol to Oil molar ratio ,only 72% was achieved. In this research, CaO obtained by Calcining eggshells at 900^{0}C was used in the transesterification of Sunflower oil and ethanol at 75^{0}C and oil/ethanol molar ratio of 1:9 and the conversion obtained was 92%. From the above analysis, it can be seen that the most viable heterogeneous catalyst for transesterification reaction is CaO.

This means that the obtained value of mole ratios is better considering that in the reaction, ethanol which is a long chain alcohol and hence susceptible to stearic hindrance, compared to methanol used in the above literature review by other researchers, gave a conversion of 92%.

Table 3.2 Combined table used for production yield model equation and 3D surface plot

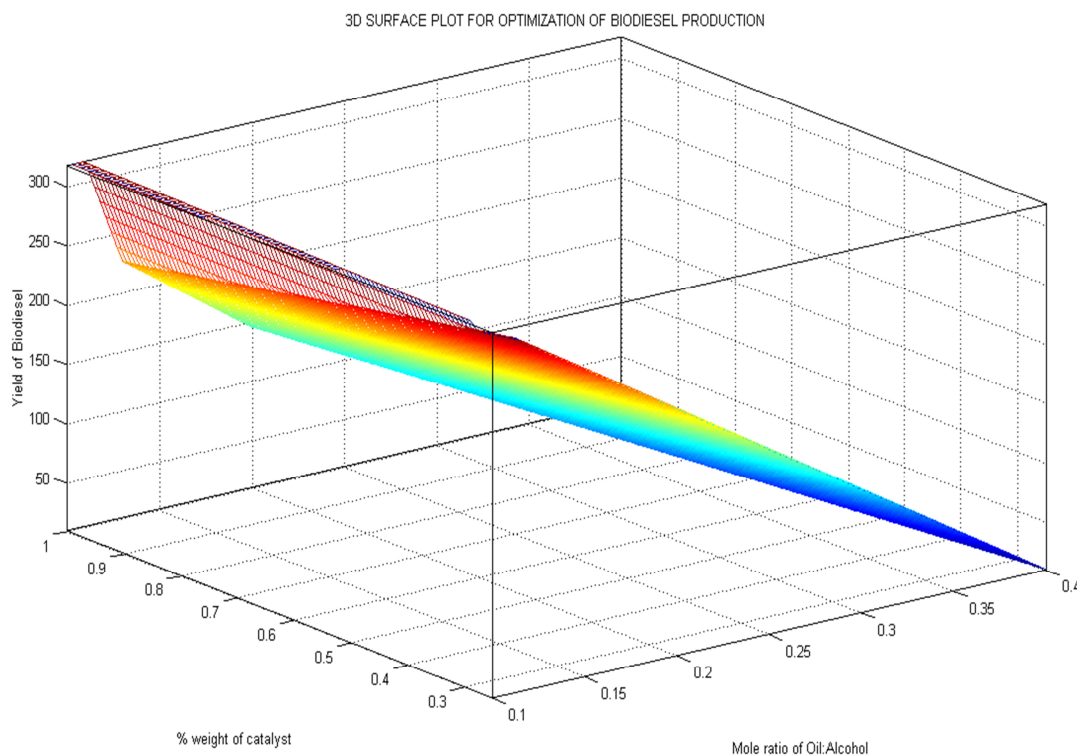| Mole ratio of Oil: Alcohol	Catalyst Amount (%)	Volume of biodiesel
0.10(1:10)	1	316.5
0.11(1:9)	1	316.5
0.11(1:9)	0.25	310
0.13(1:7.5)	1	226
0.2(1:5)	1	145
0.4(1:2.5)	1	16
0.4(1:2.5)	0.25	10

Fig 3.1 3D Surface Plot for Optimization of Biodiesel from mat lab using experimental data.

The 3D surface plot indicated above shows a comparison of the effect of changing mole ratio of oil: alcohol and the percentage weight of catalyst. It can be observed that the optimum yield of biodiesel was obtained when the optimum oil: alcohol mole ratio and optimum weight of the catalyst was used. To come up with the coefficients

of the production yield model, the data below was input to excel and by use of excel solver the production yield model was developed.

The production yield model obtained by using excel is given below.

$$Z=21+68x+254y+195xy+132x^2+12y^2+9x^2y^2$$

3.3 Physico- Chemical Properties of Sunflower Oil and Biodiesel.

The specific gravity, density, kinematic viscosity, acid value, free fatty acid composition, Saponification number, flash point and higher heating value of the sunflower oil were determined and the results are given in Table 3.1.

Table 3.3 Physico-chemical properties of sunflower oil

Property	Experimental Result	Unit
Specific Gravity	0.9496	-
Density at 21^0C	0.9496	g/ml
Kinematic viscosity at 40 ^{o}C	110.745	mm^2/s
Acid Value	0.2417	mg KOH/g oil
Composition of Free Fatty Acid	0.12085	%
Saponification Number	183.79	mg KOH/g oil
Flash point	-	^{o}C
Higher Heating Value	50.065	MJ/Kg
Iodine value	-	g I2/100g
Refractive index	1.4721	

The refractive index is a characteristic property of fats and oils and may be used as a fast measurement of advance of hydrogenation operation. A merrien reports a refractive index (n_D) of regular sunflower oil in the range 1.474-1.476 at 20^0C.The variation of the viscosity occurred due to dependence of chemical composition on agro climatic conditions where the plants are grown. The saponification number was in agreement with the reported value by Purdy , except calorific value, which is higher than the reported value of 26 MJ/ kg, which can be attributed to differences in the agro-climatic conditions.

Table 3.4 Physico-chemical properties of Biodiesel oil

Property	Experimental Result	Unit
Specific Gravity	0.9002	-
Density at 21^0C	0.9002	g/cm^3
Kinematic viscosity at 40 ^{o}C	4.47	mm^2/s
Acid Value	0.664	mg KOH/g oil
Composition of Free Fatty Acid	0.332	%
Saponification Number	150.05	mg KOH/g oil
Flash point	143	^{o}C
Higher Heating Value	46.47024	MJ/Kg
Iodine value	114.70	g I2/100g
Refractive index	1.4575	

The density of the biodiesel produced was performed and observed to be 900.2kg/m^3. When we compare the average of the results with the ASTM D6751 for biodiesel 870–890 kg/m^3 the experimental value was slightly above the standards by 1.1% and this could be as a result of the variation of agro-climatic conditions.

The viscosity is a very important property related to the biodiesel utilization in direct injection diesel engines. High values of viscosity give rise to a poor fuel atomization, incomplete combustion, and carbon deposition on the injectors.

Therefore, the biodiesel viscosity must be low. The viscosity of the biodiesel was determined at 21 ^{o}C and found to be 4.47mm^2/s, which was within the ASTM D 445 specifications (1.9 to 6.0 mm^2/s).

Iodine value is a measure of total unsaturated (double bonds) within the FAEE product. Iodine absorption occurs at double bond positions thus a higher IV indicates a higher quantity of double bonds in the sample and greater potential to polymerize in engine and hence lesser stability. The process of transesterification reduces the iodine value to a small extent. The ASTM requirement is a maximum of 115.

The iodine value from the experiments was found to be 114.70, which was in agreement with the ASTM Standards. The acid value of biodiesel was determined to be 0.664mg of KOH/g, which is within the

ASTM specification ($\leq$ 0.8). The flash point of biodiesel was 143 ^{o}C, which was well above the minimum ASTM specification (i.e., 130 ^{o}C) and can be considered safe for storage and transportation. The high heating value was found to be 46.47, which is higher than the minimum of 45 specified by ASTM standards. This implies that the biodiesel has a high energy output when used in the engine.

4.0 CONCLUSION

The result obtained shows that biodiesel production using eggshells as a catalyst, is a considerable potential in biodiesel production process, mainly because of simplification of separation process (decrease of production cost).At Ethanol to sunflower oil ratio of 9 and 1wt% of catalyst, an optimum fatty acid ethyl ester yield of 92% was obtained.The experimental results show that eggshells have an excellent activity during transesterification. It has a potential for industrial application in the transesterification of biodiesel. Hence, eggshells have a good catalytic performance.

Therefore, it can be concluded that eggshells is an effective catalyst for the production of biodiesel from sunflower oil via heterogeneous transesterification. The fatty acid ethyl ester amount increased with increasing catalyst concentration at a low ethanol-to-oil molar ratio. The fatty acid ethyl ester amount increased with the increasing ethanol-to-oil molar ratio for a low reaction temperature.

Physicochemical properties determined for the biodiesel produced meet the ASTM specification except density but which is also within the acceptable limits.

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