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IN-SITU-TRANSESTERIFICATION OF COTTON SEEDS OIL (GOSSYPIUM SPP) USING CaO DERIVED FROM EGG SHELL AS CATALYST

Y . Ibrahim, Abba Maman Manirou & Surajo Ali
Department of Chemistry and Physics, Umar Suleiman College of Education Gashua
Community Health Department, College of Health and Technology Nguru, Nigeria.
Email:ibrazuby@yahoo.com

ABSTRACT
In-situ-transesterification of cottonseed oil (Gossypium spp) was carried out with 5g calcium oxide derived from egg shell as catalyst using soxhlet extraction apparatus and 1:1 of n-hexane to methanol. All the transesterification reactions were carried out at 60^{0}C for 2 hrs. The results produced a biodiesel with 35.75% yield, water and sediment content 0.08%, density 0.85g/cm^3, specific gravity 0.85, saponification value 16.83mgKOH/g, acid value 0.79mgKOH/g, iodine value 59.22I_2/100g, cetane number 357.28, and high heating value 47.85MJ/kg. The GC/MS results indicated the presence of tetradecanoic acid methyl ester, hexadecanoic acid methyl ester, 11-octadecenoic acid methyl ester, 6-octadecenoic acid (z)-methyl ester, octadecanoic acid methyl ester, n-hexadecanoic acid oleic acid and 2-ethyl-2-hexanal. Thus, the processing of cottonseed oil into methyl ester using soxhlet extraction method is recommended as it required low energy input as compare to conventional method.
Keywords: transesterification; biodiesel, cottonseed; GC/MS.

INTRODUCTION

Due to the increasing consumption of worldwide petroleum fuels and the environmental concerns, there is a great demand for alternative resources of petroleum-based energy (Li *et al.*, 2011).Thus, the search for substitute sources of new, sustainable and renewable energy such as biomass, solar, hydro, and wind has become necessary (Aliero *et al.*, 2013).

Biodiesel is one of the major renewable alternatives which is produced through an transesterification process, in which mono-alkyl esters of long chain fatty acids are produced when alcohol, such as methanol or ethanol, in the present of acid or base catalyst chemically react with triglycerides (vegetable oil or animal fats). It is often used in compressed ignition engines for energy generation (Muhktar *et al.,* 2015).

Currently biodiesel is produced using homogeneous transesterification method (Borges and Diaz, 2012). But disadvantages of using homogeneous catalysts which includes its hygroscopic nature, may lead to the formation of soap with high free fatty acid feedstock. It generates a lot of wastewater during the washing stage which may pollute the environment (Sharma and Singh, 2011).

Homogenous Catalysis for Biodiesel Production

The biodiesel production process has been established and mainly commercialized using homogenous catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) dissolved in methanol. Homogeneous catalysts are difficult to separate from the product mixture. Thus, considerable amount of polluted water were created to remove the basic catalyst from the biodiesel product (Atadashi *et al.*, 2013).

Heterogeneous Catalysis for Biodiesel Production

Heterogeneous catalysts are promising for the transesterification reaction of vegetable oil to produce methyl esters (biodiesel). Heterogeneous catalysts can be easily separated from the reaction mixture and reused many times. The major difficulty with heterogeneously catalyzed is its slow reaction rate compared with homogeneous catalysis. To overcome this major challenge, the reaction conditions of heterogeneous catalysis are intensified by increasing reaction temperature, catalyst amount and methanol/oil molar (Boro *et al*., 2014: Shuli *et al*., 2010). Heterogeneous catalysts are classified as conventional and non-conventional catalysts. The conventional catalysts are chemically synthesized catalysts, such as zeolite and single component metal oxide (ZnO) while the non-conventional catalysts are those derived from waste products such as waste egg shells of chickens, mollusks, oyster shell and lots more (Nakano *et al*., 2010).

This paper studied the synthesis of biodiesel from cottonseed using soxhlet extraction method; generation of calcium oxide (CaO) catalyst from waste egg shell, and analyzing the physicochemical properties of biodiesel. The biodiesel produced was also characterized using GC-MS analysis.

MATERIALS AND METHODS

Sample Collection and Purification

The delinted cotton seeds (*Gossypium spp)* were obtained from Zaria Textile Industry Limited (ZAMTEX), Zaria.The seeds were identified as *Gossipium spp* at the Botany unit, Department of Biological Sciences, Ahmadu Bello University Zaria. Impurities were removed by hand-picking and the seed was grounded using mortar and pestle into fine powder, sieved to reduce the particle size and to ensure homogeneity and stored in airtight polythene bag before the analyses. Eggshells were also collected from nearby coffee shops at the Ahmadu Bello University Zaria, hostel mini market.

Catalyst Preparation

The eggshells were washed thoroughly with tap water to get rid of any unnecessary materials adhered on its surface, and rinsed twice with distilled water. The washed eggshells were shed-dried to remove moisture (Boey *et al.*, 2009), grounded using mortar and calcined in a muffle furnace under static air condition at 600°C for 2 hrs to transform calcium carbonate in the shell to CaO particle as reported by Boey *et al.*, (2009).

$$CaCO_3 \xrightarrow{600^{o}C} CaO + CO_2$$

Analytical Procedures

Transesterification

40g of cotton seed was weighed inside the thimble, 200cm^3 of 1:1(v/v) n-hexane and methanol mixture was measured and transferred into 250cm^3 round bottom flask and 5g of CaO derived from egg shell was added to the solvent mixture. The round bottom flask was fitted with a soxhlet extractor. The reaction was carried out at 60^{o}C for 2 hrs with constant stirring. At the end of the transesterification reaction, the round bottom flask was removed from soxhlet extractor apparatus and allowed to cool. The liquid phase was decanted from the solid phase, transferred into a separating funnel and allowed to settle down overnight. Two layers were formed, the lower layer was dark brown in colour containing glycerol and the upper layer was yellow containing fatty acids methyl esters which were separated using separating funnel. The biodiesel then evaporated using a rotary evaporator to remove the remaining n-hexane and methanol. Gas Chromatography- Mass Spectroscopy (GC-MS) was used to determine the chemical composition of biodiesel produced, biodiesel yield was calculated using equation below.

$$Biodiesel\ yield\ (\%) = \frac{Mass\ of\ crude\ biodiesel}{Mass\ of\ the\ sample}\ X\ 100$$

Water and sediment content was determined using the formula reported by (Muhktar *et al.*, 2015), density was also determined using the formula reported by (Almustapha *et al.*, 2009). The remaining fuel properties were determined using methods reported by AOCS, (2011). While cetane number, high heating value (HHV) were calculated using equations reported by Sokoto *et al.*, (2011).

RESULTS

Cotton seed crude biodiesel quality produced under reaction conditions (1:1 methanol to n-hexane ratio, 60°C and 2 hrs using different amount of catalyst with constant stirring) are presented in the table below:

Table 1: Physicochemical properties of Biodiesel from cottonseed.

Parameters	Cottonseed Biodiesel	EN14214	ASTM6571
Biodiesel %	35.75		
Water/sediment (v)%	0.08		0.05max
Density g/cm^3	0.85		0.90max
Specific gravity	0.85		0.90max
Saponification valuemgKOH/g	16.83		
Acid value mgKOH/g	0.79	0.5max	0.8max
Iodine value I_2g/100g	59.22	120max	115max
Cetane number	357.28	51min	47min
High heating value MJ/Kg	47.85	35min	

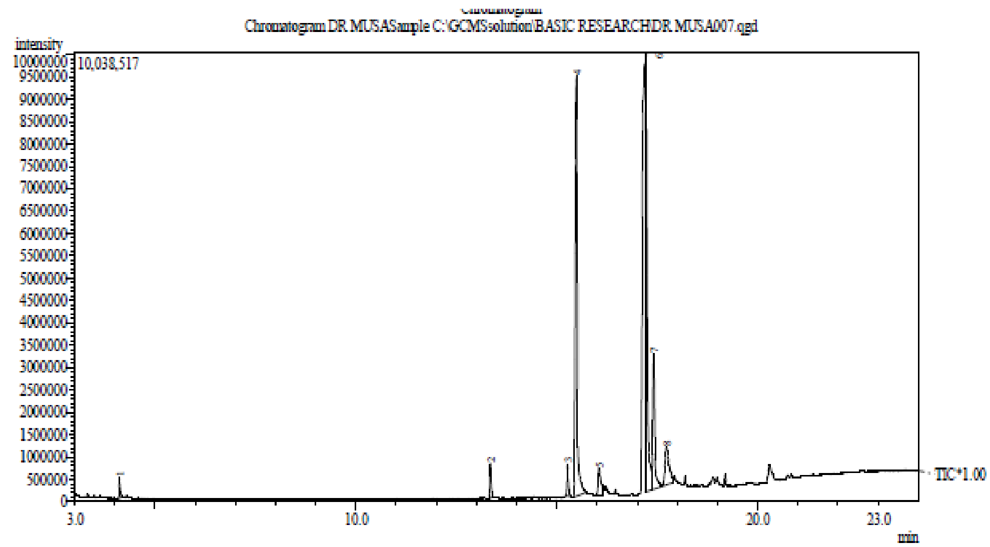

Figure 1: GC/MS Chromatograph of fatty acid methyl ester.

Table 2: Composition of cottonseed biodiesel by GC/MS.

Retention time (mins)	Possible compounds	Percentage composition (%)
13.35	Tetradecanoic acid methyl ester	2.24
15.49	Hexadecanoic acid methyl ester	40.09
15.27	11-octacecenoic acid methyl ester	1.93
17.22	6-octadecenoic acid (z)-methyl ester	33.14
17.41	Octadecanoic acid methyl ester	10.49
16.05	n-Hexadecanoic acid	3.60
17.73	Oleic acid	7.35
4.11	2-ethyl-2-hexanal	1.15
	Total FAME Content	99.99

DISCUSSION

Physicochemical Parameters

From table 1, water and sediment content, the result exceeded the 0.05% maximum accepted in the standard ASTM6571 (2007) which according to Mukhtar and Dabai (2015) is a measure of fuel cleanness (Muhktar and Dabai, 2016), was found to be high (0.08%) which exceeds 0.05% of ASTM6571 (2007) recommended for biodiesel. Water interacts with the methyl ester biodiesel to form free fatty acids which results in microbial growth in the storage tank. This indicates that, cottonseed biodiesel require further post-treatment such as centrifugation to prevent microbial growth and ester hydrolysis in storage tank (Muhktar and Dabai, 2016).

Density is one of the vital fuel quality parameter related to fuel injector system. Its value must be maintained within a tolerable limit to allow for optimal air to fuel for complete combustion (Galadima *et al.*, 2008).Table 1 showed that the density of biodiesel obtained was 0.85g/cm^3 which is within the accepted value of 0.90g/cm^3 recommended by ASTM6571 (2007) for biodiesel. However, it is lower than the value obtained by (Demirbas, 2008; Sivaramakrishnan, 2011) which was found to be 0.87g/cm^3. But is slightly higher than that of diesel fuel 0.81g/cm^3 (Almustapha *et al.*, 2009). The result indicates good combustion and ignition properties of biodiesel, and may not cause engine knock.

Knowledge of specific gravity gives a broad indication of the fuel type and for fuel of known type; it serves as general inspection check for the presence of contaminants (Hassan and Sani, 2007). From thetable 1 above it shows that the specific gravity of the biodiesel was 0.85 which is within tolerable limit of 0.90 recommended by ASTM6571 (2007) for biodiesel. As such, if the biodiesel is use it will not cause low spontaneous-ignition temperature and a corresponding high resistance to diesel knock (Hassan and Sani, 2007).

Saponification value is the amount of alkali necessary to saponify a definite quantity of the test sample. It is expressed as the number of milligrams of potassium hydroxide (KOH) required to saponifying 1g of the test sample. Saponification value is inversely proportional to relative molar mass, (Mukhtar and Dabai, 2016). The saponification value of the biodiesel was found to be 16.83mgKOH/g, this value suggests that it has higher molecular weight which may be responsible for higher density (0.85g/cm^3) of cottonseed oil biodiesel.

The acid value is an important fuel property; it is measure of free fatty acids in a given product (Mukhtar *et al.*, 2015). It is also refers to the number of KOH required to neutralize 1g of oil and it is measure used to estimate storage quality of the biodiesel (AOCS, 2011). Higher acid content can caused severe corrosion in fuel supply system of an engine. The acid value obtained in this research work was 0.79mgKOH/g which is almost close to the minimum requirement by ASTM6571 (2007) (0.80max) and aboveEN14214 (0.5max) standard for biodiesel to be used as fuel. The presence of higher free fatty acids content from the GC/MS result such as (3.60% n-Hexadecanoic acid and 7.35% Oleic acid) may be responsible for higher acid value of cottonseed oil methyl ester. The result proof that direct usage of this biodiesel may lead to severe corrosion in fuel supply system (Atabani *et al.*, 2012; Fernando *et al.*, 2007). It is recommended that the biodiesel should undergo further acid treatment to reduce the high acidity before being used in diesel engine.

According to Sokoto *et al.*, (2011), Iodine value measures the total unsaturation within a mixture of fatty acids. It is the amount of iodine required to iodize all the double bonds in the biodiesel. High amount of iodine value can lead to polymerization during combustion. From table 1 above it shows that the biodiesel has iodine value of 59.22I_2 /100g which is within the tolerable limit of both ASTM6571(2007) (115max) and EN14214 (120max). This shows that small amount of the biodiesel can be used to cover long distance compared to petroleum diesel.

The higher the cetane number of fuel, the better it is ignition property and the greater quality of methyl ester to be used as a diesel. High cetane numbers help ensure good cold start properties and minimize the formation of white smoke (Sokoto *et al.*, 2011). The cetane number obtained in this work which was shown in table 1 above was (357.28). According to EN14214 specification, biodiesel should have minimum cetane number of 51 while ASTM6571 (2007) is 47as the minimum for biodiesel. based on these two standards, cottonseed oil methyl ester has good ignition quality, because its cetane number exceeds the minimum standards value, this higher cetane number may be as a result of the presence of higher proportion of Hexadecanoic acid, methyl ester and 6-0ctadecenoic acid, (z)-methyl ester.
Heat of combustion is an important parameter for estimating fuel consumption (Sokoto *et al.*, 2011). High heating value is not specified in the biodiesel standards ASTM6571(2007) but 35Mj/Kg as minimum for EN14214.The high heating value obtained from this research work as shown in table 1,

(47.85Mj/Kg) falls within the standard recommended by EN 14214. This indicates that cottonseed oil biodiesel may serve as substitute fuel in tropical region due to its moderate unsaturation level.

GC-MS analysis shows that the major fatty acid methyl ester of *Gossypium spp* seed oil were tetradecanoic acid, methyl ester, hexadecanoic acid, methyl ester, 11-octadecenoic acid, methyl ester, 6-octadecenoic acid, (z)-methyl ester. Other fatty acids present include oleic acid and n-hexadecanoic acid. The result indicates the successful conversion of *Gossypium spp* seed oil to methyl ester during the transesterification process using 5g CaO derived from egg shell as catalyst.

CONCLUSION

The paper studied biodiesel production via*in situ* transesterification of cotton seed. It was found that generally, it is possible to produce fatty acid methyl ester (biodiesel) via *in situ* transesterification of cotton seedwith CaO alkali catalyst using soxhlet extraction method. From the results obtained, it was concluded that *Gossipium spp* methyl ester could be utilized in place of diesel fuel for diesel engines. It has also shown that density, specific gravity, iodine value, cetane number, and high heating value of the biodiesel when compared to ASTM6571 and EN14214 standards are all within the approved specification for biodiesel to be used as fuel. This is an indication that the biodiesel obtained from cotton seed can be use in diesel engines with regard to these properties. Although, the produced biodiesel was found to have high acid value, and the biodiesel have high water and sediment content. Hence biodiesel from cotton seed would be an efficient renewable substitute to diesel fuel which at the same time would be more environmentally friendly and cheaper than the conventional diesel if properly utilized.

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