Effects of Catalyst Type and Concentration on Biodiesel Yield and Quality

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Abstract: This paper present study report the effect of catalyst type and concentration on yield and quality of biodiesel produced from cotton seed oil. This was achieved through the production of biodiesel from refined cottonseed oil via the transesterification process by studying the effects of various catalysts on biodiesel yield. The catalysts studied include; sodium hydroxide, potassium hydroxide, iron sulphate and potassium carbonate at different concentrations. The yield of biodiesel decreased with increase in catalyst concentration from 0.25 to 0.75 wt % thus, highest conversion was obtained at 0.25 wt % concentration for sodium hydroxide (NaOH), potassium hydroxide (KOH), iron sulphate (FeSO4) and potassium carbonate (K_2CO_3) catalysts with corresponding yields of 96 %, 94 %, 92 % and 82 %. The fuel properties from the transesterified refined cottonseed oil show its suitability with the ASTM standard for the production of biodiesel.

Keywords: *Biodiesel, Catalyst Type, Catalyst Concentration, Cottonseed Oil*

1 Introduction

The search of newer sources of energy has been triggered by the decline in the available fossil fuel reserve, limitations of its usage, the threat to environment resulting from the emission of green house gases that results from the combustion of fossil derived fuel and technological changes that promotes newly available energy forms (Dias *et al.*,2012). Vegetable oils have been perceived as a renewable alternative to compete with petroleum derived diesel fuel but in early 1980s difficulties were encountered due to their high viscosity and low ignition power (Agarwal, 2008). These have led to the emergence of biodiesel; a promising alternative to diesel fuel which has received considerable attention over the years due to its unique properties: it is biodegradable, renewable, non toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal diesel, absence of carcinogens and lower sulphur content than the mineral diesel (Fan *et al.*, 2011).

Biodiesel is mostly produced from transesterification (alcoholysis); a process whereby an alcohol (such as methanol and ethanol) are reacted with vegetable oil in the presence of a catalyst (e.g. base, acid or an enzyme depending on the properties of the raw material) (Bugaje and Mohammed, 2008). Common vegetable oil in the Nigeria includes palm oil, palm kernel oil (PKO), peanut oil, cottonseed oil and soybean oil (David, 2006).

However, there are a lot of vegetable sources still available have not been extensively investigated as prospective feedstock for biofuel production, examples are Cotton seed, Sesame, seed etc.

Cotton plant is a perennial grown warm-weather tree that grows naturally. The plant belongs to the *Malvaceae* family, the tribe *Gossypieae,* and the genus *Gossypium*. The principal domesticated species of cotton of commercial importance are *hirsutum, barbadense, arboreum, and herbaceum*. Cottonseed bears oil that has finds extensive application in the production of biscuits, crackers, doughnuts and potato chips and the preparation of ice cream substitutes. Other industrial uses of cottonseed oil include alkyl resins for interior paints, special lubricants and soft soaps (Orhevba and Efomah, 2012). The oil is reported to contain high levels of saturated fat, and tends to have high levels of pesticide residue as well; hence it is not healthy for human consumption (Fan *et al*., 2011). Due to presence of gossypol a natural toxin that protects the plant from insects (Olaibi, 2011). In the last three decades, the proportion of cotton seed being crushed to produce oil and meal has dropped from 91% to less than 40 %. Instead the seed are used as feed for cattle (Ash and Dohlman, 2008). This can be attributed to the protein, energy and fiber content of the overall seed (Blasi and Drouillard, 2002).However the presence of gossypol, is a probable problem for cattle when whole seed is consumed rather than meal. Other reason for the decreased in demand for cottonseed oil in the food industry is as a response to various health concerns that are likely to emanate from it consumption (Santos *et al.*, 2005). In recent times it has been reported for biodiesel production (Fan *et al.*, 2011; Abdulwakil *et al.*, 2012). This is because the use of cottonseed oil as a feedstock for biodiesel would not have a large impact on food-grade vegetable oil supplies. Ash and Dohlman (2008) reported that United State (US) net consumption of all edible fats and oils was 30.1 x 10^9 pounds, of which only 708 x 10^6 pounds (2%) was from cottonseed. The author added the diversion of use of this seed oil from food related uses to fuel is not anticipated to have a considerable impact on food value. The benefits of cottonseed oil are mainly viewable from a manufacturing standpoint. It has an incredibly long shelf life and also a very high smoke point (450 degrees) (Abdulwakil *et al*., 2012). The oil content the seed have been reported to be 15.05 % wt of seed (Orhevba and Efomah, 2012).

This study report the effect of different catalyst type and concentration of the yield and quality of biodiesel from cotton seed oil.

2 Methodology

The characterization of cotton seed oil was done in accordance with the report of Akpan *et al.*, (2005). The properties characterized includes specific gravity, acid value, free fatty acid, saponification value, moisture content, iodine value, refractive index, peroxide value and viscosity. The biodiesel was produced in accordance to the literature of Musa *et al*., (2012). The transesterification of the triglyceride from cotton seed oil was conducted using four different catalysts (which include sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and iron sulphate ($FeSO_4$)) at different catalyst concentrations of 0.25, 0.5 and 0.75 % at constant reaction time (1 hour), temperature (60 ^oC) and mole ratio of oil to alcohol (1:6). The biodiesel produced from the use of the each catalyst was characterized for specific gravity, flash point, cloud point, kinematic viscosity and pour point. This was done in accordance to the American

Standard for Testing and Material (ASTM) reported by Musa *et al.*, (2012).

3 Results and Discussion

The result of the characterization of the commercially obtained cottonseed oil is shown in Table 1. The properties of the oil were compared with the standard and the values reported by other researchers.

Table 1: Characterization of the cottonseed oil

Properties	Units	ASTM Limit	Experimental Values	Ankapong (2010)
Moisture Content	%	0.2max	0.12	-
Specific Gravity	-	0.918-0.926	0.917	0.938
Acid Value	mgKOH/g	0.6max	1.12	3.45
FFA	% Oleic	< 1	0.56	1.73
Refractive Index	-	1.468-1.472	1.468	1.474
Iodine Value	g/100 oil	98.0-118.0	111	121.0
Saponification Value	mgKOH/g	189-198	193	192
Peroxide Value	meq/kg	< 1	0.90	-

Table 2: Percentage Yield using NaOH

Runs	NaOH	Glycerol (ml)	Yield	
			ml	%
1	0.25	6	48.0	96
2	0.50	15	47.0	94
3	0.75	22	38.5	77

Table 3: Percentage Yield using KOH

Runs	KOH	Glycerol (ml)	Yield	
			ml	%
1	0.25	10	47.5	94
2	0.50	13	46.0	92
3	0.75	18	36.0	72

Table 4: Percentage Yield using $FeSO_4$

Runs	$FeSO_4$	Glycerol (ml)	Yield	
			ml	%
1	0.25	4	46.0	92
2	0.50	5	43.0	86
3	0.75	6	41.0	82

Hence, from the result obtained for each of the catalyst, the optimum yield was obtained using 0.25 % catalyst concentration.

Table 5: Percentage Yield using K_2CO_3

Runs	K_2CO_3	Glycerol (ml)	Yield	
			ml	%
1	0.25	5	41.0	82
2	0.50	6	40.0	80
3	0.75	8	27.0	54

3.1 Effect of Catalyst Concentration

The results for all catalyst types (Table 1-4) shows a decrease in yield as the catalyst concentration increased. The decrease in ester yield may be due to soap formation at higher catalyst concentrations hence loss of methyl ester during washing (Oghome and Ibe, 2008). Ankapong, (2010) reported that, ester yield increases as the amount of catalyst increased from 0.25 to 1.0wt% for refined soybean, unrefined soybean and palm kernel oil.

Table 6: Properties of biodiesel produced using different catalyst type

Test	Unit	ASTM	Biodiesel produced using Different catalyst			
			NaOH	KOH	$FeSO_4$	K_2CO_3
Specific gravity@ 25 °C	-	0.88 – 0.95	0.88	0.88	0.92	0.89
Density	g/ml	0.875 – 0.95	0.95	0.95	0.99	0.96
Kinematic viscosity	mm^2/s	1.9-6.0	3.2	3.8	4.8	4.0
Flash point	°C	130 min	146	138	139	130
Pour point	°C	-	3	2	-5	-4
Cloud point	°C	-	5	4	1	2

3.2 Effect of catalyst type

The various catalysts used for this study had different effect on the methyl ester yield produced. The result shows sodium hydroxide catalyst gives the best yield with refined cottonseed oil with a yield of 96 %. This is in agreement with the European norm which ipulate a minimum of 96.5 wt %.

3.3 Properties of Biodiesel

The flash point is a key property in the determination of the flammability of a fuel. The flash point obtained from this work shows sample produced ranging from 130 -148 °C for all catalyst type as shown in Table 1. These values are consistent with the ASTM standard.

These results also show that the biodiesel produced using the various catalysts were safe for handling. This is because a typical flash point of pure methyl esters should be greater than 93°C, classifying them as "non-flammable" (Gerpen *et al.,* 2004). However, during production and purification of the biodiesel, not all methanols may be removed thus making the fuel flammable and more dangerous to handle and store if flash point falls below 130 °C. Excess methanol may also affect engine seals and elastomer and corrode metal components (Gerpen *et al.*, 2004).

The cloud point is the temperature at which a cloud of wax first appears in a liquid when it is cooled down under conditions prescribed in ASTM D2500 test method (Gerpen *et al.,* 2004). The value determined for the cloud point in this work for the various catalysts ranges from 1 °C - 5 °C, for all catalyst used. The cloud point is a critical factor in cold weather performance for all diesel fuels. For temperatures below these cloud point temperatures, biowax begins to form which thickens the oil and clog fuel filters and injection in engines. This shows biodiesel produced using $FeSO_4$ can be use in a cooler region than the other catalyst.

Pour point is a measure of the fuel gelling temperature, at which point the fuel can no longer be pumped. The values of pour point for the biodiesel produced in this work shows $FeSO_4$ with a value of -5 °C as the lowest compare to the other catalyst. According to ASTM standard D 6751, no limit is specified for Pour point. The reason is that the climate conditions in the world vary considerably, thus affecting the needs of biodiesel users in a specific region.

The standard for biodiesel states that the fuel should have a density between 0.875 and 0.950 g/ml. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel. The results obtained showed that for the four catalysts studied, NaOH and KOH with a density of 0.95 each fall within the acceptable range of the ASTM standard while $FeSO_4$ and K_2CO_3 have a density of 0.99 and 0.96 respectively, which are slightly above the ASTM standard. Density increases with decreasing chain length and increasing number of double bonds, this explains the high values for fuels rich in unsaturated compounds (Ankapong, 2012).

According to ASTM D 6751, for biodiesel to be used in diesel engines, the kinematic viscosity must be between 1.9 and 6.0 mm^2/s. The kinematic viscosities of the biodiesel produced from the four catalysts ranged from 3.0 to 4.8 mm^2/s. The values are in agreement with the standard specified by ASTM. Viscosity is closely related to the fatty acids composition of a given biodiesel sample. It increases with increasing length of fatty acid chain. Viscosity is inversely related to the number of double bonds. This explains the high viscosity ratings for biodiesel obtained from saturated materials such as palm oil (6.20mm^2/s) and palm kernel oil (5.92mm^2/s) and low ratings for highly unsaturated compounds such as soybean methyl ester (4.14mm^2/s). Unexpected high viscosity value of methyl ester above the ASTM standard may be attributed to high fuel ageing during storage (Ankapong, 2010).

4 Conclusion

This work showed cottonseed oil to exhibit good physiochemical properties and could be useful as biodiesel feedstock. Among the catalyst studied, NaOH gives the optimum yield of 96 % at 0.25 wt% catalyst concentrate. However all the biodiesel produced from various catalysts satisfactory qualify for diesel engine application.

It was obvious that biodiesel yield is dependent on catalyst type and concentration but the quality of the biodiesel does not depend on the catalyst type.

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