Effect Of High Free Fatty Acid Feedstock On Methyl Esters Yield Using Bulk Calcium Oxide Catalyst

Ibrahim Haruna, Mohamed Fatima. Verlaine Ndam

Abstract: Presence of free fatty acids in biodiesel feedstock has been source of concern to biodiesel producers, hence this investigation was carried out to determine its effect on methyl esters yield by transesterification using solid base catalyst. *Jatropha curcas* oil of different free fatty acid compositions and methanol were transesterified with bulk calcium oxide catalyst in a stoichiometric ratio. The feedstock with 0.22% free fatty acid had 99.99% methyl ester, that with 1.00% FFA had 99.11% methyl esters, the one with 3.92% FFA had 94.76% methyl esters, the ome with 7.8% FFA had 87.49% methyl esters and that with 8.16% FFA had 84.42% methyl esters. This indicates that methyl esters yield decrease with increase FFA of feedstocks. The presence of acid in the feedstock reduces the quantity of biodiesel produced when solid base catalyst is used.

Index Terms: effect, feedstock, high FFA, methyl esters, yield

1 INTRODUCTION

Biodiesel is produced from vegetable oil and animal fats. Biodiesel is one of the important alternative energy sources [1]. The most common feed stock is the vegetable oils. The vegetable oil and animal fats are made of esters which when reacted with alcohols in the presences of catalyst biodiesel (fatty acid alkyl esters) is produced. However, some vegetable oils contain high free fatty acids (FFA) which affect the yield of biodiesel if not treated before production. Improper handling of oil would cause it to oxidize in the presence of water to free fatty acid [2] due to hydrolysis and oxidation of the triglycerides. Transesterification of these feedstocks with high acid using acid catalysts convert the acids into methyl esters [3] thereby reduce or rather eliminated acid in the final products. Heterogeneous acid catalysts performed less activity, but they are favorable for low-qualified oil feedstocks with high FFAs [4]. Oils with higher fatty acid content lead to the formation of soap during homogeneous catalytic transesterification [5] and this reduces the production capacity. The soap formed partially consumes the catalyst, reduces products yield and interferes with the separation of glycerol [6]. Biodiesel can be produced from vegetable oils and animal fats depending on which source is readily and cheaply available. The source for biodiesel production is chosen according to the availability in each region [7]. Since the prices of edible vegetable oils are higher than that of fossil diesel, the use of edible vegetable oil for biodiesel production is not commercially viable.

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These edible vegetable oils are referred to as first generation biodiesel feedstocks. Their use for biodiesel production has generated heated debate of energy security for food crisis. This debate has changed the direction of biodiesel research into the use of non-edible oil sources referred to as second generation biodiesel feedstock of which *Jatropha curcas* is one. *Jatropha curcas* oil is highly acidic especially when left uncared for. The oil will undergo hydrolysis and oxidation in the presence of moisture and air which raises its acidity. This study is aimed at producing biodiesel from *Jatropha* oil of different acid values using bulk CaO (solid base) catalyst and compares their yields with refined oil feedstock. This will enable us establish the effect of feedstock acid value on methyl ester yield by transesterification.

2. MATERIALS AND METHODS

The materials used for this study include; *Jatropha curcas* seed oils of different content of free fatty acid (FFA), analytical grade methanol, 0.1 M KOH solution, bulk calcium oxide catalyst, magnetic stirrer, 250 mL conical flask, plastic funnel and sheet cloth. A mass of 1.0 g of *Jatropha curcas* oil was titrated against 0.1 M KOH to pink colour to determine the acid value of the oil. This was done for five different samples of *Jatropha curcas* oil.100 g of each of the five samples of the *Jatropha* oil was transesterified with 10.8 g of methanol and 1.0 g of bulk CaO catalyst making 3:1 methanol to oil molar ratio. The mixture of methanol and catalyst was prepared by missing 10.8 g of methanol with 1.0 g of CaO. This mixture was added to the oil at 60^{o}C and transesterified at this temperature for 60 minutes. The products were filtered and the filtrates were analyzed for yield with GC-MS. The GC-MS analysis was done by diluting biodiesel samples with n-hexane. 2 mL of the solution was collected into a sample bottle and injected into the GC-MS machine. The composition of methyl esters, acid, glycerol and other impurities were calculated from area% of the GC-MS analysis. This analysis was performed on GCMS-QP2010 PLUS SHIMADZU/JAPAN in the Quality control unit NARICT, Zaria

3. RESULTS AND DISCUSSION

Methyl esters compositions from the five productions are presented in Table 1. Methyl esters yield decreases with increase in FFA content of the feedstocks. The feedstock with acid value of 0.44 (0.22%) has 99.99% methyl ester, no

glycerol and acid. The feedstocks with 1.00%, 3.92%, 7.8% and 8.16% free fatty acid had 99.11%, 94.798%, 87.49% and 84.42% methyl esters; no glycerol (except the one from feedstock with 3.92% acid) and their acid value were 0.178%, 2.256%, 4.56% and 5.748% respectively. The non-methyl esters in the products are presented in Table 2.

Table 1: Methyl esters yield

Methyl ester composition	MF	Feedstock Acid Value (%)				
		0.22	**1.00**	**3.92**	**7.80**	**8.16**
Methyl 10-undecenoate	$C_{12}H_{22}O_2$		3.312			
Methyl palmitoleate	$C_{17}H_{32}O_2$	0.356	0.6		0.264	0.244
Methyl-7 hexadecenoate	$C_{17}H_{32}O_2$	0.178	0.3		0.132	0.122
Methyl hexadecanoate	$C_{17}H_{32}O_2$	7.5	3.044	6.088	5.656	5.572
Methyl 14-methylpentadecanoate	$C_{17}H_{34}O_2$	7.5	3.044	7.130	5.656	5.572
Methyl 15-methylhexadecanoate	$C_{18}H_{36}O_2$	3.75	1.522	4.464	3.964	3.926
Methyl 8-(2-hexylcyclopropyl) octanoate	$C_{18}H_{34}O_2$	0.178	0.3		0.132	0.122
Methyl -3-octadecenote	$C_{19}H_{36}O_2$	14.458	15.01			
Methyl 9-octadecenoate	$C_{19}H_{36}O_2$	14.458	15.01			12.836
Methyl oleate	$C_{19}H_{36}O_2$			12.688	26.804	25.672
Methyl elaidate	$C_{19}H_{36}O_2$	28.916	30.02		13.402	12.836
Methyl-12-hydroxy-9-octadecenoate	$C_{19}H_{36}O_2$		1.656			
Methyl 6-octadecenoate	$C_{19}H_{36}O_2$			26.068		
Methyl 7-octadecenoate	$C_{19}H_{36}O_2$			12.688	13.402	12.836
Methyl 8-octadecenoate	$C_{19}H_{36}O_2$	14.458	15.01	12.688	13.402	
Methyl-10 -octadecenoate	$C_{19}H_38O_2$					0.122
Methyl n-octadecanoate	$C_{19}H_{38}O_2$	6.448	5.336	4.260	4.544	4.56
Methyl 16-methylheptadecanoate	$C_{19}H_{38}O_2$	1.612	1.334			
Methyl -10-nondecenoate	$C_{20}H_{38}O_2$	0.178	0.3		0.132	
Methyl ricinoleate	$C_{19}H_{36}O_3$		3.312			
Total Methyl esters		**99.99**	**99.110**	**94.760**	**87.490**	**84.42**

None of the feedstocks with high acid value yielded methyl esters content of 96.5% which is the minimum methyl esters content for EN standard requirement for biodiesel [7]. The methyl ester content decreases with increase in feedstock acid value as presented in Table 1. Hence, CaO a base catalyst cannot esterify, the free fatty acid in the feedstock after transesterification acid reappeared in the product almost unchanged. The formation of Methyl 8-(2-hexylcyclopropyl) octanoate ($C_{18}H_{34}O_2$) could be the reaction of glycerol backbone (C_3H_5) with methanol as illustrated in the Eqn. 1 since there were no cyclopropane (∇) and glyceryl octanoate in *Jatropha curcas* oil. The lowest triglyceride in *Jatropha curcas* oil is glyceryl trimysritate (tritetradecanoate) [2]. This is also an indication that the catalyst could have catalyzed the isomerization of glycerol backbone (C_3H_5) to cyclopropyl radical (∇^+) which resulted in the formation of methyl 8-(2-hexylcyclopropyl) octanoate.

$$5C_3H_5 + 3CH_3OH \xrightarrow{CaO} CH_3O_2C(CH_2)_7\nabla CH(CH_2)_4CH_3 + H_2O + H^+ \quad (1)$$

Table 2: Non-methyl ester impurities

		Feedstock Acid Value (%)				
Non-methyl esters	**MF**	0.22	**1.00**	**3.92**	**7.80**	**8.16**
9-Octadecenoic acid, 1,2,3-propentriyl ester	$C_{57}H_{104}O_6$			0.266		
Glycerin 1-monoleate	$C_{21}H_{40}O_4$			0.492		
Glycerin 2-monoleate	$C_{21}H_{40}O_4$			0.266		
n-Pentadecanoic acid	$C_{15}H_{30}O_2$					0.658
n-Hexadececanoic acid	$C_{16}H_{32}O_2$				1.028	1.316
9-Hexadecenoic acid	$C_{16}H_{30}O_2$			0.492		
n-Heptadecoic acid	$C_{17}H_{34}O_2$				0.514	
Oleic acid	$C_{18}H_{34}O_2$			0.492		
6-Octadecenoic acid	$C_{18}H_{34}O_2$			0.492		
n-octadecanoic acid	$C_{18}H_{36}O_2$				0.514	
n-Octadecenoic acid	$C_{18}H_{34}O_2$					0.658
Arachidic acid	$C_{20}H_{40}O_2$				0.514	0.658
13-Docosenoic acid	$C_{20}H_{42}O_2$			0.492		
cis-Linoleic acid	$C_{18}H_{32}O_2$		0.178		1.99	2.458
Linoleic acid chloride	$C_{18}H_{31}ClO$			0.288		
(Z)-6-Pentadecen-1-ol	$C_{15}H_{30}O$		0.178		1.99	
cis-9-Octadecen-1-ol	$C_{18}H_{36}O$		0.178		1.99	2.458
9-Hexadecenal	$C_{16}H_{30}O$			0.266	3.98	4.916
9-Octadecenal	$C_{18}H_{34}O$			0.266		
13-Tetradecenal	$C_{14}H_{26}O$		0.178			2.458
Linoleyol chloride	$C_{18}H_{31}ClO$		0.178			
Total non-methyl esters		**0**	**0.890**	**3.812**	**12.51**	**15.58**

The hydrogen ion produced in Eqn. 1 could be used to reduce some of the fatty acids to alkanal. For example, the 9-hexadecenal could have been produced from the reduction of 9-hexadecenoic acid as illustrated in Eqn.2.

$$C_{16}H_{30}O_2 + 2H^+ \xrightarrow{CaO} C_{16}H_{30}O + H_2O \quad (2)$$

There was a complete conversion of feedstock that had 0.22% acid value to methyl esters. But as the acid value increases the methyl esters yield decreases as shown in Fig. 1 and the acid content of the biodiesel products increases. Glycerol the co-product of biodiesel was not produced except from the feedstock that had 3.92% free fatty acid (FFA) value. It can be deduced that the catalyst is perfectly good for transesterification of acid free feedstock but not effective for high acid feedstock. It promoted the production of other impurities such as aldehydes as shown in Table 2. High acid feedstock reduces the quality and quantity of product. The remnants of crude and partially esterified *Jatropha curcas* oils were stored for a long time not properly cared for. The oils compositions changed due to hydrolysis and oxidation of triglycerides in the presence of moisture and air [2]. The degradation of the oils results in the high free fatty acid content. High free fatty acid feedstock if not properly refined a lot of impurities will be formed which will reduces the quality of the biodiesel produced. It would raise the cost of production due to refining of the biodiesel product to meet required specification. The biodiesel product has to be neutralized with base solution and washed to reduce its acid content as it affect the engine on which it would be used for. Production of biodiesel from feedstock with high free fatty acid has to be refined but refining further increases production costs as a result of the additional equipment, time, and manpower that are required [9].

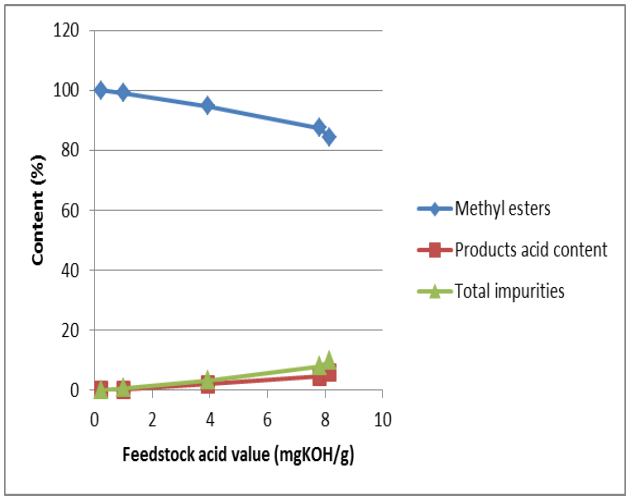

Figure 1: *Composition of product components*

4. CONCLUSIONS

Jatrpha curcas oil feedstocks with different free fatty acid contents were transesterification with methanol using bulk calcium oxide catalyst. The methyl esters contents decrease with increase free fatty acid composition of the feedstocks. The feedstocks free fatty acid appeared in the products indicating that the catalyst bulk calcium oxide (a base solid catalyst) could not transform the free fatty acids into methyl esters as do solid acid catalysts. The increase in concentration of free fatty acid in the feedstocks increased the impurities in the products. The feedstock with low acid (0.22%) was converted to methyl esters completely. Therefore, it pays to refine feedstock satisfactorily before transesterification.

5. ACKNOWLEDGMENT

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REFERENCES

[1] Kritana Prueksakorn and Shabbir H. Gheewala, Energy and Greenhouse Gas Implications of Biodiesel Production from Jatropha curcas L., The 2nd Joint International Conference on “Sustainable Energy and Environment (SEE 2006)

[2] Hanny Johanes Berchmans and Shizuko Hirata. Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresource Technology 99 (2008) 1716–1721, Available online at www.sciencedirect.com

[3] Yogesh C. Sharma and Bhaskar Singh, Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel, 2010 Society of Chemical Industry and John Wiley & Sons, Ltd | Biofuels, Bioprod. Bioref. 5:69–92 (2011); DOI: 10.1002/bbb

[4] Feng Guo and Zhen Fang (2011). Biodiesel Productionwith Solid Catalysts, Biodiesel - Feedstocks and Processing Technologies, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-713-0, InTech, Available from: http://www.intechopen.com

[5] A.P. Singh Chouhan, A.K. Sarma, Modern heterogeneous catalysts for biodiesel production: A comprehensive review, Renewable and Sustainable Energy Reviews, 15 (2011) 4378– 4399

[6] Pin Pin Oh, Harrison Lik Nang Lau, Junghui Chen, Mei Fong Chong and Yuen May Choo, A review on conventional technologies and emerging process intensification (PI) methods for biodiesel production, Renewable and Sustainable Energy Reviews 16 (2012) 5131–5145

[7] A.B.M.S. Hossain and M.A. Mazen, Effects of catalyst types and concentrations onbiodiesel production from waste soybean oil biomass as renewable energy and environmental recycling process, Australian Journal of Crop Science, AJCS 4(7):550-555

[8] Istvá n Barabá s and Ioan -Adrian Todoruţ (2011). Biodiesel Quality, Standards and Properties, BiodieselQuality, Emissions and By-Products, Dr. Gisela Montero (Ed.), ISBN: 978-953-307-784-0, InTech, Available from: http://www.intechopen.com

[9] Bryan R. Moser, Biodiesel production, properties, and feedstocks, In Vitro Cell.Dev.Biol.—Plant (2009) 45:229–266, DOI 10.1007/s11627-009-9204-z