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New non-edible resource for biodiesel production in Ghana

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ABSTRACT
Allanblackia floribunda oil, a by-product of pharmaceutical factory was investigated for potential non-edible feedstock for biodiesel production through alkali-catalyst transesterification using methanol with KOH as catalyst. The variables affecting the yield were studied. The optimum reaction conditions for producing the biodiesel included oil-to-methanol molar ratio of 1:10, catalyst amount of 1%, reaction temperature of 60 °C and reaction time of 1.5 h. The maximum yield of the biodiesel was 82.3 %. From the result, it was clear that the qualities of the biodiesel produced from Allanblackia floribunda oil at the optimum transesterification reaction conditions were within the international standards (ASTM D 6751 and European EN 14214). The results indicate that Allanblackia floribunda oil could be used as a new potential non-edible feedstock for biodiesel production.

Keywords: Allanblackia floribunda oil; biodiesel; non-edible feedstock; by-product; transesterification

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I. INTRODUCTION

Due to the frequent changes in the price of crude petroleum and its products coupled with air pollution caused by the combustion of fossil fuels, alternative fuels have gain attension (Singh & Singh, 2010, Feng et al., 2011). Among the available alternative fuel sources, biodiesel can be much preferred. This is as a result of its efficient biodegradability, non-toxic, inherent lubricity and relatively high flash point. It also reduces most of the regulated exhaust emissions (Bi et al., 2010, Zhu et al., 2008) and can be used without any modification in diesel, boilers or combustion engines (Zabeti et al., 2010).

Biodiesel has been produced using edible feedstocks such as soybean, cannola, rapeseed, sunflower, palm oil etc. (Lin et al., 2011). The use of edible oils for biodiesel production has increased the problem of food versus fuel. According to Mustafa (2011), the non-food uses of edible oils are worsening the problem of food shortages which consequently affects the economy.

The tallow tree (Allanblackia floribunda) is a woody dicotyledonous and underutilized plant belonging to the Guttiferae family. It is an evergreen plant that thrives well in wet places especially in the rainforest regions. The tree is widely distributed in most parts of Africa including Sierra Leone, Cameroon, Gabon, Congo Brazzaville and Uganda. In Ghana, it is found growing in the Western, Central, Ashanti and Eastern regions (Doehmer et al., 2011). Traditionally, the oil extracted from the seeds is used for preparing medicines and making soap. Properties of the oil including the high melting point makes it superior to alternatives like palm oil. The seeds of parkia contain 6.0% water, 2.2% ash, 3.6% crude protein, 3.1% crude fibre, 20.7% carbohydrate and 64.4% oil (Li et al. 2012). The oil content of the cake ranges from 4 to 6% or even up to 10%, depending on the oilseed and the processing equipment

II. MATERIALS AND METHODS

2.1 Materials

The crude Allanblackia floribunda oil was obtained from Rhyte Aid Pharmaceutical Co., Ltd (Ghana). Methanol, potassium hydroxide, n-heptane and tetradecane were obtained from Rhyte Aid Pharmaceutical Co., Ltd (Ghana) and were all of analytical reagent (AR) grade.

2.2 Alkali-catalyzed transesterification

Methyl esters were prepared by refluxing the oil at a preset temperature with a certain volume of methanol containing potassium hydroxide as catalyst for 1.5 h in a 250 mL three-neck reaction flask equipped with a condenser. Two layers were then formed in a separatory funnel. The upper layer consisted of methyl esters, traces of methanol, residual catalyst etc. The methyl ester layer was purified with 10% sulphuric acid and washed with deionized water and then finally dried at 70 °C with a rotary evaporator.
Methyl ester yields and composition were determined by the GC and GC-MS respectively.

III. RESULTS AND DISCUSSION

3.1 Characterization of the crude Allanblackia floribunda oil

Table 1 shows the GC-MS results of fatty acid contents of the crude oil sample. The overall content of unsaturated and saturated fatty acids was 83.9% and 16.1% w/w, respectively. These affect alkali-catalyzed transesterification. FFA of oil should be less than 1% prior to alkali-catalyzed transesterification (Hayyan et al., 2011). The oil used in this study had a FFA content of 0.9% hence standard for one-step process of alkali-catalyzed transesterification.

Table 1: Contents of Fatty acid of Allanblackia floribunda oil and Peroxide value of biodiesel with and without antioxidant with time.

Fatty acid[a]	Amount[b] (%)	Time (day)	Peroxide value (meq/kg) (No Anti-oxidant)	Peroxide value (meq/kg) With Anti-oxidant
C14:0 Myristic acid	0.13%	1	11.23	2.42
C16:0 Palmitic acid	7.76%	5	22.12	9.24
C18:0 Stearic acid	4.70%	10	52.15	12.18
C18:1 Oleic acid	20.56%	15	76.37	20.73
C18:2 Linoleic acid	62.69%	20	92.51	24.51
C20:0 Arachidic acid	1.99%	25	100.17	30.25
C20:1 Gadoleinic acid	0.65%	30	105.4	39.15
C22:0 Behenic acid	1.43%			

[a] Fatty acid was determined by GC-MS.
[b] Esters amount was determined by GC, using tetradecane as an internal standard.

3.2 Influence of transesterification reaction conditions

Transesterification process consists of a sequence of three consecutive reversible reactions viz; triglyceride to diglyceride, monoglyceride and finally to glycerin and FAME. Stoichiometrically, 3 moles of methanol is required for 1 mol of oil. But in practice, more methanol is needed to drive the reaction to the product. From Fig. 1, as the methanol to oil molar ratio was increased (from 6:1 to 10:1), the yield also increased till maximum of 81.7% at 10:1. The yield however reduced after 10:1 molar ratio was exceeded. The excessively added methanol had no significant effect on the production yield. The reason might be that the catalyst content decreased with increase in methanol. To elevate biodiesel production yield, an excess methanol was effective to some extent. It can be concluded that molar ratio of 10:1 was enough to achieve good yield (82.3%) at relatively short time (1.5h).

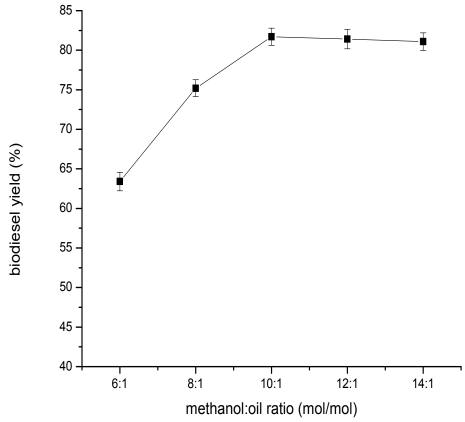

Fig.1 Evolution of the biodiesel yield at methanol/oil ratio: reaction temperature 60 ℃, catalyst amount 1.5 wt%, reaction time 120 min

From Fig. 2, when the amount of catalyst was increased from 0.25 wt% to 1.0 wt%, the biodiesel yield increased and reached maximum (82.5%) at 1.0 wt%. The yield decreased after the catalyst amount exceeded 1.0% possibly due to saponification reaction.

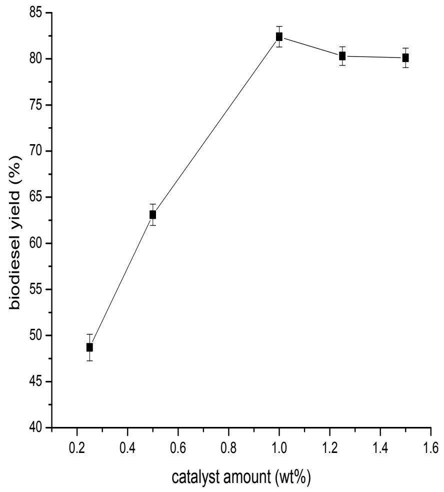

Fig. 2 Effect of catalyst amount on the biodiesel yield: methanol to oil molar ratio 10:1, reaction temperature 60 °C, reaction time 120 min

Temperature factor is a reversible chemical reaction at equilibrium. As shown in Fig.3, the reaction rate was slow at low temperatures (40, 50 ^{0}C), but the biodiesel yield first increased and then decreased with further increase in the reaction temperature. Generally, a more rapid reaction could be obtained at high temperatures as a result of endothermic nature of transesterification reaction (Wen et al. 2010). At the higher temperatures, methanol might have vaporized and formed a large number of bubbles which inhibited the reaction interface. The optimum reaction temperature was 60 ℃with of yield of 84.5%.

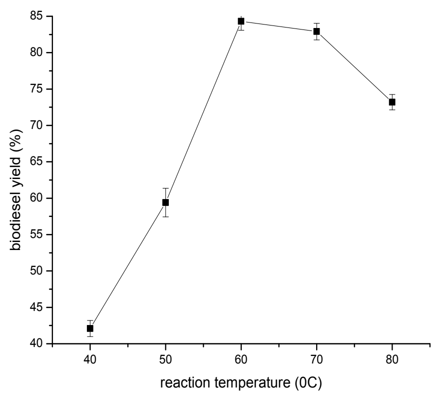

Fig. 3 Effect of reaction temperature on the biodiesel yield: methanol to oil ratio 10:1, catalyst amount 1.0 wt%, reaction time 120 min

The dependence of the biodiesel yield on the reaction time was investigated. The reaction time was varied in the range of 30 to 160 min. Fig. 4 revealed that at the beginning (30 min), the reaction was slow due to the mixing and dispersion of the methanol onto the oil and the biodiesel yield increased fast in the reaction time range of 30 and 60 min. Moreover, excess reaction time lead to a reduction in the yield due to backward reaction resulting in loss of esters and causing fatty acids to form soap. The optimum reaction time was 90 min.

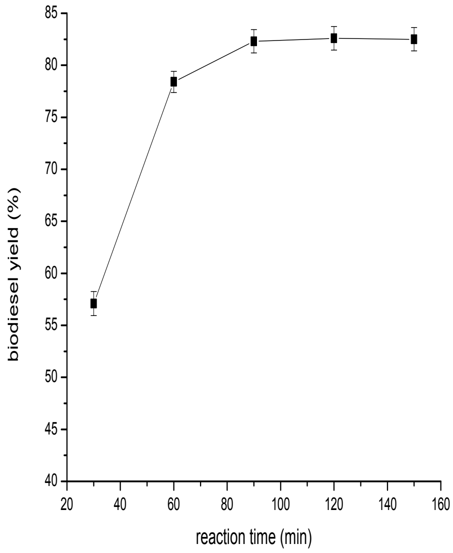

Fig. 4 Effect of reaction time on the biodiesel yield: methanol to oil molar ratio 10:1, catalyst amount 1.0 wt%, reaction temperature 60 ℃

3.3 Properties of the Allanblackia floribunda biodiesel

Since the quality of any proposed new biodiesel fuel is essential for the performance and emission characteristics of diesel engines, it is necessary that the silybum marianum biodiesel undergo testing with standard methods. The results of the study with international standards are listed in table 2.

Cetane number as one of the most significant properties specifying the ignition quality of fuel for use in a diesel engine indicated a high value which implies better ignition properties. This is associated with esters of saturated fatty acids (palmitic acid (C16:0)) and mono-unsaturated compounds (oleic acids (C18:1)) (Martín et al., 2010). The cetane number (51) was within the standards of ASTM D 6751 and EN 14214.

The key cold flow properties of biodiesel include cloud points (CP), pour point (PP) and cold-filter plugging point (CFPP). The CP, PP and CFPP observed for the biodiesel were 6 ˚C, 2 ˚C and 13 ˚C, respectively. These values were relatively higher than the conventional biodiesel from edible resource (rapeseed, sunflower and soybean) except peanuts biodiesel with CFPP of 16 ˚C (Bryan R, 2012). The poor cold flow properties of the biodiesel are possibly caused by methyl esters of long carbon chain saturated fatty acids (Bryan R, 2012). Winterization was used to improve the low temperature properties (Table 2). From Table (2), the low CP, PP and the CFPP were reduced from 2, 6 and 13 to -3, -3 and 0 ^{0}C respectively.

Ascobic acid was used as antioxidants to improve the oxidation stability of biodiesel. Peroxide value (POV) was determined using GB/T 5538 method. The value at 105.4 meq/kg at 30st day was reduced to 39.15 meq/kg upon adding ascorbic acid as anti oxidant (Table1). The kinematic viscosity, flash point, cid value and sulfur content were all within the international recommended standards (PRC, ASTM D6751 and EN 14214) (Table 2).

Table 2: Comparison of properties of the Allanblackia floribunda biodiesel and the standards of biodiesel United States and Europe and improvement of Key Cold Flow Properties.

Fuel property	Method	Allanblackia floribunda biodiesel	ASTM D6751	EN 14214	CFP (After Winterization)
Cetane number	ASTM D6890	51	≥47	≥51	
Kinematic viscosity (mm2/s; 40 ◦C)	ASTM D445	4.298	1.9-6.0	3.5-5.0	
Oxidative stability (h)	EN 14112	2.87	≥3	≥6	4.25
Cloud point (˚C)	D 2500	2	Report[d]	Country specific[d]	-3
Pour point (◦C)	D 2500	6	Report[d]	Country specific[d]	-3
cold filter plugging point (˚C)	GB/T 2540	13	-	-	0
Flash point (˚C)	ASTM D93	152	≥93	≥120	
Sulphur content (%, w/w)	ASTM D4294	NG	≤0.05	0.020	
Ash content (%, w/w)	GB/T508	0.018	≤0.02	≤0.02	
Acid value (KOH mg/kg)	ASTM D664-01	0.454	≤0.5	≤0.5	
Water (mg/kg)	ASTM D6304	0.4	≤0.05	≤0.05	
Density (20 ˚C)	SH/T0248	865	-	860-900	
Free glycerin (%, w/w)	EN 1405	0.01	≤0.02	≤0.020	
Total glycerin (%, w/w)	SH/T0796	0. 14	0.24	≤0.25	

NG= Negligible
CFP = Cold flow properties
[d] Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser.

IV. CONCLUSION

This study revealed that biodiesel can be produced successfully from crude silybum marianum oil through alkali-catalyst transesterification using methanol with KOH as catalyst. The optimum transesterification conditions for producing the biodiesel included oil-to-methanol molar ratio of 1:10, catalyst amount of 1%, reaction temperature of 60 ˚C and reaction time of 1.5 h with the maximum yield being 84.5%. The properties of the obtained biodiesel were within the international standards (PRC, ASTM6751 and EN14214). Subject to further testing on diesel engine performance otherwise, Allanblackia floribunda oil could be a new potential non-edible feedstock for biodiesel production.

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