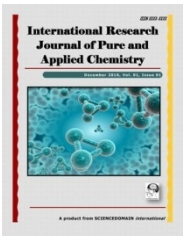

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Determination of Optimum Catalyst Concentration for Biodiesel Yield from Coconut (*Cocos nucifera*) Oil

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Authors' contributions

The first and corresponding author AUO designed the study, wrote the protocol, and wrote the first draft of the manuscript. The third author IEU carried out some aspects of the experimental work. Authors AUO, CNI and IEU managed the analyses of the study. All authors read and approved the final manuscript

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ABSTRACT

The determination of optimum catalyst concentration for biodiesel yield from Coconut (*Cocos nucifera*) oil was studied. The oil was transesterified using potassium methoxide as catalyst to obtain the crude biodiesel. The reaction was carried out at different catalyst concentrations of 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1.0%, 1.1% and 1.2% w/v KOH, while the speed of stirring, reaction time (60 min), alcohol to oil ratio (6:1) and reaction temperature (60^{o}C) were kept constant. The crude biodiesel were purified by washing with water severally to obtain the relatively pure biodiesel. They were dried using solar dryer for a period of four (4) days to obtain moisture-free pure biodiesel. They were subsequently analyzed for various parameters; Kinematic viscosity, acid value, free fatty acid (FFA), specific gravity, iodine value, ash value and flash point. The different variants gave results of the parameters analyzed comparable to International standards of biodiesel. The results of the study showed that, the optimum yield was obtained at 0.7% w/v catalyst concentration giving a biodiesel yield of 87.2%. At the

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catalyst concentrations of 1.1% and 1.2%, no biodiesel yield were obtained, instead there was formation of emulsion. General results obtained show that the optimum yields of biodiesel obtainable from Coconut oil when transesterified using KOH/methanol at the catalyst concentration of 0.7% w/v KOH is about 87%. Overall results indicate that Coconut oil can serve as a veritable feedstock for biodiesel production.

Keywords: Transesterification; biodiesel production; biodiesel yield; coconut oil; catalyst concentration.

1. INTRODUCTION

There is an ever increasing campaign for cleaner burning fuel in order to safeguard the environment and protect man from the inhalation of genotoxic substances. The exhaust gases from petroleum products especially diesel are known to be toxic and carcinogenous in nature, since they contain polycyclic aromatic hydrocarbons. There has also been a surge in the prices of petroleum products worldwide and it is quite doubtful if these prices would ever down-plunge since their rising trend has been consistent. There is therefore a global search for alternative sources of fuel which could be cheaper, safer and more importantly environmentally friendly [1]. Biodiesel is a fuel produced from the reaction of vegetable oil and fats with alcohol in the presence of a catalyst usually alkali (NaOH, KOH etc.). Biodiesel is biodegradable, non-toxic and has low emission profiles when compared to fossil fuel and its usage will allow balance between agriculture, economic development and the environment [2]. Biodiesel is produced through a chemical process known as transesterification. Transesterification of vegetable oils with low molecular weight simple alcohols (methanol, ethanol, propanol, butanol and amyl alcohol) has been established as the best option to reduce the high viscosity, low volatility, heavy engine deposits and toxic substance formation associated with the direct use of vegetable oils [3,4]. A wide variety of feedstock have been identified as suitable for biodiesel production including; seeds, nuts, fruits, leaves, stems, roots and tapped exudates etc.[5]. Others include known oil plants like soybean, canola, sunflower, safflower, *Jatropha curcas*, peanut, tigernut, coconut etc. [6,7]. However, some of these oil sources are commodities whose prices are strongly dependent on the International market. Coconut (*Cocos nucifera*), is a tropical plant and is commonly found in the western part of Nigeria and will find good use as a feedstock for biodiesel production. Coconut oil is heat stable. Its smoke point is about 180^{o}C. Because of its stability, it is slow to oxidize and thus resistant to rancidity, lasting up to two years due to high saturated fat content [8]. Coconut oil is a fat consisting of about 90% saturated fat. The oil contains predominantly medium chain triglycerides with 86.5% saturated fatty acids, 5.8% monounsaturated fatty acids and 1.8% polyunsaturated fatty acids [9]. Of the saturated fatty acid, coconut oil is primarily 48% lauric acid, 16% myristic acid and 8.5% palmitic acid, although it contains seven different saturated fatty acids in total. Its only monounsaturated fatty acid is oleic acid (6.5%) while its only polyunsaturated fatty acid is linoleic acid (2%). Ugheoke et al., [10] studied the optimum catalyst concentration for biodiesel yield from tigernut oil using potassium hydroxide and methanol at levels of 0.5 to 1.2% w/v KOH. Their findings concluded that the optimum concentration was 0.9% w/v catalyst level yielding 67% methyl ester. Some other research works have been carried out using coconut oil for biodiesel production. Alamu et al., [11] considered the use of coconut oil for the production of renewable and environmentally friendly biodiesel as an alternative to the conventional diesel fuel. Test quantities of coconut diesel were produced through transesterification reaction using 100 g coconut oil, 20% w/v ethanol, 0.8% potassium hydroxide catalyst at 65^{o}C

reaction temperature and 120 min reaction time. The result showed that low yield of the diesel (10.4%) was obtained. Awaluddin and Wahyuningshi [12] studied the optimum conditions of biodiesel production by methanolysis reaction between coconut oil and methanol using a heterogeneous catalyst ($CaCO_3$) calcined for 1.5 h at 90°C. Experimental parameters studied include catalyst concentration (1 – 3 wt %) and alcohol to oil ratio (4:1 – 12:1). They concluded that the catalyst concentration of 2% and alcohol to oil ratio of 8:1 at 60°C produced the highest conversion of cocodiesel of 75.02%. Highina et al, [13] studied biodiesel production from Jatropha curcas oil in a batch reactor using zinc oxide catalyst. The optimum conditions were found to be 1% ZnO, 18:1 methanol to oil ratio and temperature of 67°C giving the highest biodiesel yield of 98%. Puna et al, [14] studied the use of CaO modified with Li catalyst which showed very good catalytic performances with high activity and stability with yields higher than 92% without expensive intermediate reactivation procedures. The present work seeks to determine the optimum catalyst concentration for maximum biodiesel yield from crude coconut oil using the single stage process of transesterification in the first instance.

2. MATERIALS AND METHODS

2.1 Materials

The fresh, extracted coconut (*Cocos nucifera*) oil was procured from Badagry in Lagos state Nigeria. The methanol, analytical grade (Scharlau Chemie S.A, Sentmenat, Spain) and potassium hydroxide (Kalium hydroxide, Riedel-DeHaeneg, Seelze- Hannover) were used as purchased without further purification. This study was carried out in the National Centre for Energy Research and Development, University of Nigeria Nsukka between April and June, 2012. Other materials used were; 1 liter biodiesel reactor, thermo- regulator heater equipped with stirrer (Heizung Chauffage, MGW- LAUDA, D6970, Lauda- Königshofen, Germany), electronic digital weighing balance (Ohaus, Adventurer, model- AR 3130), separatory flasks, Oven (BTOV 1423), Vecstar furnace LF3, Ferranti portable viscometer model VL, Abbe refractometer (Searchtech Instruments No:820310110289, England), SYD-3536 Cleveland open cup flash point tester (Shanghaichangi Geological Instrument Co. Ltd), A greenhouse type passive solar dryer (constructed at The National Center for Energy Research and Development, UNN), operating at a temperature of 50 – 65°C.

2.2 Experimental Procedure

Potassium hydroxide (2.37g) representing 0.5% w/v catalyst concentration was added to absolute methanol (125 ml) in a 250 ml conical flask and tightly stoppered. It was swirled and kept overnight to ensure complete dissolution of the KOH in methanol. 500 ml of coconut oil was measured into the 1 liter biodiesel reactor. The oil was heated to 60°C while stirring at the same time. At the set temperature of 60°C, the potassium methoxide was gradually poured in the reactor and stirring continued at a constant speed at the same temperature. The reaction was carried out at different catalyst concentrations of 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1.0%, 1.1% and 1.2% while their speed of stirring, reaction time (60 min), alcohol to oil ratio (6:1) and reaction temperature (60°C) were kept constant. At the end of the reaction time, the mixtures were poured into different separatory flasks and left overnight to bring about gravity separation of the two layers. The lower layer (glycerol) was drawn off carefully leaving the methyl ester upper layer. The crude biodiesel was collected and measured. Their pH was recorded. Purification of the biodiesel was carried out by washing with distilled water (20% by volume of the oil used). The washing was done by

pouring the measured quantity of water and stirring vigorously to ensure proper removal of residual catalyst and methanol including soaps and other impurities. The washing was carried out four times to obtain very clear water. The purified biodiesel was put in the solar dryer for a period of four (4) days to dry, after which the samples were measured and the final yield obtained while their final pH were also taken.

2.3 Physicochemical Analysis

Odour, colour and physical state of the oil were estimated by sensory evaluation. The oil and biodiesel samples were characterized for specific gravity using specific gravity bottle, pH were determined using pH paper, moisture and ash content by AOAC (2010) method [15], kinematic viscosity using a viscometer, refractive index using Abbe refractometer, and flash point using the SYD-3536 Cleveland open cup flash point tester [16]. Other properties analyzed were the saponification values determined by titrimetry using the methods of the Palm Oil Research Institute of Malaysia [17]. Acid value, iodine value, peroxide value and free fatty acid (% FFA as lauric) were determined by titrimetry according to FAO [18, 19]

3. RESULTS AND DISCUSSION

Table 1 shows the result of the physicochemical properties of the coconut oil. Free fatty acid and acid value of the oil was higher than that observed from some other feedstock including *Jatropha curcas* kernel oil (2.26%, 4.47 $mgKOHg^{-1}$), *Arachis hypogea* oil (2.61%, 1.31 $mgKOHg^{-1}$) and *Luffa cylindrica* (2.47%, 1.23 $mgKOHg^{-1}$). It was however lower than that of *Azadirachta indica* (6.07%,12.08 $mgKOHg^{-1}$) [20,21].

Table 1. Physicochemical properties of the crude coconut oil

Parameters	Results
Viscosity (Cpoise)	11.57
Acid value ($mg/KOHg^{-1}$)	9.87
Free fatty acid (%)	4.96
Specific gravity (g/cm^{3})	0.92
Iodine value (g/100g)	63.70
Peroxide value (Meq/g)	3.76
Saponification value ($mg/KOHg^{-1}$)	240.25
Moisture content (%)	2.0
Ash content (%)	0.009

Acid value measures the presence of corrosive free fatty acids and oxidation products. This is actually an important variable in considering the quality of oil because the lower the free fatty acid, the better the quality of oil. The acceptable limit for edible oils for human consumption is ≤10 [22]. FFA concentration of the oil was somehow higher than the maximum limit of 2.0% reported for high-grade Codex Alimentarius [23]. Vegetable oils containing high free fatty acids have significant effects on the transesterification with methanol using alkaline catalyst. It also interferes with the separation of fatty acid ester and glycerols [24]. This indicates that the oil may be better converted to biodiesel using the two-stage process of esterification followed by transesterification, saponification followed by transesterification [25,26] or using heterogenous catalysts [14]. Specific gravity of all the oils was in the range of 0.85–0.93, which is close to the ASTM standard range of 0.87–0.90 for biodiesel [27]. Density and other gravities are important parameters for diesel fuel injection

systems. The values must be maintained within tolerable limits to allow optimal air to fuel ratios for complete combustion. High-density biodiesel or its blend can lead to clogging of fuel lines due to poor conversion of triglycerides to methyl esters [28]. The saponification value was high and therefore implies the possible tendency to soap formation and difficulties in separation of products if utilized for biodiesel production. This would also suggest that using the oils for biodiesel production would lead to low yields of the methyl esters. The peroxide value of the oil was okay indicating that the oil possesses good stability properties and would not easily go rancid as oils high in peroxide value are known to easily go rancid and therefore have short shelf life [29].

Table 2 shows the physicochemical properties of the biodiesel from the coconut oil. The flash point of the biodiesel was well within the ASTM standard specification of 120^{o}C min (Table 2). This indicates that their use will eliminate the fear of fire outbreaks on storage. The viscosity was also within the ASTM standard specification of 1.9-6.0 mm^2/g. This again indicates that transesterification effectively took care of the high viscosity of the oil that makes it unsuitable for use as a direct fuel in diesel engines. The iodine value was also within the standard specified which is also 120 max. High iodine value indicates high un-saturation in oils and fats. This shows that the transesterification took care of the unsaturation in the oil. The saponification value was lower than that obtained for peanut oil (224.74 and 218.09 mg/KOH) and from Jatropha oil (193.55mg/KOH) as reported by Arkbar et al. [30]. The ash content was lower than the maximum limit indicating that the biodiesel would leave minimal or no deposits during combustion in the exhaust pipe. The specific gravity was well within the standard limit. The free fatty acid was high, indicating that the two stage process of esterification or saponification before transesterification may be the preferred production route for this oil type.

Table 2. Biodiesel physicochemical properties

Parameters	Results	ASTM D6751 - 20
Kinematic viscosity (mm^2/g)	5.31	1.9 – 6.0
Acid value (mg/KOHg^{-1})	2.31	0.8 max
Free fatty acid (%)	1.22	-
Specific gravity (g/cm^3)	0.87	0.875 – 0.9
Iodine value (g/100g)	72.51	120 max
Saponification value (mg/KOHg^{-1})	126.23	-
Moisture content (%)	0.85	0.05
Ash content (%)	0.014	0.02
Flash point (^{o}C)	123	120 min

The catalyst concentration level β was calculated based on the formula:

β = (weight KOH)/(oil volume)*100

Also, biodiesel yield % γ was obtained from:

γ = (Product Volume)/(Oil Volume) *100 [10].

The biodiesel volumetric yield at the different catalyst concentrations is graphically presented in Fig. 1 below. The biodiesel yield before purification by washing showed that the variants at catalyst concentration of 1.1 and 1.2% had no yield at all (Table 3). The reaction yielded soap indicating that the catalyst concentrations were too high. The 0.7% concentration had the highest yield.

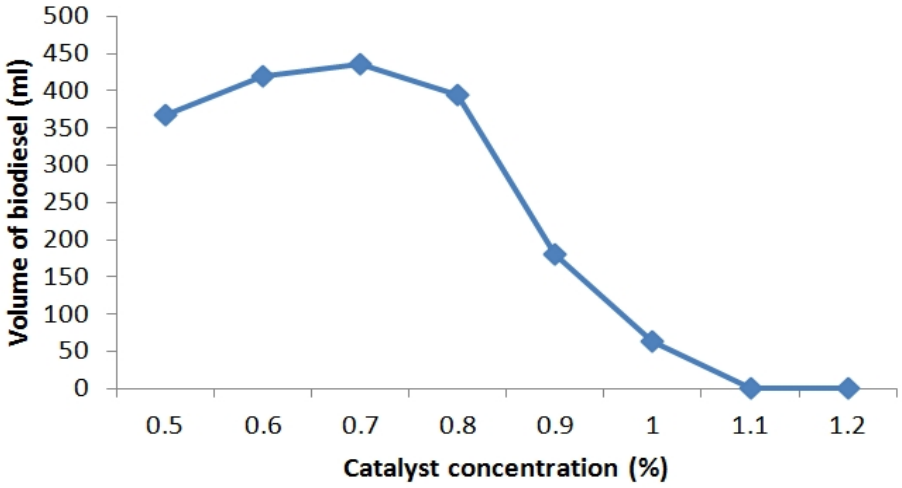

Fig. 1. Biodiesel yield at different catalyst concentrations

Table 3. Biodiesel yield properties

Catalyst concentration β (%w/v)	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Crude biodiesel yield (ml)	480	490	489	466	202	135	0	0
pH of crude biodiesel	9.0	9.0	9.0	9.0	9.0	9.0	-	-
Pure biodiesel yield (ml)	368	420	436	395	180	64	-	-
pH of pure biodiesel	6.0	6.5	6.4	6.5	6.5	6.5	-	-
Biodiesel yield (%)γ	73.6	84	87.2	79.0	36.0	12.8	0	0

After purification by washing, the yields of the different variants reduced, indicating that impurities like KOH, residual methanol, glycerol and some un-reacted materials were in high content. It was observed that the losses were high indicating low conversion efficiencies of the biodiesel. From Fig. 1 and Table 3, it was observed that the product volume increased steadily from 0.5% w/v concentration of the catalyst (KOH) until it peaked at 0.7% w/v of catalyst concentration and thereafter, a decrease was witnessed. It is clear therefore that increment in concentration level of the catalyst would not yield further volume increase in biodiesel obtainable from coconut oil. This could be explained from the viewpoint of the reversible nature of the transesterification process as reported by Darnoko [31]. Catalyst concentration levels greater than 1 may have favoured the backward reaction- the formation of glycerine, hence the yield of methyl ester at concentration level of 1.1 and 1.2 was nil. Ugheoke *et al*., [10] reported an optimum catalyst concentration of 0.9% w/v for tigernut oil resulting to a yield of 67%. This result is lower than that obtained for coconut oil in this study. The report by Awaluddin and Wahyuningshi [12] obtained a yield of 75.02% from coconut biodiesel using methanol and $CaCO_3$. Again, the work of Jansri and Prateepchaikul [26] on high free fatty acid coconut comparing the two stage methods showed that the highest yield achieved was 86.6% methyl ester with the TSP (esterification followed by transesterification). The processing conditions used were 0.5% NaOH at 60^{o}C and reaction time of 14.25 h. In this study, a higher yield of 87.2% was obtained at the catalyst concentration of 0.7% w/v of KOH. This indicates that at the prevailing operating conditions

of reaction temperature and time, 0.7% w/v KOH is the optimum catalyst concentration for coconut oil.

4. CONCLUSION

The study has shown the optimum catalyst concentration for a single stage transesterification of biodiesel from coconut oil using methanol and potassium hydroxide. The results have shown higher yields of biodiesel obtainable from coconut oil than those reported in literature from the same coconut oil. This indicates that coconut oil is a good feedstock for biodiesel production. The results further indicate that applying this catalyst concentration to the two stage process may give a higher yield of the biodiesel. The use of some heterogeneous catalysts in the transesterification of the coconut biodiesel may also give a better yield and would be investigated at different operating conditions from ones cited.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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