

Comparison of the Biodiesel Production from Coconut (*Cocos Nucifera*) Oil using the Two-Stage Method and the Single Stage Base Method

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Abstract - Comparison of the biodiesel production from Coconut (*Cocos nucifera*) oil was carried out using both the two stage method (esterification followed by transesterification) (Ac-Bs-M) and the single stage base-transesterification method (Ss-M). For the two stage biodiesel production, the esterification was carried out using conc. H_2SO_4 . The reaction was carried out for a total stirring time of 2 h and methanol quantity of 8% by volume of oil at a constant low stirring speed. The transesterification was carried out after 8 h of the esterification using potassium methoxide (0.65%) as catalyst at $60^\circ C$ and reaction time of $2\frac{1}{2}$ h also at a constant low stirring speed. The single stage base-transesterification was carried out at catalyst concentration of 0.7%, reaction temperature of $45^\circ C$ and reaction time of 45 min while keeping the speed of stirring constant. The methyl ester obtained from the two systems was 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. They were also analyzed according to ASTM D 6751-20 for some parameters including, free fatty acid (FFA), flash point, cloud point, pour point, ash content, moisture content, specific gravity and kinematic viscosity. The results of the parameters analyzed were comparable to International standards of biodiesel. The results of the study showed that the volumetric yield obtained from the two-stage method was 50% while that obtained from the single stage method was 82%. The results indicate that for this oil type with low free fatty acid, the two stage method is not the appropriate method for converting the coconut oil to biodiesel.

Keywords - Coconut oil, acid – base method, single stage method, biodiesel production, transesterification, biodiesel yield

1. INTRODUCTION

Renewable energy sources and biofuels, including biodiesel, have been gaining increasing attention recently as a replacement for fossil fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. The alternative diesel fuel can be termed as biodiesel. However, their implementation in the general market depends on making these fuels more competitive by the right choice of feedstock. 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 (Meher et al., 2004). Biodiesel is produced through a chemical process known as trans-esterification. 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 (Schwab et al., 1987; Teseer et al., 2005).

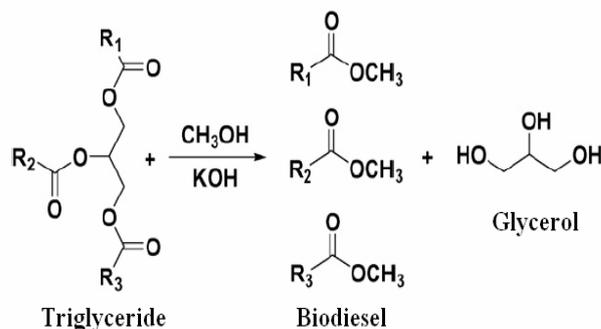


Fig. 1: Reaction of biodiesel production by base-catalyzed transesterification with methanol (Kolesárová et al., 2010)

Various edible and non edible vegetable oils, such as rice bran oil, coconut oil, *Jatropha curcas* oil, castor oil, cottonseed oil, mahua, karanja which are either surplus and are non-edible type can be used for the preparation of biodiesel (Freedman et al., 1986; Malhotra and Das, 1999; Shah et al., 2004). 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°C. Because of its stability, it is slow to oxidize and thus is resistant to rancidity, lasting up to two years due to high saturated fat content (James, 2001). 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 (Kincs, 1985). Of the saturated fatty acid, coconut oil is primarily 46.5% lauric acid, 19.2% myristic acid and 9.8% palmitic acid, although it contains seven different saturated fatty acids in total. Its only monounsaturated fatty acid is oleic acid (6.9%) while its only polyunsaturated fatty acid is linoleic acid (2.2%). Some research works have been carried out using coconut oil for biodiesel production. Alamu *et al.*, (2011) 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°C reaction temperature and 120 min reaction time. The result showed that low yield of the diesel (10.4%) was obtained. Awaluddin and Wahyuningshi (2010) studied the optimum conditions of coco-diesel production by methanolysis reaction between coconut oil and methanol using a heterogeneous catalyst (CaCO₃) calcined for 1.5 h at 90°C. Experimental parameters studied include catalyst concentration (1 – 3 wt %) and oil to alcohol ratio (4:1 – 12:1). They concluded that the catalyst concentration of 2% and oil to alcohol ratio of 8: 1 at 60°C produced the highest conversion of coco-diesel of 75.02%. In a previous study by Ofoefule *et al.*, 2013 and 2014, the effect of catalyst concentration, reaction temperature and reaction time on the biodiesel yield of coconut oil reported the optimum parameters to be catalyst concentration of 0.7%, reaction time of 45min, reaction temperature of 45°C and methanol to oil ratio of 16:1. The present study seeks to compare the volumetric yield of biodiesel from coconut oil using the two stage method of esterification followed by transesterification (Ac-Bs-M) and that from the single stage base catalyzed method (Ss-M) by combination of all the parameters from the previous study to find the best production method for this oil source

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), potassium hydroxide (Kalium hydroxide, Riedel-DeHaeneg, Seelze- Hannover) and conc. Sulphuric acid 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, 2013. Other materials used were; 1 liter biodiesel reactor, 5ml graduated syringe, thermo- regulator heater equipped with stirrer (Heizung Chauffage, MGW-LAUDA, D6970, Lauda- Königshofen, Germany), electronic digital weighing balance (Ohaus, Adventurer, model- AR 3130), digital pH meter (Jenway 3510), separatory flasks, Oven (BTOV 1423), Vecstar furnace LF3, Ferranti portable viscometer model VL, Abbe refractometer, semiautomatic Cleveland flash point tester, thermometer (-10 – 110°C), Oxygen Bomb calorimeter (XRY – 1A: Shanghai Changai, China) and 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

2.2.1 Preparation of Potassium Methoxide

Two Stage Acid –Base Methoxide (Ac-Bs-M)

Potassium hydroxide (2.9 g) representing 0.65% 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.

Single Stage Base Methoxide (Ss-M)

Potassium hydroxide (3.22 g) representing 0.7% w/v catalyst concentration was added to absolute methanol (163 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.

2.2.3 Acid- Base Biodiesel Production (Ac-Bs-M)

This was carried out according to Kac (2007) method. The coconut oil (500ml) was measured into the biodiesel reactor. The thermo-regulator heater was adjusted to the temperature of 35°C and maintained there while stirring the oil at a constant speed. Methanol (8% by volume of the oil) was added to the heated oil and stirred for 5 min. conc. H₂SO₄ (0.5ml) was added to the oil/methanol mixture while stirring. This was stirred at 35°C for a period of 1 h after which the heating was stopped and stirring continued for another 1hr (bringing the total stirring time for this stage to 2 h). At the end of the stirring, the mixture was left to sit for 8 h. After 8 h, half of the prepared potassium methoxide was poured into the unheated mixture and stirred for 5 min (this was expected to neutralize the H₂SO₄ and boost catalysis). It was then heated to 60°C and the second half of the methoxide added to the heated mixture. The stirring continued at a low speed for a period of 2½ h bringing the reaction to a stop. At the end of the reaction time, the mixture was poured into a separatory flask 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. The pH was recorded.

2.2.4 Single Stage Base Biodiesel Production (Ss-M)

This was carried out according to Ofoefule et al 2013 and 2014 method. 500 ml of coconut oil was measured into the 1 liter biodiesel reactor. The oil was heated to 45°C while stirring at the same time. At the set temperature of 45°C, the potassium methoxide was gradually poured in the reactor and stirring continued at a constant speed at the same temperature. The stirring was carried out for 45min. At the end of the reaction time, the mixture was poured into a separatory flask 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. The pH was recorded.

2.2.5 Biodiesel Purification

Purification of the biodiesel produced by the two methods was carried out by washing with warm 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 washings were carried out four times to obtain very clear water. The purified biodiesel were put in the solar dryer for a period of four (4) days to dry, after which the samples were measured and the final yields obtained while the final pH were also taken.

2.2.6 Physicochemical Analyses

Odour, colour and physical state of the oil was 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, kinematic viscosity was determined using a viscometer, refractive index using Abbe refractometer, and flash point using the SYD-3536 Cleveland open cup flash point tester (Van Gerpen, 2005). Other properties analyzed were the saponification values determined by titrimetry using the methods of the Palm Oil Research Institute of Malaysia (Anon, 1995). Iodine value, peroxide value and free fatty acid (% FFA as lauric) were determined by titrimetry according to FAO (1991). Acid value was determined as % FFA * 2.

3. RESULTS AND DISCUSSION

Table 1 shows the physicochemical properties of the raw oil. The free fatty acid and acid value of this sample

of coconut oil were low unlike that in the previous study which had a higher free fatty acid and acid value (4.9635% and 9.8678 mg/KOHg⁻¹) (Ofoefule et al., 2013 and 2014). These values for free fatty acid and acid value were also lower than those 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) (Joshua et al., 2011; Ibeto et al., 2012). This indicates that this sample of coconut oil should be a good feedstock for single stage biodiesel production. All the other parameters including the specific gravity, iodine value, saponification value and ash content were okay and within standard specification for a good biodiesel feedstock.

Table 1: Physicochemical properties of the raw crude oil

Parameters	Results
Viscosity (Pa.s)	75.71
Free fatty acid (%)	0.31
Acid value (mgKOHg ⁻¹)	0.62
Specific gravity (g/cm ³)	0.92
Iodine value (g/100g)	163.5
Saponification value (mgKOHg ⁻¹)	266.2
Ash content (%)	0.08

Table 2 shows the physico-chemical properties of the coconut biodiesel from the two methods of production. The yield of the biodiesel from the Ac-Bs-M was much lower than that of the Ss-M method. It was also lower than that reported in the previous studies which were 87.4%, 87.2% and 88% (Ofoefule et al., 2013 and 2014). It was again lower than most high yielding ones (95% and above). For instance, Highina et al., (2012) reported 97% biodiesel yield from *Jatropha curcas* while Meka *et al.* (2007) reported 96.85% biodiesel yield from Safflower. The biodiesel yield was only comparable to 50% reported by Itodo et al. (2009). The free fatty acid and acid value were okay indicating that the biodiesel is good and would not pose any problem on usage. The viscosity was also within the standard ASTM range, showing that transesterification took care of the high viscosity of the raw oil. The flash point was within the ASTM 6751 standard specification. This indicates that with its use, the fear of fire outbreaks would be eliminated. The ash content was slightly above the ASTM standard. Even though this suggests that it may likely have higher mineral contents leading to some level of air pollutants like SO_x and NO_x, however, the level was quite insignificant. The cloud point and the pour point of the biodiesel were well within the standard. One of the problems associated with biodiesel is its cold flow properties represented by the pour point. The pour point



is the lowest temperature at which frozen oil can flow and is used to specify the cold temperature instability of fuel oil.

Table 2: Biodiesel Physicochemical Properties

Parameters	Ss-M	Ac-Bs-M	ASTM D6751 - 20
Biodiesel yield (%)	82	50	> 95
Kinematic viscosity (mm ² /s)	5.07	5.07	1.9 – 6.0
Ash content (%)	0.09	0.09	0.02
Free fatty acid (%)	0.08	0.08	-
Acid Value (mgKOHg ⁻¹)	0.16	0.16	0.8 max
Specific gravity (g/cm ³)	0.877	0.877	0.875 – 0.900
Moisture content (%)	3.57	3.57	0.05
Flash point (°C)	130	130	120 min
Cloud point (°C)	-2	-2	-50 - 6
Pour point (°C)	-6	-6	-55 - 150

The result of the experiment described the comparison between the two methods of biodiesel production for the coconut oil in order to ascertain the route that will give the higher yield and hence the best production method. The result obtained in this study showed a much lower volumetric yield from the Ac-Bs-M when compared with that obtained from the Ss-M and individual studies earlier on. The result of the acid-base method showed that the volumetric yield obtained from the biodiesel was 50%, while that obtained from the Ss-M by combination of the parameters from the previous study was 82% and that at optimum catalyst concentration, optimum reaction and optimum reaction temperature for the previous studies were 87.2%, 87.4% and 88.0% respectively. Other reports have obtained yields above 90%. A test of the pH of the oil showed that this particular oil sample was not acidic and confirmed the low level of free fatty acid observed in the analysis. This indicates that the conversion efficiency for the Ac-Bs-M for this oil sample was not good at all. The Ss-M yield was closer to that obtained from the individual reports earlier. The result confirms that the Ac-Bs-M route is not the best route for converting this oil type with low FFA to biodiesel.

4. CONCLUSION

The study has shown the comparison between the two methods for converting coconut oil to biodiesel. The results have shown that coconut oil is a good feedstock for biodiesel production, however, the two stage acid-base method is not the best for transesterifying the oil to biodiesel especially when the free fatty acid content is very low. The result further showed that the single stage base method is better for the conversion to biodiesel especially when the optimum conditions reported in the previous study are adhered to. Further research would still be carried out in order to optimize the yield obtainable from this oil feedstock.

REFERENCES

- Alamu, O. J., Dehinbo, O. and Sulaiman, A. (2011). Production and testing of coconut oil biodiesel fuel and its blends. *Leonardo J. Sci.* 9: 95-104.
- Anon. (1995). Palm Oil Research Institute of Malaysia, Ministry of Primary Industries, Bangi, Malaysia.
- AOAC. (2010). Official methods of Analysis. Association of Analytical Chemists. 14th ed. Washington, USA. 22209.
- Awaluddin, P.A. and Wahyuningshi, S. (2010). Making biodiesel from coconut oil by reaction metanolysis heterogeneous catalyst. In *Proc. Energy and sustainable Development: Issues and strategies (ESD)*, 2 – 4, June, Chiang Mai, Thailand.
- FAO. (1991). Guide to Specifications for General Notices, General Analytical Techniques, Identification Tests, Test Solutions, and other Reference Materials, vol. 5 of FAO Food and Nutrition, Rome, Italy.
- Freedman, B., Butterfield, R.O. and Pryde, E. H. (1986). Transesterification kinetics of soybean oil. *J Am Oil Chem Soc*; 63(10): 1375-80.
- Highina, B.K., Bugaje, I.M. and Umar, B. (2012). Biodiesel production from *Jatropha curcas* oil in a batch reactor using zinc oxide as catalyst. *J. Appl. Phytotech. Environ. Sanit.* 1(6): 61-66.
- Ibeto, C.N., Okoye, C.O.B. and Ofoefule, A.U. (2012). Comparative study of the physicochemical characterization of some oils as potential feedstock for biodiesel production. *ISRN Renew. Energy*, 1-5. Doi: 10.5402/2012/621518.
- Itodo, I.N., Oseni, M.I. and Wergba, C. A. (2009). Comparative study of the properties and yield of biodiesel from soy and groundnut oils. *Nig. J. Solar Energy*, 21:124-128.
- James, D. (2001). Compliance demonstration for solvent extraction for vegetable oil production. NESHAP, North Carolina. Pp 161- 173.



Joshua, M., Garba, M.A., Chidi, N., Audu, A.A. and Abduljalal, D. (2011). Comparative study of biodiesel from kernel oils of *Jatropha curcas* and *Azadirachta indica* in Zaria Nigeria. *J. Pharm. Res. Innov.*, 4:10-15.

Kac, A. The foolproof way to make biodiesel: free fatty acid to ester conversion, http://journeytoforever.org/biodiesel_aleksnew.html. 10/02/2007

Kincs, F.R. (1985). Meat Fat Formulation. *J. Amer. Oil Chem. Soc.*, 62: 815 – 818.

Kolesárová, N., Hutňan, M., Špalková, V. and Lazor, M. (2010). Biodiesel by-products as potential substrates for biogas production. 37th Int. Conf. of SSCHE. May 24-28, Tatranske Matliare, Slovakia..

Malhotra, R. K. and Das, L.M. (1999). Biofuel as blending components for motor gasoline and diesel fuels, *Journal of Scientific and Industrial Research*, Vol. 61, 91.

Meher, L.C., Sagar, D. V. and Naik, S. N. (2004). Technical Aspect of Biodiesel Production by transesterification-A Review. *Renewable Sustainable Energy Rev.* 3.

Meka, P.K, Tripathi, V and Singh, R.P. (2007). Synthesis of biodiesel fuel from safflower oil using various reaction parameters. *J. Oleo Sci.*, 56 (1): 9-12.

Ofoefule, A.U., Ibeto, C.N. and Ugwuamoke, I.E. (2013). Determination of optimum catalyst concentration for biodiesel yield from Coconut (*Cocos nucifera*) oil. *Int. Res. J. Pure & Appl. Chem.*, 3 (4): 357 – 365.

Ofoefule, A.U., Ibeto, C.N., Ugwu, L.C. and Eze, D.C. (2014). Determination of optimum reaction temperature and reaction time for biodiesel yield from Coconut (*Cocos nucifera*) oil. *Int. Res. J. Pure & Appl. Chem.* 4 (1): 108 – 117.

Schwab, A.W., Baghy, M.O. and Freedman, B. (1987). Preparation and properties of Diesel fuel from vegetable oils, *Fuel*, 66: 1372 – 1378.

Shah, S., Sweta, S. and Gupta, M.N. (2004). Biodiesel Preparation by Lipase catalyzed transesterification of *Jatropha* oil. *India Energy & Fuels*, 18: 154-159.

Tesser, R., Di Serio, M., Guida, M., Nastasi, M. and Santacesaria, E. (2005). Kinetics of Oleic acid etherification with methanol in the presence of Triglycerides. *Ind. Eng. Chem.. Res.*, 44: 7978- 7982.

Van Gerpen, J.H. (2005). Biodiesel processing and production. *Fuel Processing Technology*. 2005 86(10):1097–1107.