@2016 Journal of PU, Part: B
Vol. 3 No:2, July 2016 pp 11-17
PRESIDENCY UNIVERSITY
ISSN: 2224-7610

Ricinoleic acid methyl ester (RAME): Synthesis, characterization and determination of optimum process parameters

M. A. Usman, R.U. Owolabi and E.N Onoh

ABSTRACT

The quality of biodiesel has been said to depend strongly on the reaction parameters or process variables. The parameters/variables such as methanol to oil molar ratio, reaction temperature and time, catalyst concentration and stirring rate have been explored in this study using the one variable at a time technique. The step by step exploration was carried out on the synthesis of castor oil (ricinoleic acid) biodiesel (ricinoleic acid methyl ester) in methanol solvent environment using potassium hydroxide as catalyst. Optimum condition of 12:1 methanol to oil molar ratio,60 minutes reaction time,1.5%w/w catalyst concentration,65^0 reaction temperature and 125 rotation per minutes stirring rate presented a biodiesel yield of 82-96%.The fuel properties of the RAME and the infra-red spectral obtained through optimized condition were mostly found to be within acceptable standards.

Key words: Ricinoleic acid, RAME, Fuel properties, Infra-red spectral

INTRODUCTION

The process for biodiesel synthesis has been extensively and consistently studied in the past especially by researchers such as, Lapuerta (2009), Canoira (2008, 2007, 2006), Alcantara et al. (2000). The biodiesel synthesis from castor oil (Ricinoleic acid) has also been earlier reported by Varma and Madras (2007), Meneghetti et al.(2007,2006),Silva et al.(2006) and Oleveira et al.(2005). Owolabi et al.(2011) and Saloua et al.(2010) reported that the renewed interest in biodiesel as alternative energy sources for reducing greenhouse effects in line with Kyoto principle agreement, and further conserving of fossil fuel reserves is on the basis of its direct use without any modification in diesel engines, boilers or other combustion equipment. Examples of this include the first successful trial run on a superfast passenger train which was conducted on December 31, 2002 by Indian railway on Delhi-Amritsar Shatabdi Express with use of 5% biodiesel, which helped railways in fuel bill reduction, Sreenivas et al. (2011), and the first trial to test run a fossil diesel generator for hours at the University of Ilorin, Kwara state, Nigeria (Longitude 8.50 ^{0}N and Latitude 4.55^{0}E), Owolabi et al. (2012). Biodiesel is produced by a simple technology called trans-esterification. By this, triglycerides which are the main components of bio-sourced oil react with an alcohol to produce fatty acid mono-alkyl esters (Biodiesel) and glycerol as a by-product.

University of Lagos, Chemical and Petroleum Engineering Department, Akoka, Yaba, Lagos State, Nigeria. e-mail: mawwal04@yahoo.com

The review of Owolabi et al. (2012) reported lengthy list of oil source for biodiesel in different countries. Furthermore, the suitability of fatty acid methyl esters (FAMEs) of seed oils as fuel in diesel engines has been documented in the case of many plant species, Azam et al.(2005) and Ramos et al.(2009).Castor oil has been selected for the synthesis of biodiesel in this study. The fatty acids of this oil consist of approximately 80–90% ricinoleic, 3–6% linoleic, 2–4% oleic, and 1–5% saturated fatty acids, Murat et al.(2013).The dominance of the ricinoleic in the castor oil gave rise to the name ricinoleic acid methyl ester (RAME) as the castor oil biodiesel. Lavanya (2012) reported that the presence of about 90% ricinoleic acid in castor oil results in its solubility in alcohol at 30 ^{0}C. High ricinoleic acid facilitates trans esterification without heating and lowers the cost of production. Castor oil is an important oil resource. Outside, its recent use as biodiesel feedstock, it finds application in the manufacturing of surfactants, coatings, greases, fungi stats, pharmaceuticals, cosmetics, Jose et al. (2013).As against earlier reports of, Muktar et al. (2008), Kumar et al. (2008) and Ravindrababu (2006) on Jatropha, the work of Ogunniyi (2006) and book authored by Weiss (2000) on oil seeds claimed that castor has a higher percentage (47-49%) of oil. Earlier studies concluded that some factors such as free fatty acid (FFA) and moisture contents of feedstock, quantity of alcohol, the amount and type of catalyst, the reaction temperature and time , and stirring rate affect the yield of biodiesel, Jeong et al., (2006a,2006b,2007,2009) and Freedman et al.(1984).

EXPERIMENTAL METHODS

Reagents and materials

Refined castor oil was purchased from Hollyland Chemicals Ltd, Ojota, Lagos state, Nigeria. Latitude 6.5833 and Longitude 3.75. It is a characteristically brownish viscous liquid packaged in 6-liter white plastic bottle. Analytical grade methanol (99.5%) packed in amber color bottled was purchased from Evans Chemicals Ltd, Ilasamaja, Lagos, Nigeria. KOH was provided by the management of Chemical Engineering Petroleum Laboratory II of the University of Lagos, Nigeria. All reagents were analytical grade and were used without purification. The physico-chemical properties of castor oil were determined using standard methods.

Trans esterification reaction

About 100grams of Castor was weighed in a beaker and heated mildly to evaporate any moisture present. The oil was allowed to cool while the temperature was monitored to the set reaction temperature. 44.20 grams of methanol and 1.5% w/w of Potassium Hydroxide (KOH) pellets used as catalyst were put together for dissolution. The Castor oil beaker was partially immersed in the water bath set-up (at 65^{o}C reaction temperature) with magnetic stirrer set at 250 rpm. The Methanol- KOH mixture was introduced into the stirred castor oil immediately for a period of time as depicted in the chemical reaction contained in Fig 1.The experiment was carried out repeatedly for reaction times of 30, 45, 60, 90, 120 and 180 minutes while keeping molar ratio, catalyst amount, reaction temperature and stirring rate

constant. The resulting reaction mixture was allowed to cool, settle and was separated using the separation funnel. The Biodiesel (topmost layer) was separated from the glycerin (bottom layer) and the little catalyst solution mixed with soap solution (thin middle layer).The Biodiesel was washed with 2% water amount for three times to obtain purer biodiesel and its percentage yield was calculated. The experiment was repeated six times each while varying molar ratio (1:3, 1:6. 1:12, 1:15, 1:20,1:25) and keeping reaction time, catalyst amount, reaction temperature and stirring rate constant at 60 minutes, 1.5% w/w, 65^{o}C and 250 rpm respectively. The same experiment was repeated six times each while varying catalyst amount (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0% w/w) and keeping molar ratio, reaction time, reaction temperature and stirring rate constant at 1:12, 60 minutes, 65^{o}C and 250 rpm respectively. The experiment was also repeated six times each while varying reaction temperature (50, 60, 65, 70, 75 and 80^{o}C) and keeping molar ratio, reaction time, catalyst amount and stirring rate constant at 1:12, 60 minutes, 1.5% w/w and 250 rpm respectively. The experiment was lastly repeated six times each while varying stirring rate (100, 125, 250, 350, 400 and 500 rpm) and keeping molar ratio, reaction time, catalyst amount and reaction temperature constant at 1:12, 60 minutes, 1.5% w/w and 65^{o}C respectively. The resulting Biodiesel at optimal parameters (molar ratio, reaction time, catalyst amount, reaction temperature and stirring rate) was analyzed using FTIR.

The molecular weight (MW) of the oil was determined from the saponification (S.V) and acid value (A.V) in mgKOH/g oil using approach(eq.1.0) adopted by Cheng et al.(2008)

$$MW = \frac{56.1 \times 1000 \times 3}{SV - AV} \qquad (1)$$

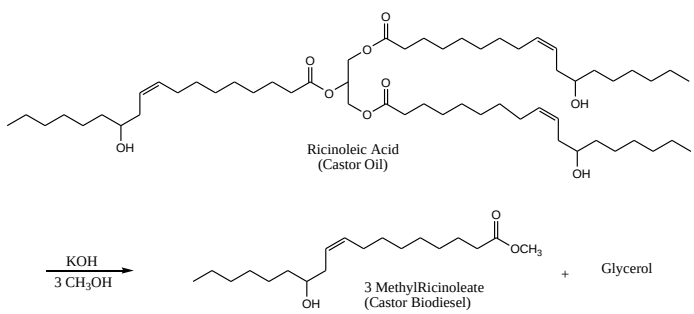


Fig 1. Methyl trans esterification of castor oil using a lye catalyzer

DISCUSSION OF RESULTS

Saponification value and acid value of the castor oil was determined using ASTM D6751 and was found to be 200.48 and 6.74, mgKOH/g respectively. The oil molecular weight was calculated using eq.1.0 to be 868.69 g/mol. The physic-chemical analysis of the biodiesel (Table 1.0) was carried out at Bato Chemical Laboratory Isolo, Lagos, Nigeria. Biodiesel synthesis is influenced by the properties of the oil. Canakci (2001) reported that high rates of acidity and moisture reduce the reaction yield and that acceptable values for biodiesel

production are between 0.5 to 0.8 mg KOH/g oil and a moisture content of 0.04. However, earlier reports have been silent on specific effects of other oil properties prior to biodiesel synthesis.

Table 1: Physico-Chemical Analysis of Castor Oil

Properties	**Value Obtained**	**ASTM Standard**	**EN Standard**
Appearance	Brrownish Liquid		
Volatile matter	2.28		
Moisture content, % w/w	0.04	0.05 (ASTM D6751)	0.05 (EN 14214)
Viscosity (kinematic) at 40^{o}C, mm/s^{2}	21.76	1.9-6.0 (ASTM D6751)	3.5-5.0 (EN 14214,)
Acid value, mgKOH/g	6.74	0.8 (ASTM D6751)	0.5 (EN 14214)
Free fatty acid,%	2.37		
Peroxide Value,mEg/Kg	1.96		
Saponification Value, mg/KOH	200.48		
Unsaponifiable matter g/Kg	14.5		
Specific gravity at 25^{o}C	0.9560	0.86-0.90 (ASTM D6751, ASTM D287)	0.86-0.90 (EN 14214)
Iodine value, g/100g	107.1	<130 (ASTM D6751)	<120 (EN 14214)
Refractive index	1.4870		

OPTIMIZATION OF CASTOR OIL BIODIESEL SYNTHESIS

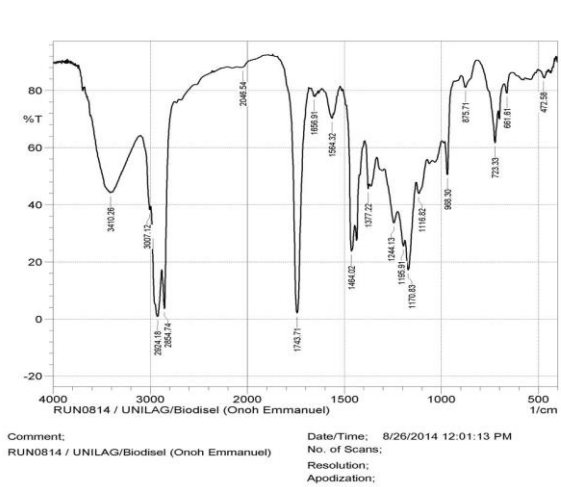
Six process variables were considered and at any point, one of the process parameters is varied while others remain constant. Over 90% biodiesel yield was obtained at 6:1 and 12:1 methanol to oil molar ratio. The maximum biodiesel yield of 95% at methanol to oil molar ratio 6:1.This same ratio was obtained for maximum yield by Kang and Wang (2013). At methanol to oil molar ratio 15:1 and beyond, the excess methanol has no significant effect on the biodiesel yield and at this point, the separation of glycerol becomes increasingly difficult. Molar ratio 12:1 is the optimum ratio.

The reaction was found to strongly depend on the reaction time. The yield was lower at low reaction times and later peaks at 60 minutes reaction before declining. This decline at higher reaction time may be due to the tendency of a reversed reaction leading to loss of RAME as well as increasing the tendency of soap formation. The optimum reaction time is therefore 60 minutes. For the catalyst concentration, no particular trend was observed, however, the maximum yield was obtained when the catalyst concentration was 1.5% w/w. Beyond 1.5% w/w of the catalyst, there is tendency of increased soap formation and as a result reduces the biodiesel yield. At lower reaction temperature, the biodiesel synthesis follows the normal temperature effects on reaction rate. The yield was low at lower temperature, reaches maximum of about 93% at 65 ^{0}C.A fall in the yield was observed at temperatures higher than 65 ^{0}C. Kang and Wang (2013) attributed the fall in yield at higher temperatures to the vaporization of methano and the subsequent formation of large number of bubbles in the interface, which inhibit the increase in the yield. Stirring of reaction mixture enables

components distribution homogeneity to be quickly attained and in most cases, favors the progress of the reaction towards getting the required yield output. In this work, stirring rate between 125 and 350 rpm actually showed relatively no remarkable increase (only 2 to 4%) in yield of biodiesel. Higher increases in stirring rate to 400 and 500rpm gave reduced yield of biodiesel.

FT-IR SPECTROMETRY

The procedure as reported by Yordanov et al. (2013) was adopted. The FT-IR spectra were recorded using Shimadzu spectrometer at ambient temperature in the wave number 4000-400 cm^{-1}.The resulting IR spectra of the RAME synthesized at optimum condition are contained in Fig 2.0 and can be interpreted as follows: There is a brand for triglycerides at 1743.71 cm^{-1}.An indication for unsaturated compounds is at 3007.12 cm^{-1} and deformation vibrations at 1464.02 cm^{-1}.The brands at 2924.18 cm^{-1} and 2854.74 cm^{-1} belong to the valence vibrations of CH_2- group. The brand at 723.33 cm^{-1} is typical for more than four CH_2- groups present in the spectra
Of compounds containing CH_2- long chain higher fatty acids.



SHIMADZU

	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	472.58	84.555	0.437	486.08	470.65	1.044	0.014
2	661.61	79.087	4.641	675.11	636.53	3.107	0.247
3	723.33	61.677	14.175	810.13	705.97	11.023	1.634
4	875.71	81.049	5.638	896.93	817.85	5.578	1.151
5	968.3	50.532	17.861	983.73	931.65	8.507	1.058
6	1116.82	43.924	5.632	1128.39	1074.39	17.097	1.695
7	1170.83	17.169	15.916	1186.26	1130.32	30.803	6.407
8	1195.91	25.546	4.131	1224.84	1188.19	18.845	0.782
9	1244.13	33.665	7.774	1294.28	1226.77	26.248	2.365
10	1377.22	45.578	5.521	1394.58	1371.43	6.27	0.142
11	1464.02	23.784	26.172	1489.1	1446.66	17.559	4.556
12	1564.32	70.272	2.621	1610.61	1558.54	6.427	0.232
13	1656.91	77.932	0.96	1670.41	1653.05	1.763	0.04
14	1743.71	2.061	82.941	1830.51	1683.91	51.406	41.58
15	2046.54	88.124	0.097	2048.47	1992.53	2.806	0.05
16	2854.74	3.609	26.3	2881.75	2756.37	58.56	15.01
17	2924.18	0.899	24.289	2996.55	2883.68	131.425	65.586
18	3007.12	38.159	4.678	3057.27	2997.48	19.1	0.437
19	3410.26	44.147	0.12	3414.12	3406.4	2.735	0.004

Fig 2. IR Spectra of RAME synthesized under optimum condition.

Viscosity as a physical property is one of the important qualities of biodiesel. The value obtained for the castor oil viscosity (Table 3.0) is slightly above the standard set by ASTM D6751 and EN 14214.The RAME produced has acid value lower than the recommended. The specific gravity, iodine value, and cold filter plugging point all fall within acceptable limits. Flash point of biodiesel is important during storage to avoid explosion. The flash point of biodiesel can be affected by the level of unreacted methanol in the biodiesel. Ferlizardo et al.(2006) showed that an increase in 0.5% in methanol content of biodiesel can lead to 50% decrease in biodiesel flash point. Specific gravity of 0.862 reported in this work is in

consistent with EN 14214 and ASTM D6751standard.Akihama et al.(2002) reported that Higher degrees of unsaturation is undesirable for fuels because of its oxidation reaction which generally take place at high temperatures during combustion, may result in irreversible polymerization to plastic-like substances. Iodine value is known for the determination of the degree of unsaturation of the biodiesel fuel and as such influences fuel oxidation tendency. The tendency of such oxidation is low for the synthesized biodiesel because of the very low iodine value obtained. Other fuel property was either slightly above or below set standard. Further treatment could be carried out to correction any batch synthesized with serious deviation from standards. Baig (2010), Berrios et al.(2011) and Atadashi et al.(2011) for instance, attributed higher acid values of biodiesel to leaching of the sulponic group which they corrected through water stripping, a common processing step for the industrial production of biodiesel.

Table 2: Fuel Properties of castor oil synthesized biodiesel

Properties	**Value Obtained**	**ASTM Standard**	**EN Standard**
Moisture content, % w/w	0.071	0.05 (ASTM D6751)	0.05 (EN 14214)
Flash point, ^{o}C	154	130 (ASTM D6751)	120 (EN 14214)
Heating value, J/kg	$36.72x10^{6}$	($10x10^{6}$ to $35x10^{6}$ (ASTM 6751)	$35.0x10^{6}$ (EN 14213)
Viscosity (kinematic) at 40^{o}C, mm/s^{2}	6.56	1.9-6.0 (ASTM D6751)	3.5-5.0 (EN 14214,)
Acid value, mgKOH/g	0.29	0.8 (ASTM D6751)	0.5 (EN 14214)
Ash Content, %	0.09	0.02 (ASTM D6751)	<0.02 (EN 14214)
Specific gravity at 25^{o}C	0.862	0.86-0.90 (ASTM D6751)	0.86-0.90 (EN 14214)
Iodine value, g/100g	26.22	<130 (ASTM D6751)	<120 (EN 14214)
Cetane Number	55.2	45 min (ASTM D613)	51 min (EN 4264)
Cloud Point, ^{o}C	3.7	-1 (ASTM D2500)	<-1(EN 116)
Cold Filter Plugging Point (CFPP), ^{o}C	-16	(-28 to 0)(ASTM D2500)	<0 (EN 116,EN 14214)

CONCLUSION

In this study of castor oil biodiesel synthesis at optimum condition of 12:1 methanol to oil molar ratio, 60 minutes reaction time, 1.5%w/w catalyst concentration,65^{0} Creation temperature and 125 rotation per minutes stirring rate, biodiesel yield of 82-96% was obtained using potassium hydroxide as catalyst. Apart from the flash point, and iodine value, all other fuel properties of the RAME were within standard limits. The synthesis of biodiesel from castor oil may be improved through further processes and the optimization to obtain biodiesel desired quality.

REFERENCE

[1] Akihama, K.,Takatori, Y., Nakakita, K (2002) Effect of Hydrocarbon Molecular Structure on diesel exhaust emissions: A research report, R & D Review of Toyota CRDL; 37, 3.

[2] Alcantara, R., Amores, J., Canoira, L., Fidalgo, E., Franco, M.J, Navarro, A (2000) Catalytic production of biodiesel from soybean oil, used frying oil and tallow. Biomass Bioenergy, 18, 515–27.

[3] Atadashi,I.M., Arou,M.M.,AbdulAziz,A.R.,Sulaiman,N.M.N (2011) Refining technologies for the purification of crude biodiesel.Applied energy,88,4239-4251.

[4] Azam, M.M., Waris, A., Nahar, N.M (2005) Prospects and potential of fatty acid methyl esters of non traditional seed oil for use as biodiesel in India. Biomass Bioenergy ,29,293-302.

[5] Baig,A.,NG FTT (2010) A single step solid acid catalyzed process for the production of biodiesel from high free fatty acid feedstocks.Energu fuels,24,4712-4720.

[6] Berrios,M.,Martin,M.A.,Chica,A.F., Martin,A (2011) Purification of biodiesel from used cooking oils.Applied energy,88:3625-3631.

[7] Canoira, L., Alcantara, R., Garcı´a-Martı´nez, M.J., Carrasco, J (2006) Biodiesel from Jojoba oil-wax: transesterification with methanol and properties as a fuel. Biomass Bioenergy, 30, 76–81.

[8] Canoira, L., Alcantara, R., Torcal, S., Tsiouvaras, N., Lois, E., Korres, D.M (2007) Nitration of biodiesel of waste oil: nitrated biodiesel as a cetane number enhancer. Fuel ,86, 965–71.

[9] Canoira, L., Rodrı´guez-Gamero, M., Querol, E., Alcantara, R., Lapuerta, M., Oliva, F (2008) Biodiesel from low-grade animal fat: production process assessment and biodiesel properties characterization. Industrial and Engineering Chemistry Research, 47,7997–8004.

[10] Cheng, J., Li,Y., He,S.,Shen,W., Liu,Y.,Song,Y (2008) Reaction kinetics of transesterification between vegetable oil and methanol under super critical conditions.Energy Source.Part A,30,681-688.

[11] Felizardo P, Neiva M.J, Raposo I, Mendes J.F, Berkermeire R, Bordodo J.M (2006) Production of Biodiesel from Waste Frying Oil; 'Optimization of Biodiesel Production ': Fuel Process Technology, 87, 883-90.

[12] Freedman, B., Pryde, E. H., & Mounts, T. L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oilsJournal of the American Oil Chemists' Society, 61,1683–1643.

[13] Jeong, G. T., & Park, D. H. (2006). Batch (one- and two-stage) production of biodiesel fuel from rapeseed oil.Applied Biochemistry and Biotechnology, 129–132, 668–679.

[14] Jeong, G. T., Oh, Y. T., & Park, D. H. (2006). Emission profile of rapeseed methyl ester and its blend in a diesel engine Applied Biochemistry and Biotechnology, 129–132, 165–178.

[15] Jeong, G. T., Kim, D. H., & Park, D. H. (2007). Response surface methodological approach for optimization of free fatty acid removal in feedstock Applied Biochemistry and Biotechnology, 136–140,583–594.

[16] Jeong, G. T., Yang, H. S., & Park, D. H. (2009). Optimization of trans esterification of animal fat ester using response surface methodology Bio resource Technology, 100, 25–30.

[17] José, R.S. .L., Antonio, C.D.A., Eduardo, S.S., Carlos, A. B.O., L, Ivandro, F¸ S (2013) Seasonal and interannual variations of evapotranspiration, energy exchange, yield and water use efficiency of castor grown undertrained conditions in northeastern Brazil José, Industrial Crops and Products 50, 203– 211

[18] Kang, L and Rui, W., (2013) Biodiesel production by Tran esterification of duck oil with methanol in the presence of alkali catalyst, Petroleum and Coal, 55(1):68-72.

[19] Lapuerta, M., Rodrı´guez-Ferna´ndez, J., Oliva, F., Canoira, L (2009) Biodiesel from low grade animal fats: diesel engine performance and emissions. Energy Fuels, 23,121–129.

[20] Lavanya, C., Murthy,I.Y.L.N., Nagaraj,G., Mukta,N (2012) Prospects of castor (Ricinus communis L.) genotypes for biodiesel production in India, Biomass and Bioenergy 39, 204 -209

[21] Murat, K., Başak, B. U., Ersan, P., Ayşe, E. P (2013) Optimization of biodiesel production from castor oil using factorial design, Fuel Processing Technology 111,105–110.

[22] Ogunniyi, D.S (2006) Castor oil: a vital industrial raw material. Bioresource Technology, 97,1086–1091

[23] Owolabi, R.U, Adejumo A.L and Aderibigbe, A.F (2012) Biodiesel: Fuel for the Future (A Brief Review), International Journal of Energy Engineering, 2(5):223-231.

[24] Owolabi , R.U , Osiyemi , N. A, Amosa, M .K and Ojewumi , M. E (2011) Biodiesel from Household/Restaurant Waste Cooking Oil (WCO), Journal of Chemical Engineering & Process Technology 2, 1-4.

[25] Ramos, M.J., Fernandez, C.M., Casas, A., Rodriguez, L., Perez, A (2009) Influence of fatty acid composition of raw materials on biodiesel properties. Bioresource Technology 100,261-268

[26] Saloua, F., Saber, C., Hedi, Z (2010) Methyl ester of [Maclura pomifera (Rafin.) Schneider] seed oil: biodiesel production and characterization. Bio resource Technology 101,3091-3096.

[27] Sreenivas ,P., Venkata, R. M., Chandra, S.K (2011) Development of Biodiesel from Castor Oil, International journal of energy science, 1 (3): 192-197.

[28] Yordanov,D.I., Tsonev,Z.B.,Palichev,T.V.,Mustafa,Z.A (2013) A new approach for production of coffee oil from waste coffee as a feedstock for biodiesel, Petroleum and Coal, 55(2):74-81.