

Muna M. Khudhair

Ministry of Science and Technology, Directorate of Materials Research, Baghdad, Iraq. tao_t15@yahoo.com

Sajeda A. Husain

Ministry of Science and Technology, Directorate of Materials Research, Baghdad, Iraq.

Zahraa M. Jassim

Ministry of Science and Technology, Directorate of Materials Research, Baghdad, Iraq.

Shefaa M. Salih

Ministry of Science and Technology, Directorate of Materials Research, Baghdad, Iraq.

Received on: 20/09/2016

Accepted on: 20/07/2017

Transesterification of Castor Oil by Using Methanol and Ethanol (50/50) Mixture

Abstract- Biodiesel is gaining considerable attention as a renewable source of energy, as an alternative to petroleum fuel and can be used in engine without modification in this paper, the profile of preparation of fatty acid methyl ethyl ester from castor oil via a base-catalyzed transesterification was investigated. The variables chosen for the study were reaction time, oil to (methanol and ethanol) mixture ratio, and reaction temperature at constant concentration of KOH (catalyst). The effects of these variables on viscosity and specific gravity were studied.

Keywords- Alkyl Ester, Biodiesel, Castor oil, Fatty Acids, Transesterification.

How to cite this article: M.M.Khudhair, S.A. Husain, Z.M. Jassim and S.M. Salih, "Transesterification of Castor Oil by Using Methanol and Ethanol (50/50)Mixture," *Engineering and Technology Journal*, Vol. 36, Part B, No.1, pp.59-63, 2018.

1. Introduction

The consumed energy in several countries generates from crude oil, coal, and natural gas. The convention energy sources may be depletion of the energy sources with time, and thus it need to research on renewable materials to gain the required energy [1]. Biodiesel is one of the resources that has great important in the latest years [2,3]. According to the American Society for Testing and Materials (ASTM) biodiesel fuel is defined as mono alkyl esters of long chain fatty acids derived from vegetable oil or animal fat [4,5]. Biodiesel molecules are simple hydrocarbon chains free from sulfur and aromatics. The importance of biodiesel is summarized as fellow [6]:

1. Biodiesel is a renewable fuel.
2. The toxic exhaust emissions from biodiesel are lower than for petroleum fuel.
3. Biodiesel reduces greenhouse effect.
4. Biodiesel provides an additional source of income to farmers.
5. Biodiesel has good lubricity.

6. Biodiesel is biodegradable fuel [6].

Pyrolysis, dilution, microemulsification, and transesterification are essential routes to produce biodiesel from vegetable oils namely. Currently, the most practical method is transesterification by using alkaline catalyst because it required short time and low cost [7-8].

According to previous studies, castor oil is the best vegetable oil for producing biodiesel because it is soluble in alcohol and the consequent energy requirement in transforming them into fuel is lower than other vegetable oils. Castor oil has an unusual chemical composition of a triglyceride of fatty acids related to hydroxyl group presence and double bond in chain of fatty acid represented ricinoleic acid at percentage about 80-90[9]. Methanol is typically used to preparation biodiesel, which represented fatty acid methyl ester. As known, methanol is produced from petrochemical processes and the resulted biodiesel have low temperature performance and lubricity. Ethanol is also used to produce fatty acid

ethyl ester (biodiesel) which has higher viscosity than fatty acid methyl ester [10].

For above reasons, Kulkarni et al. and Joshi et al. had studied transesterification of some vegetable oil like canola oil by using 1:1 molar ratio of mixture of methanol and ethanol [9-10]. Doshpande et al. studied the transesterification of castor oil using methanol in the presence of KOH and evaluated the biodiesel quantity by viscosity and specific gravity properties [11]. Very little information is available and, no in-depth studies concerned the conditions of preparation of fatty acid methyl ethyl ester derived from castor oil. Thus, we have carried out a systematic study of methanolysis and ethanolysis together of castor oil in the presence of KOH catalyst. Thus, the aim of this research was to study the experimental parameters of ester production from castor oil employing methanol and ethanol(50/50) mixture with KOH as catalyst in terms of change in viscosity and specific gravity with the variables like reaction time, temperature, and oil to alcohols mixture ratio.

2. Experimental

I. Materials

Anhydrous methanol of 99.95% purity, anhydrous ethanol of 99.95%, and potassium hydroxide of analytical reagent grade were obtained from Sigma company. Castor oil was obtained from Mom company in India which have viscosity 193 cSt at 40°C and specific gravity 0.956 at 20°C.

II. Transesterification reaction

The reaction was carried out by differing molar ratio of (mixed methyl and ethyl) alcohol and castor oil, using potassium hydroxide 1% under constant mixing at different temperature and different reaction time. At the end of the reaction alkyl esters were obtained, allowed to stand for 1h to separate the soap. The mixture was separated by using separation funnel. After 24 hours, two phases were observed: the top layer represents alkyl esters and the glycerine layer in the bottom. The crude biodiesel was neutralized by using HCl solution, then washed with water and characterized [12,13].

III. Study the optimum conditions of transesterification reaction

To obtain real data from castor oil transesterification reaction progression, the ester was produced at different times (1,2.5,4,6)hours, different temperature (30,40,50,60) °C, and different molar ratio of oil methanol and ethanol (50/50) mixture (1:6, 1:12, 1:18, 1:24) at constant

speed mixing(700rpm) and constant catalyst concentration(1%). Mean value of triplicate experiments were taken.

IV. Determination of physical properties

1-Determination of viscosity according to ASTM D445 [14].

2-Determination of specific gravity according to ASTM D941-55 [15].

3. Results and Discussion

Figure 1, shows a schematic diagram of the preparation of methyl ethyl ester of castor oil. In the first step, it was prepared mixture of methanol and ethanol to ensure the complete mixing and give each alcohols the same opportunities to react with castor oil [16].

After transesterification reaction is completed, water is added to improve glycerol separation and then removed the excess methanol and ethanol. Acid is added to mixture to neutralize the remained catalyst and remove the soap, which may have formed through transesterification reaction. The acid reacts with soap to form salts that soluble in water, then water-washing step is intended. Calcium chloride is added to biodiesel to absorb the remained water [17]. The castor oil methyl ethyl ester that obtained during various runs was analyzed for viscosity and specific density. Hence, the quantity of biodiesel is discussed in terms of change in above properties with variables like reaction time, temperature, and oil to alcohol ratio.

I. Study the optimum conditions of the transesterification reaction

Viscosity is a measure of resistance to flow of liquid and it is one of the important fuel properties. The viscosity value affects the atomization of fuel and combustion in addition of formation of engine deposits. The viscosity of vegetable oil is higher than that of biodiesel derived from it. As known, castor oil has high viscosity in comparison with other vegetable oil. Transesterification process was used to reduce viscosity value of castor oil [12].

The density is the key properties of the fuel, which directly affect the performance of the machine. It is affecting the mass of fuel injected into the combustion chamber and thus in the proportions of air to fuel. This is because fuel injection pump meter by volume not mass, and the fuel has most density contains greeter mass than the fuel has less density to the same size. So changes in the density of the fuel will affect the energy coming out of the machine because of the various mass of fuel injected. As known, the density of biodiesel based

on ester content and remained alcohol. Thus, the choice of vegetable oil greatly affects the density of biodiesel [18].

II. Effect of reaction time

Several authors had found that the reaction time of methanolysis of castor oil was 1hour and of ethanolysis was 6 hour, hence it was selected the range of 1-6hour of reaction time for transesterification keeping other parameter constant like reaction temperature 60 °c, oil to alcohol mixture ratio 1:24, stirring speed 700rpm, and 1% catalyst percentage.

Figure 2 shows the changes of viscosity of castor oil methyl ethyl ester for different reaction time which decreases with increasing time from 1hour to 2.5 hour, and hence the optimum reaction time may be considered as 2.5hour with lowest viscosity value 10 cSt.

The variation of specific gravity with reaction time appears as similar trend as that of viscosity. The specific gravity decreases from 0.917 to 0.908 as reaction time increased from 1hour to 2.5 hours, thus optimum reaction time may be considered as 2.5hour according to the lowest value of specific gravity (Figure3.).

III. Effect of temperature

Experimental work were carried out varying the temperature of reaction in the reactor from 30-60°C keeping other parameter like reaction time 6 hour, oil to alcohol mixture ratio 1:24, stirring speed 700rpm, and 1% catalyst percentage.

It was observed that the 40°C gave the lower viscosity 10 cSt, thus the optimum temperature is considered as 40 °C (Figure 4.).

Specific gravity is decreased from 0.918 to 0.906 as changing the temperature from 30°C to 40°C, thus the optimum temperature is 40°C according to the specific gravity value as shown in Figure 5.

IV. Effect of molar ratio of oil to methanol and ethanol mixture

Figure(6)presents the effect of molar ratio of alcohol mixture to oil(6:1,12:1,18:1,24:1) on the viscosity of castor oil methyl ethyl ester at reaction time 6hour, reaction temperature 60°C, stirring speed 700rpm, and 1% catalyst percentage.

As expected an increase molar ratio promotes lower viscosity .Thus, the optimum mole ratio on was 18:1 (Figure 6).

The lower specific gravity was observed for the variety of molar ratio of alcohol mixture to oil at 18:1 which shown in figure 7. The value of specific gravity was 0.906 at 18:1 molar ratio of alcohol mixture to oil.

Although the stoichiometric calculations of molar ratio of castor oil to alcohols is 1:3, it was taken 1:6 molar ratio and higher to shift the transesterification towards the products.

4. Conclusion

In conclusions, we presents here a methodology to improve some important properties of castor oil to make it the asymptotic properties of mineral oil by transesterification with mixture of methanol and ethanol to produce biodiesel. It was observed that in the optimum conditions of transesterification, the result ester has viscosity and specific gravity values higher than the limited value in ASTM specification and EN14214 of biodiesel, it would therefore be necessary to improve these properties by mixing with other esters or mineral diesel.

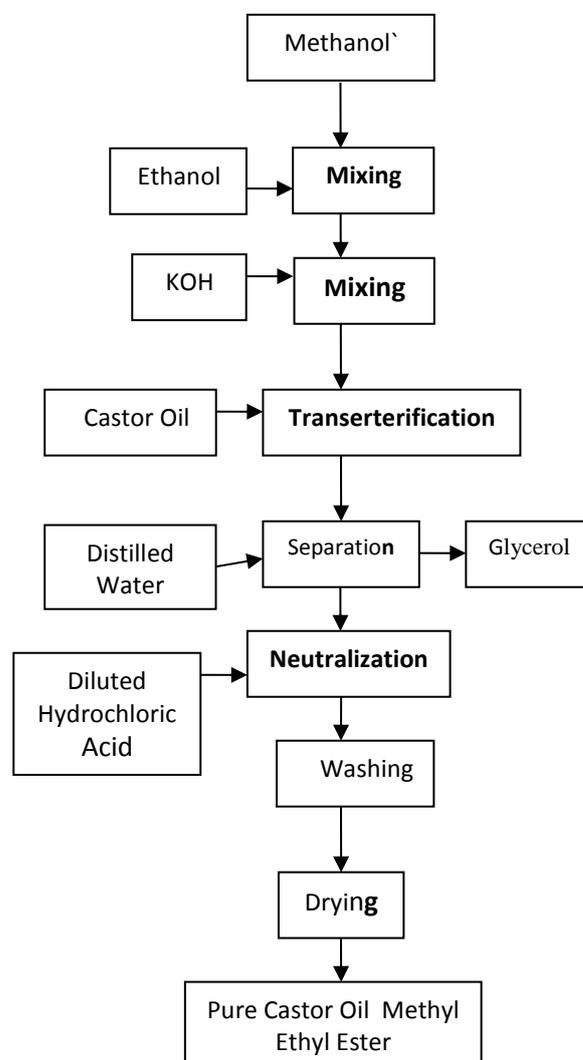


Figure 1: Schematic diagram of the preparation of biodiesel

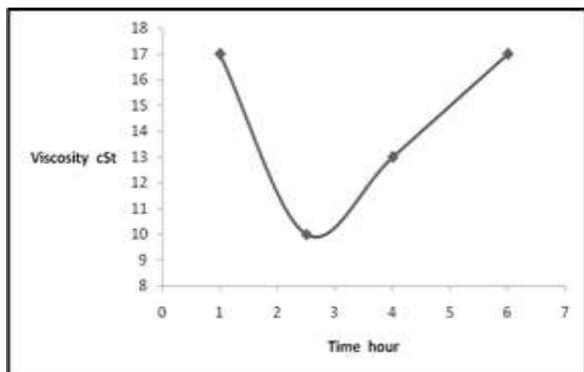


Figure 2: Variation of specific gravity with reaction time

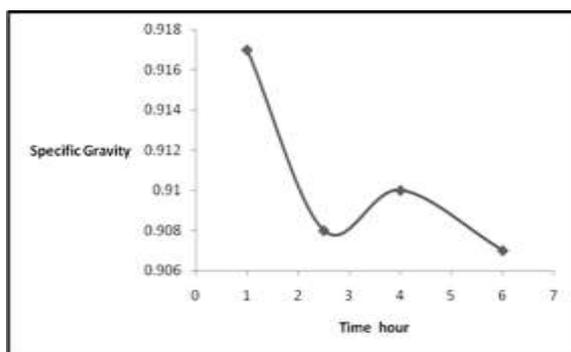


Figure 3: Variation of specific gravity with reaction time

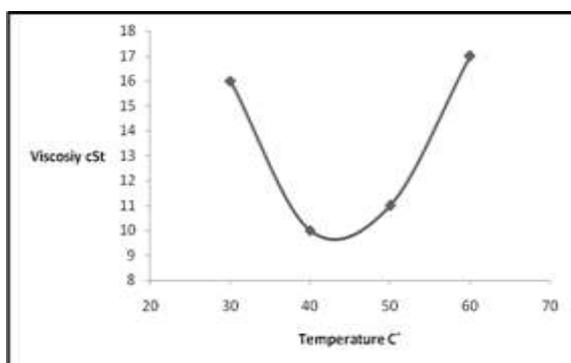


Figure 4: Variation of viscosity with temperature of reaction

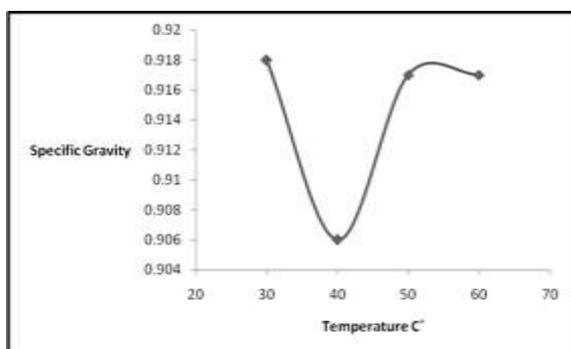


Figure 5: Variation of specific gravity with temperature of reaction

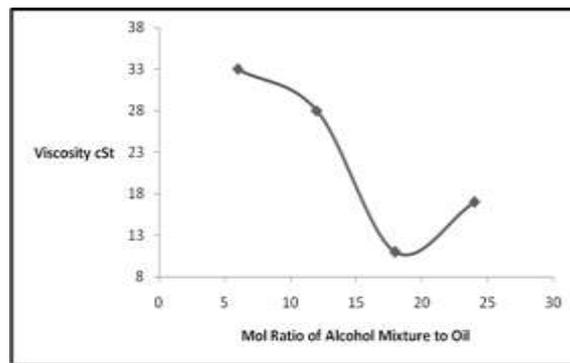


Figure 6: Variation of viscosity with molar ratio of methanol and ethanol

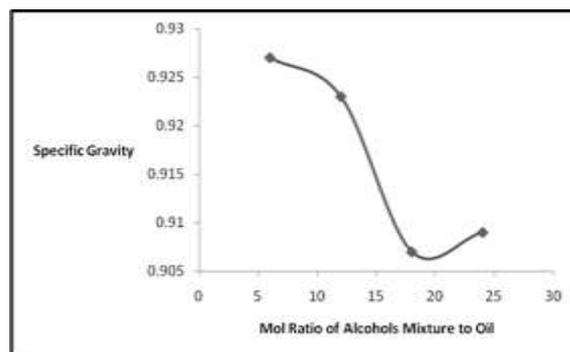


Figure 7: Variation of specific gravity with molar ratio of methanol and ethanol

References

- [1] A.S. Nataly, L.A. Marileiod, R. Rosenhaim, F.C. Silva, V.J. Fernandes, M.G. Ieda and A.G. Souza, "Thermogravimetric and Calorimetric Evaluation of Babassu Biodiesel Obtained by the Methanol Route," *Thermal Analysis and Calorimetry*, Vol. 87, No.3, pp. 649-652, 2007.
- [2] F. Ma and M.A. Hanna, "Biodiesel Production: a review," *Bioresources Technology*, Vol.70, No.1, pp.1-15, 1999.
- [3] Y.C. Sharma, B. Singh and S.N. Upadhyay, "Advancements in Development and Characterization of Biodiesel: a review," *Fuel*, Vol. 87, pp. 2355-2373, 2008.
- [4] N.D. Silva, C.B. Batistella, R.M. Filho and M.R. Maciel, "Biodiesel Production from Castor Oil: Optimization of Alkaline Ethanolysis," *Energy Fuels*, Vol. 23, No. 11, pp. 5636-5642, 2009.
- [5] Y. Zhang, M.A. Dubé, D.D. McLean and M. Kates, "Biodiesel Production from Waste Coking Oil: Process Design and Technological Assessment," *Bioresources Technology*, Vol. 89, No. 1, pp. 1-16, 2003.
- [6] J.M. Encinar, J.F. González, G. Martínez, N. Sánchez and, C.G. González, "Synthesis and Characterization of Biodiesel Obtained from Castor Oil Transesterification," *International Conference on Renewable Energies and Power Quality. Las Palmas de Gran Canaria (Spain), 13th to 15th April, 2010.*

- [7] A. Srivastava and R. Prasad, "Triglycerides-based Diesel Fuels," *Renewable and Sustainable Energy Reviews*, Vol. 4, pp. 111-133, 2000.
- [8] K. Liu, "Preparation of Fatty Acid Methyl Esters for Gas-Chromatographic," *Analysis of Lipids in Biological Materials*, Vol. 71, No. 11, pp. 1179-1187, 1994.
- [9] B. Freedman, E.H. Pryde, and T.L. Mounts, "Variable Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils," *Journal of the American Oil Chemical Society*, Vol. 61, No. 10, pp.1638-1643, 1984.
- [10] M.G. Kulkarni, A.K. Dalai and N.N. Bakhshi, "Transesterification of Canola Oil in Mixed Methanol/Ethanol System and Use of Esters as Lubricity Additive," *Bioresources Technology*, Vol. 98, No. 10, pp. 2027-2033, 2007.
- [11] H. Joshil, J. Toler, B. R. Moser and T. Walker, 2009, "Biodiesel from Canola Oil Using a1:1 Molar Mixture of Methanol and Ethanol," *European Journal of Lipid Science and Technology*, Vol. 111, pp. 464-473, 2007.
- [12] D.P. Doshpande, S.S. Haral, S.S. Gandhi and V.N. Ganvir, "Transterification of Castor oil," *Journal of Engineering Sciences*, Vol. 1 , No.1, pp. 2-7, 2012.
- [13] G. Knothe and K.R. Steidley, "Kinematic Viscosity of Biodiesel Fuel Components and Related Compounds. Influence of Compound Structure and Comparison to Petro Diesel Fuel Components," *Fuel*, Vol. 84, pp.1059-1065, 2005.
- [14] E. Alptekin and M. Canakci, "Determination of the Density and the Viscosities of Biodiesel-Diesel Fuel Blends," *Renewable Energy*, Vol. 33, pp. 2623-2630, 2008.
- [15] ATSM Standard D445: Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids and Calculation of Dynamic Viscosity. American Society for Testing and Materials, West Conshohocken, PA (USA) 2006.
- [16] ATSM Standard D4052: Standard Test Method for Density and Relative Density American Society for Testing and Materials, West Conshohocken, PA (USA) 2006.
- [17] W.D. Stidham, D.W. Seaman, M.F. Danzer, "Method for Preparing a Lower Alkyl Ester Product from Vegetable Oil," US Patent No.6, 127, 560, 2000.
- [18] T. Wimmer, "Process for the Production of Fatty Acid Esters of Lower Alcohols," US Patent No. 5, 399, 731, 1995.
- [19] Z.J. Predojevic, "The Production of Biodiesel from Waste Frying Oils: a Comparison of Different Purification Steps," *Fuel*, Vol. 87, pp. 3522-3528, 2008.