

Exploring the Transesterification of Castor Oil to Produce Second Generation Biodiesel using a Novel Catalyst

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Abstract– In this study, the crude oil of Malaysian castor bean *Ricinus communis L.* which is non-edible oil was extracted by microwave-assisted extraction (MAE) using ethanol and follow by transesterification reaction by using heterogeneous activated cement clinker catalyst (ACCC). MAE procedure takes 15-30 min and uses small solvent volumes (50% of weight oil). The biodiesel yield when using 1% was 88.61 % which is highest compare with catalyst loading 0.5%,0.75%,1.25% and 1.5 wt/wt%. Reaction time affected positively the catalytic activity since the conversion percentage increased steadily with the reaction time with 2 hours is the best reaction time give yield percentage is 93.91%. Experiment works were carried out varying oil to methanol ratio 1:3, 1:6 and 1:9 keeping other parameter constant, reaction temperature, 60 °C and reaction time in 2 hour. It show that, best oil to methanol ratio was 1:6 with give biodiesel yield 96.90% .

Keywords: *Castor Oil, Non-Edible Oil, Biodiesel, Microwave-Assisted Extraction, Heterogeneous Catalysts, Transesterification*

I. INTRODUCTION

Energy consumption is inevitable for human existence. There are various reasons for the search of an alternative fuel that is technically feasible, environmentally acceptable, economically competitive, and readily available. There are three reasons important of alternative fuel [1]. The first foremost reason is the increasing demand for fossil fuels in all sectors of human life, transportation, power generation, industrial processes, and residential consumption [2]. This effect increasing demand gives rise to environmental concerns such as larger CO² and greenhouse gas emissions, and also global warming. World energy consumption doubled between 1971 and 2001 and the world energy demand will increase 53% by the year 2030. For example, petroleum consumption will rise from 84.4 to 116 million barrels per day in USA until year 2030 [4,5]. Second reason is fossil-fuel resources are non-renewable, and they will be exhausted in the near future [5]. Some reports claimed that oil and gas reserves will be depleted in 41 and 63 years, respectively, if the

consumption remains constant [6]. The price instability of fuels like crude oil also one of reason in rapid searching for alternative fuel [7]. There are several alternatives such as wind, solar, hydro, nuclear, biofuel, and biodiesel which is have higher potential in producing energy in future.

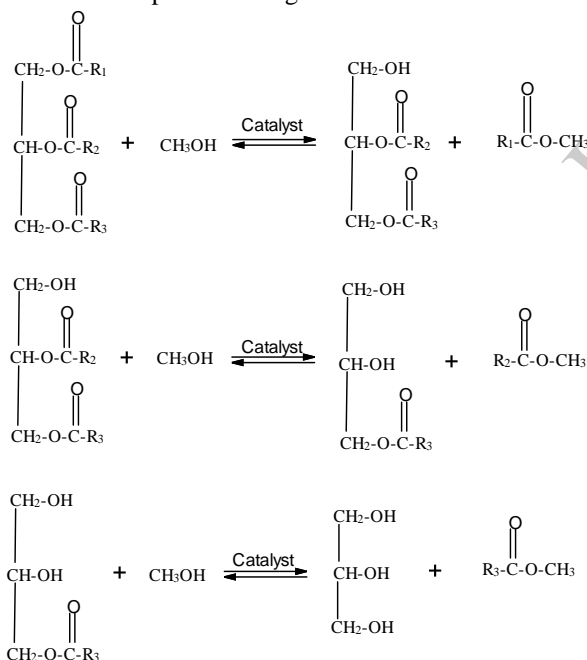
Biodiesel is a mixture of various fatty acid methyl ester oils produced from vegetable oil or animal fat for use as fuel in diesel engine and in compliance with American Society for Testing and Materials (ASTM) standards. Biodiesel was first introduced by Rudolph Diesel in 1911 [8]. Biodiesel is considered as the best alternative to substitute petrodiesel after the world oil crisis in 1970's. Biodiesel can be used alone or mixed with petroleum-based diesel as an alternative efficient fuel and can be used in any diesel engine without modification [9]. The most common biodiesel blends are B2 (2% biodiesel and 98% petroleum diesel), B5 (5% biodiesel and 95% petroleum diesel), and B20 (20% biodiesel and 80% petroleum diesel [10]. Besides that, the researcher also argued to find the alternative for petroleum based fuel biodiesel also have several advantages such its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number and higher biodegradability which contributed to greener fuel. The higher the blending ratio of biodiesel means the fewer the carbon emission to the environment [11].

Currently, more than 95% of the world biodiesel is produced from edible oil which is easily available in large scale such as palm oil [12]. However, continuous and large scale production of biodiesel from edible oil without proper planning may cause negative impact to the world such as depletion of food supply leading to economic imbalance. There are different potential feedstocks for biodiesel production. Non-edible vegetable oils which are known as the second generation feedstocks can be considered as promising substitutions for traditional edible food crops for the production of biodiesel [13]. The use of non-edible plant oils is very significant because of the tremendous demand for edible oils as food source. Moreover, edible oils' feedstock costs are far expensive to be used as fuel [14]. Therefore, production of biodiesel from non-edible

oils is an effective way to overcome all the problems with edible oils. Castor (*Ricinus communis*) oil is one of non edible oil which high potential in biodiesel production with a hydroxy fatty acid, ricinoleic acid (12-hydroxy-9(Z)-octadecenoic acid), as a major constituent (85-90%) of its fatty acid profile.

Castor oil as source of biodiesel has recently been promoted especially in Brazil as a means for economic development in the northeastern part of the country besides the aspect of using a renewable domestic feedstock [15]. Availability of castor oil was wide which India is the largest exporter follow by China and Brazil [16]. The total world production of seeds is estimated at around 1 million tons and the oil extracted is about 500,000 tons, with a productivity of 470 kg of oil per hectare [17].

Generally, there are three ways to convert vegetable oils and fats into biodiesel which is base catalyzed transesterification, direct acid catalyzed transesterification or conversion of the oil to its fatty acid then to biodiesel [18]. Base catalyzed transesterification way normally use due to low temperature and pressure in the process. The method also has high conversion ratio of almost 98% with minimal side effects and reaction time. This method is advantageous as no intermediate compound is required and the oil can directly be converted to biodiesel [19]. The chemical reaction for base catalyzed castor oil biodiesel production are present in Fig.1 below:



*R₁, R₂, and R₃: Carbon chain of fatty acid

Fig 1: Stage of transesterification reaction [20]

II. MATERIALS AND METHOD

Castor seeds was obtained from Casa Kinabalu Sdn Bhd, is the company that is responsible in the production and the planting the castor plant in Malaysia. Methyl ricinoleate, methyl oleate and methyl palmitate standards for Gas Chromatography (GC) and methanol were purchase from Sigma-Aldrich

III. EXPERIMENTAL PROCEDURE

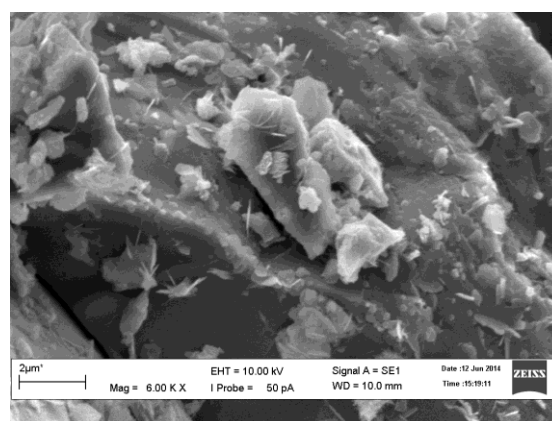
A. Cement Clinker Catalyst Activation and Characterization

Clinker was crushed to reduce the particle size around 200 μm to ensure a large surface area. The clinkers then soaked with potassium hydroxide and stirred for 24 hours. Filter and drying process at 105 $^\circ\text{C}$ for 1 hour and finally followed with calcination at 500 $^\circ\text{C}$ for 5 hours in the furnace (Carbolite, CWF1215). The activated cement clinker chemical compositions was analyzed using X-ray fluorescence (XRF model S8 Tiger, Brand: Bruker) from Germany before used in biodiesel production. The results of X-ray fluorescence analysis are as follows

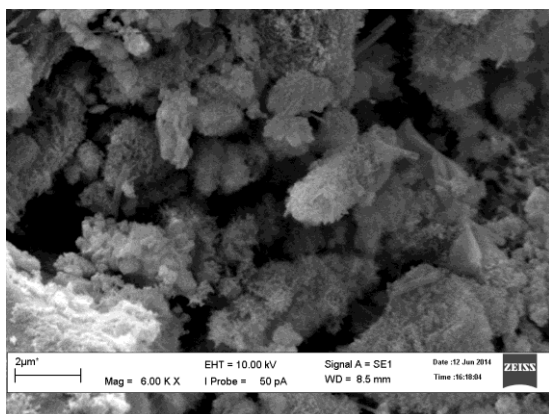
Table 1: X-Ray fluorescence of Activated Cement Clinker

Parameter	Results, %
CaO	67.78
SiO ₂	20.05
Al ₂ O ₃	4.57
Fe ₂ O ₃	3.80
MgO	1.08
SO ₃	0.97
K ₂ O	0.63
TiO ₂	0.28

The XRF analysis reveals that cement clinker has a high amount of Calcium Oxide (CaO) which is about 67.78%. This value is similar to the earlier study reported by WHM Microanalysis Consultants [21]. A higher percentage of CaO attributes to its property as a good solid base catalyst for castor oil transesterification. Scanning electron microscopy was performed for both the clinker and the catalyst to examine their surface morphology and surface area. Fig. 2 shows the SEM picture of clinker before and after activation which indicates a significant increase of porous



a) Fresh Cement Clinker Catalyst (before activation)



b) Activated Cement Clinker Catalyst (after activation)

Fig 2: SEM image of Cement clinker before and after activation at 6000X

B. Microwave Assisted Extraction (MAE)

200 g crushed seed was put into a round glass with 400 ml of ethanol for 30 minutes with 5 minutes each run until 30 minutes at power of 400 W and temperature 70 °C using microwave connected with condenser.

C. Transesterification procedure

200ml of extracted oil was measured and poured into 1L reactor, heated to the 60 °C using a water bath. The activated cement clinker catalyst (ACCC) was prepared in 250ml beaker with methanol, which is depending on molar ratio used. The mixture of catalyst and methanol was then poured into the warm oil and stirred vigorously for varies of reaction time using mechanical stirrer. The mixture was left to settle for 24 hours in a separating funnel. After settling, the upper layer which was biodiesel was decanted into a separate beaker while the lower layer which comprises of glycerol and soap was collected from the bottom of the funnel.

IV. RESULT AND DISCUSSION

A. Effect of Methanol to Oil Ratio

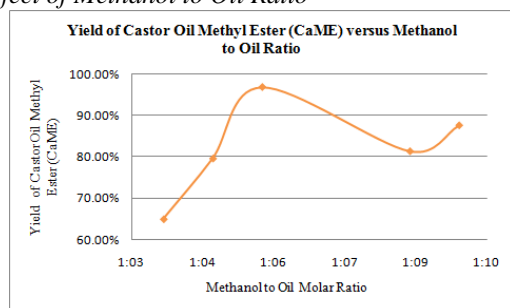


Fig 3: Yield of castor Methyl Ester (CaME) versus Methanol to Oil Ratio

Methanol to oil molar ratio played an important role in biodiesel synthesis. Thus, a different methanol to oil molar ratio was employed transesterification reaction to study their effect to methyl ester yield. 1 wt. % of activated cement clinker catalyst (ACCC) was added to castor oil and methanol under constant reaction temperature at 60 °C and stirred at 600 rpm. Theoretically 1 mole triglyceride required 3 mole of alcohol to produce 3 mole of methyl

ester and 1 mole of glycerol as the side product. However, this stoichiometry is not always possible since the reaction produced different result from different source and conditions. Figure 3 show that the methyl ester production increased with the methanol to oil molar ratio increase until 6:1 molar ratio. Further increased of the molar ratio decreased the methyl ester production because the excess methanol increase the solubility of the by-product and initiate the reversible reaction which reduced the reaction rate. The optimum methanol to oil molar ratio in this study is 6:1.

B. Effect of Catalyst Loading

The effect of activated cement clinker catalyst (ACCC) concentration on the transesterification of castor oil was investigated with its concentration varying from 0.5 wt% to 1.25 wt% (based on the weight of mixture of castor oil and methanol). From Figure 4 below, that an increase in the catalyst concentration from 0.5 wt% to 1.0 wt% results in an increase in the yield from 73.34% to 88.61%. Initially, insufficient amount of catalyst result in incomplete conversion of triglycerides into the esters as indicated lower yield of ester. 1 wt% of catalyst loading show the high ester content which is 88.61%

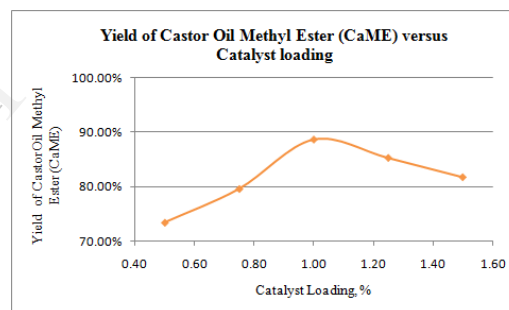


Figure 4: Yield of Castor Methyl Ester (CaME) versus Catalyst Loading

C. Effect of Reaction Time

Reaction time of transesterification reaction also gives influence to castor oil methyl ester yield. Experiments work were carried out varying the residence time in the batch reactor from 30 minutes to 150 minutes keeping other parameter, reaction temperature 60 °C, methanol to oil ratio 1:6 and catalyst loading 1.00% of mixture of oil and methanol.

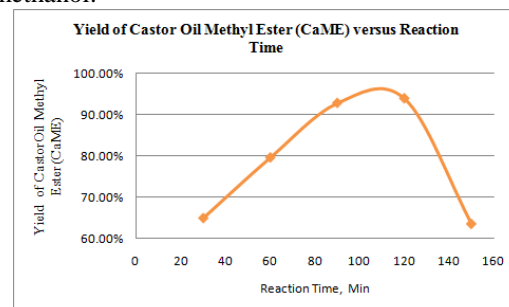


Fig 5: Yield of Castor Methyl Ester (CaME) versus Reaction Time

As shown in Figure 5, the methyl ester production increase as the reaction time increase until 120 minutes, and then drop decrease when 150 minutes reaction time was apply. The highest methyl ester content was 93.91%.

D. Effect of Reaction Temperature

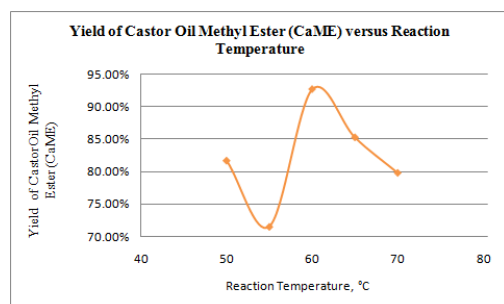


Fig 6: Yield of Castor Methyl Ester (CaME) versus Reaction Temperature

The best yield obtained for the methyl ester of *Ricinus communis* at the temperature of 60 °C with the percentage methyl ester yield being 92.63%. This is because at 60 °C, the molecules of the triglycerides of castor oil had high kinetic energy and this thus increased the collision rate and therefore, improved the overall process by favouring the formation of methyl esters while at the lower temperatures of 50°C and 55°C with corresponding percentage methyl ester yield 81.65% and 71.50% respectively, there was lesser collision of reacting molecules and thus, reduced biodiesel yield. The reason for this behaviour is due to the endothermic nature of the reaction. The higher reaction temperature would favour endothermic reaction, thus increasing the rate of reaction as well as the ester concentration [18]. Although at 65 °C, it was notice that there was a drop in percentage methyl ester yield. This is because at the 65 °C, there was increased vaporization of the methanol used in the transesterification process due to the proximity of the reaction temperature (65°C) to the boiling point of methanol (64.7°C).

E. Analysis of Extracted Castor Oil and Castor Methyl Ester (CaME)

Oil and FAME composition of seed oil was determined using gas chromatography mass spectroscopy (GC-MS) according to ASTM D6584. Samples from the extraction and biodiesel production process were taken and dissolved in HPLC grade hexane before being injected into the GC-MS. Triacylglycerides (TAG) analysis was performed on Agilent 7890A GC System equipped with Agilent 7683B Series Injector, 5975C Inert MSD and a DB-5MS column (30 m × 0.25 mm × 340°C, while the FAME produced were analyzed on HP-INNOWAX column (30 m x 0.25 mm x 0.25 µm) with a temperature range of 60°C to 325°C. Identification of the peaks was performed by comparing retention times with those of library standards analyzed under the same conditions. FAME and fatty acid composition was determined as in Table 2 and Table 3. The most abundant fatty acids in castor oil were ricinoleic acid,

linoleic, oleic, palmitic and linolenic acids while the FAME is mainly of methyl ricinoleate as shown in Fig.7 below.

Table 2: Fatty acid composition of Castor Oil

Fatty acid composition (%)	This work	Salimon.J et al. (2010)
Ricinoleic acid	85.8	84.2
Linoleic acid	3.9	7.3
Oleic acid	3	5.5
Palmitic acid	1	1.3
Linolenic acid	0.6	0.5
Other	5.7	1.2

Table 3: FAME composition

FAME content (%)	This work	Conaira et al. [22]
Methyl Ricinoleate	84.2	87.10
Methyl Linoleate	3.0	5.27
Methyl Oleate	3.0	3.81
Methyl Palmitate	0.6	1.25
Methyl Linolenate	0.4	0.81
Other	8.8	1.76

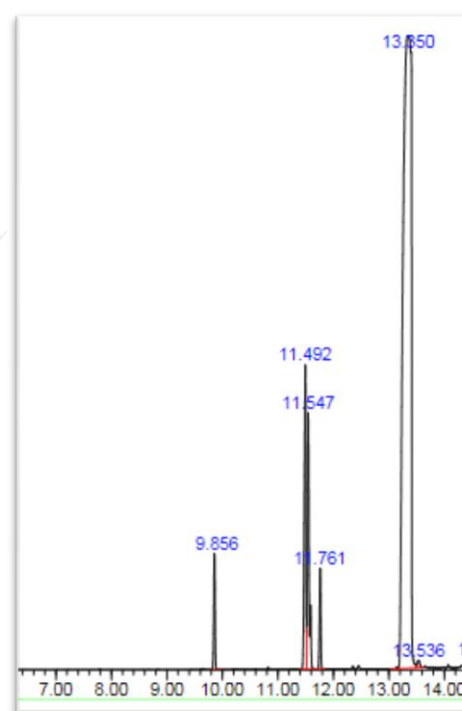


Fig 7: GC Chromatogram of Castor Methyl Ester (CaME)

5. CONCLUSION

Castor methyl ester (CaME) produced by using activated cement clinker catalyst (ACCC) give 96.90% yield of biodiesel with optimum system which is reaction temperature was 60 °C, catalyst loading 1.00% of mixture oil and methanol, reaction time 120 minutes (2 hours) and methanol to oil ratio was 1:6. The biodiesel produced in this work compared with specification described in ASTM D6751.

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REFERENCES

- [1] Talebian-Kiakalaieh, A., Amin, N. A. S., & Mazaheri, H. (2013). A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104, 683–710. doi:10.1016/j.apenergy.2012.11.061
- [2] Kafuku G, Mbarawa M. Alkaline catalyzed biodiesel production from Moringa oleifera oil with optimized production parameters. *Appl Energy* 2010;87(8):2561–5.
- [3] Bioengineering Resource Inc. <www.brienergy.com> [accessed 12.08.10].
- [4] Energy Department. <www.energy.gov> [accessed 12.08.10].
- [5] Maceiras R, Rodriguez M, Cancela A, Urrejola S, Sanchez A. Macroalgae: raw material for biodiesel production. *Appl Energy* 2011;88(10):3318–23.
- [6] Reports and Publications. Statistical review of world energy; June 2007.
- [7] Santori G, Nicola GD, Moglie M, Polonara F. A review analyzing the industrial biodiesel production practice starting from vegetable oil refining. *Appl Energy* 2012;92:109–32.
- [8] Akoh CC, Chang SW, Lee GC, Shaw JF. Enzymatic approach to biodiesel production. *J Agric Food Chem* 2007;55:8995–9005.
- [9] Demirbas MF, Balat M, Balat H. Potential contribution of biomass to the sustainable energy development. *Energy Convers Manage* 2009;50: 1746–60.
- [10] Balat, M., & Balat, H. (2010). Progress in biodiesel processing. *Applied Energy*, 87(6), 1815–1835 doi:10.1016/j.apenergy.2010.01.012
- [11] Fukuda H, Kondo A, Noda H. Biodiesel fuel production by transesterification of oils. *J Biosci Bioeng* 2001;92:405–16.
- [12] Deligiannis, A., Anastopoulous, G., Karavalakis, G., Mattheou, L., Karonis, D., Zannikos, F., Stournas, S. and Lois, S.; Castor (*Ricinus Communis* L) Seeds Oil as an Alternative Feedstocks For The Production of Biodiesel, Proceeding of the 11th International Conference on Environmental Science and Technology 2009
- [13] Atabani, a. E., Silitonga, a. S., Ong, H. C., Mahlia, T. M. I., Masjuki, H. H., Badruddin, I. A., & Fayaz, H. (2013). Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renewable and Sustainable Energy Reviews*, 18, 211–245. doi:10.1016/j.rser.2012.10.013
- [14] Ong, H. C., Silitonga, a. S., Masjuki, H. H., Mahlia, T. M. I., Chong, W. T., & Boosroh, M. H. (2013). Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha curcas*, *Sterculia foetida* and *Ceiba pentandra*. *Energy Conversion and Management*, 73, 245–255. doi:10.1016/j.enconman.2013.04.011
- [15] Scholz V, da Silva JN. Prospects and risks of the use of castor oil as a fuel. *Biomass Bioenergy* 2008;32(2):95–100
- [16] Ogunniyi DS. Castor oil: a vital industrial raw material. *Bioresource Technology* 2006;97:1086–91.
- [17] Santana G.C.S., Martins P.F., Da Silva D.L.N., Batistella C.B., Filho M.R., Maciel W.M.R. Simulation and cost estimate for biodiesel production using castor oil. *Chemical Engineering Research and Design* 2009.
- [18] Abdulkareem, A.S.; Jimoh, A.; Afolabi, A.S.; Odigire, J.O. & Patience, D. Production and characterization of biofuel from non-edible oils: An Alternative Energy Sources to Petrol Diesel
- [19] Mekhilef, S., Siga, S., Saidur, R.: A review on palm oil biodiesel as a source of renewable fuel, *Renewable and Sustainable Energy reviews* 15, 2011; 1037-1949
- [20] Hafizuddin .W.Y.(2012), Evaluation of Heterogeneous Quaternary Ammonium Catalysts for Transesterification of Triglycerides
- [21] WHM Microanalysis Consultants, 2011. Cement History. <http://www.understandingcement.com/clinker.html> [Accessed 10 October 2011].
- [22] Canoira, L., García Galeán, J., Alcántara, R., Lapuerta, M., & García-Contreras, R. (2010). Fatty acid methyl esters (FAMES) from castor oil: Production process assessment and synergistic effects in its properties. *Renewable Energy*, 35(1), 208–217. doi:10.1016/j.renene.2009.05.006