Optimization of Transesterification Parameters in Ricinus Communis L. (Castor) Seed Oil for Biodiesel Production: Reaction Temperature based at 70°C

Charmaine SJ. Lamiel [1] , Ma. Cristina Carmela C. Manocan [1] , Gino Paul M. Marasigan [1] ,
and Maria Natalia R. Dimaano [1,2,*]

[1] Department of Chemical Engineering
[2] Research Center for the Natural and Applied Sciences

University of Santo Tomas
España, Manila 1008, Philippines

Abstract—The feasibility of castor seed as feedstock for optimum biodiesel production was studied. Castor oil has been a source of methyl esters with almost 90% of its fatty acid composition as ricinoleic acid. The castor oil was extracted via methanol as solvent. It was subjected to a two-step transesterification process: esterification with H_2SO_4 followed by NaOH-catalyzed methanolysis. The reaction times of 1.0, 1.5, and 2.0 hours were each subjected to the methoxide (NaOH-CH_3OH) concentrations of 0.6, 0.7 and 0.8M. The transesterification process proceeded with the reaction temperature controlled at 70°C. The optimum parameters at 70°C were identified at 0.7 M NaOH-CH_3 and 1.0 hour based on the maximum obtained yield of 63.29% Castor Methyl Ester (CasME). The CasME was subjected to Gas Chromatography / Mass Spectrometry (GC/MS) analysis for its fatty acid composition. The fuel characterization analysis conducted indicated acceptable results with respect to kinematic viscosity of 3.60 and 3.82 for B5 and B10 blends, respectively. Other properties of B10 were also determined from its acceptable value of kinematic viscosity and provided customary results based on the set values of Philippine National Standards (PNS).

Keywords— Ricinus communis L., castor seed oil, biodiesel, transesterification

I. INTRODUCTION

The biofuel industry has penetrated the market and is now gradually expanding to reduce the world's dependency on petroleum - based diesel fuels. Blended fuels are initially being implemented in countries to contribute to the attenuation of the world's problems that are climate change and extinction of fossil fuels.

Biodiesel is environmentally safe, nontoxic, and biodegradable [1]. It is a great source of renewable energy today aside from solar, wind, nuclear, geothermal, hydroelectric power and ocean thermal energy. It could be a clean substitute for fossil fuel, since the use of biodiesel would mean less emissions of CO, NOx, SOx and soots. Biodiesel is a mixture of methyl esters consisting of long-chain fatty acids like lauric, palmitic, stearic, oleic, etc. [2]. The production of biodiesel is commonly derived from renewable resources like agricultural crops and vegetable oils.

Ricinus communis L., commonly known as the castor plant is being considered nowadays for biodiesel production as a potential biofuel alternative [3]. Castor has viscous, pale yellow, non-volatile and non-drying oil, which can be extracted from its seed [4]. It is non-edible and hence, does not raise any conflict against the food industry. Castor oil is a potential biodiesel source since it is easy to grow and cultivate particularly in the Philippines. In the production of biodiesel, a two-step process is done due to castor's high free fatty acids content [5-7]. An acid-catalyzed esterification is initially done to reduce the acid value of the oil by 2% [8]. Alkaline-catalyzed transesterification follows with sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide as catalysts [9].

Ricinus communis L. usually grows in tropical areas such as Philippines and Brazil [10]. Roots, leaves, seeds are used externally in medicinal applications. They are collected all year round except for the seeds which are collected from May to August in the Philippines [11]. Castor has a unique composition with approximately 89.5% ricinoleic acid. Ricinoleic acid is also called castor oil acid which is soluble in most organic solvents. It is distinguished for its high hydroxylated fatty acid content. Castor has attributes such as high molecular weight (298), low melting point (5°C), and very low solidification point (-12 to 18°C) which makes it useful. And although it has high viscosity, its transesterified oil has suitability to be blended with petroleum – based diesel fuel. [12].

This study aimed at determining the optimum parametric conditions varied at different methoxide concentrations and times of reaction, holding the transesterification temperature constant at 70°C. Simultaneously with this study, another group, which is part of this research, worked on the same parametric designs but at different reaction temperatures of 60°C and 80°C [13]. The solution of the optimum parameters will be based on the obtained highest % yield of the Castor Methyl Ester (CasME). Blending of CasME with FAME – based diesel oil at B5 and B10 proportions were completed to address the high kinematic viscosity of pure CasME. Further analysis of different biodiesel properties were completed using B10 blended proportion of CasME.

II. EXPERIMENTAL

A. Materials

Extracted castor oil was obtained from solvent extraction using Methyl Alcohol (Anhydrous, Mallinckrodt Chemical, USA) mixed with crushed castor seeds. Acid–catalyzed esterification was done with 6:1 ratio of methanol-sulfuric acid solution (Sulfuric Acid 98% RCl Labscan, AR Thailand). Finally, base-catalyzed transesterification was done using methanol−sodium hydroxide (solid, Merck kGaA, Germany) solution mixed with esterified oil. A schematic diagram of the whole process from oil extraction to transesterification and final conversion to its biodiesel form is shown in Figure 1.
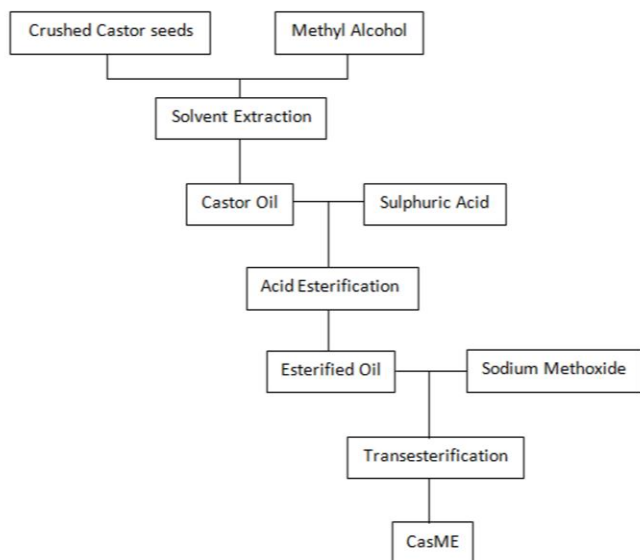

Figure 1 Schematic diagram of CasME production.

B. Transesterification

With the transesterification temperature controlled at 70°C, each run was carried out with the methoxide concentrations varied at 0.6M, 0.7M and 0.8M, while the reaction times were designated each time at 1.0, 1.5, and 2.0 hours. Each CasME produced was subjected to further boiling at 110˚C to ultimately remove its water content. Optimized sample was submitted to De La Salle University for GC / MS analysis using Clarus 500 PE Autosystem with built in autosampler. Blending of the CasME with FAME-blended diesel oil (Shell, Philippines) at B5 and B10 proportions was done. B10 blend with volume of 1.5 liters was subjected to fuel characterization and analysis at the Department of Energy (DOE), Philippines.

III. RESULTS AND DISCUSSIONS

A. Oil Analysis for Ricinus communis L.

A sack of castor seeds, which were already dehusked from its outermost shell, were given in kind by the Philippine Forest Corporation. The second layer of the shells before its kernels was removed using the fabricated mechanical decorticator situated in the Research Center for the Natural and Applied Sciences (RCNAS).

One hundred (100) to two hundred (200) grams of ground castor kernels were immersed in the solvent Analytical Reagent Methyl Alcohol (Anhydrous, Mallinckrodt Chemical, USA). The immersion followed a 1:1.5 volumetric ratio placed in clean reagent bottle. The mixture was stirred using Corning PC – 420D Stirrer / Hotplate and a magnetic stirrer for about 2.0 hours using 1100 rpm. Vacuum filtration was applied after two days of further immersion to separate the oil-solvent mixture from the castor seeds meal.

Oil was extracted by rotary evaporation. The percentage of oil obtained is shown in Table 1.

Table 1 Percentage yield of oil.

Trial	Weight of crushed seeds (g)	Weight of extracted oil (g)	Percent yield of oil
1	186.26	86.76	46.58%
2	220.15	111.95	50.85%
3	250.00	120.44	48.18%
4	250.16	122.07	48.80%
5	300.00	152.25	50.75%

Castor oil yielded as much as 51% after stirring it for 2 hours at 1100 rpm and settling for 2 days before rotary evaporation.   The result had showed about 14% greater than that reported results from the study done by Cotiangson et al [15].

B. Optimization of Methoxide Solution and Time

Methanol-NaOH solution was used varying its concentration at 0.6 M, 0.7 M and 0.8 M. The effects of methoxide solution were studied with varying time at 1.0 hour, 1.5 hours, and 2.0 hours each time. Conditions were fixed at 70° C and 300 rpm. Results are shown in Table 2.

Table 2 Optimization of methoxide solution and transesterification time.

0.6 M	1.0 hour			1.5 hours			2.0 hours		
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Weight (g)	8.16	8.36	8.16	8.24	8.56	8.44	9.85	8.43	7.60
Percent Error (%)	0.79	1.60	0.82	2.04	1.77	0.28	14.20	2.32	11.87
Percent Conversion (%)	57.39	58.77	57.37	57.96	60.21	59.33	69.28	59.26	53.46
Average Percentage (%)	57.84			59.17			60.67		
0.7 M	1.0 hour			1.5 hour			2.0 hours		
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Weight (g)	8.99	8.97	9.04	8.11	8.13	8.08	8.21	9.15	7.79
Percent Error (%)	0.15	0.30	0.45	0.05	0.31	0.36	2.10	9.15	7.05
Percent Conversion (%)	63.20	63.11	63.58	57.05	57.20	56.82	57.72	64.35	54.80
Average Percentage (%)	63.29			57.02			58.95		
0.8 M	1.0 hour			1.5 hour			2.0 hours		
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Weight (g)	8.08	8.17	8.10	8.54	8.55	8.43	6.22	8.07	6.43
Percent Error (%)	0.47	0.69	0.22	0.38	0.52	0.90	9.93	16.84	6.92
Percent Conversion (%)	56.82	57.49	56.97	60.07	60.15	59.30	43.73	56.73	45.20
Average Percentage (%)	57.09			59.84			48.55		

In this study, the highest average yield of 63.29% was reported to have been obtained at conditions of 0.7 M sodium methoxide and 1.0 hour of transesterification time.

The transesterification time of 2.0 hours showed no layer formation between CasME and glycerol. The non-formation of two layers for CasME and glycerol would mean that complete conversion of CasME had already occurred at the esterification parameters of 6:1 ratio of methanol-sulfuric acid solution. However, the transesterification done at 1.0 and 1.5 hours produced a layer of CasME and glycerol. This only meant that esterification was not a sufficient method for converting CasME employing the set of parameters. The formation of glycerol in the transesterification process only meant that the free fatty acids from the esterification were not fully converted to CasME. Transesterification was used as second step in order to completely convert the remaining free fatty acids.

The study done by the other group employing the reaction temperature of 60˚C reported an optimum value of 64.75 % at 1.0 hour in 0.6 M methoxide solution [13]. The yield was found to be higher with 60˚C compared to the results conducted at 70˚C. In another study, it was indicated that the intimate mixing of oil, alcohol and catalyst were needed to speed up the reaction at a temperature below the alcohol's boiling temperature [14]. The reaction temperature at 70˚C was higher than the boiling point of methanol which led to the degradation of the effect of methoxide in the transesterification reaction. This observation was consequently demonstrated on the varying yields (from 2 to 16 % error) of CasME that were subjected to 2.0 hours at 70˚C.

The average results of the trials based on the designated parameters of temperature, reaction time and methoxide concentrations are shown in Figure 2a. The methoxide concentration of 0.8M that was transesterified for 1.5 hours provided a maximum yield of 59.84%. The same concentration showed a drastic decrease to 48.55% yield with the transesterification time of 2.0 hours. The behavior of 0.7 M was reported to be the highest at 1.0 hour, decreased at 1.5 hours, and slightly recovered at 2.0 hours. The concentration of 0.7 M at 1.0 hour yielded the optimum value of 63.29% with respect to 0.6M, increasing the transesterification

temperature corresponded to an increasing yield without an assurance of an optimum peak.

Furthermore, longer heating required more energy consumption equating to a higher cost of CasME production. Considering the energy consumed and the time of reaction, 0.7 M provided the highest yield of CasME at 63.29%. Thus, the optimum concentration was chosen at 0.7M shown in Figure 2b.
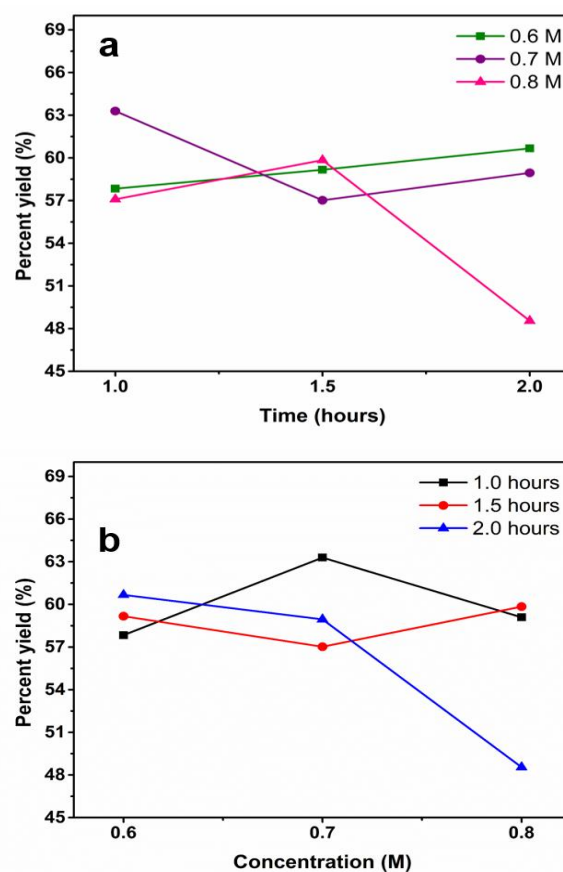

Figure 2 Percent yield for (a) for varying time and (b) for varying concentration at 70˚C.

C. Gas Chromatography and Mass Spectrometric Analysis

The optimum CasME sample produced was subjected to GC / MS analysis. The result of the chromatogram is shown in Figure 3.
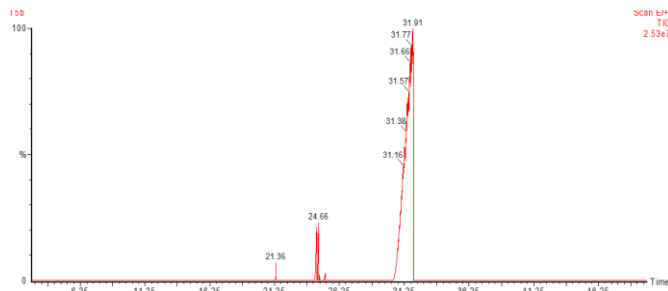

Figure 3 GC result of CasME at 46.25 minutes

In the GC analysis, many peaks were obtained from the sample. The highest was obtained at a retention time of 31.25 minutes. Analysis showed its compatibility with methyl ricinoleate. In comparison from the study done by Cotiangson et al, the same peak for methyl ricinoleate was also depicted as shown in Figure 4.
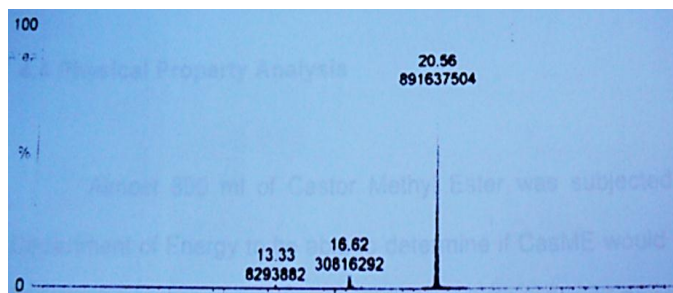

Figure 4 Chromatogram depicted in the study of Cotiangson et al.

As for the graphs before this retention time, the peaks indicated in Figure 5 manifested the formation of other esters. At around 24.73 minutes, 7-Hexadecenoic acid methyl ester was determined. However, the other esters were not identified by the service provider.
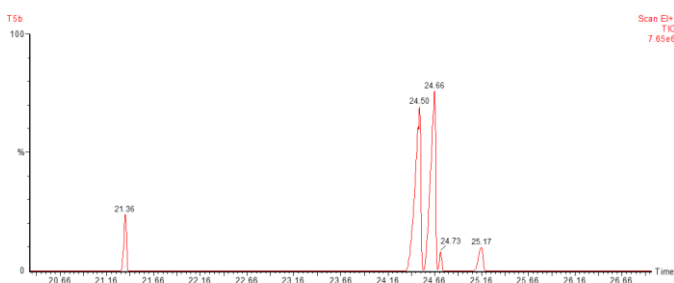

Figure 5 GC result of CasME at 26.66 minutes.

In the chromatogram shown in Figure 6, the results obtained from Cotiangson et al showed the same peaks of formation of esters. However in their study, 7-Hexadecenoic acid methyl ester was not determined. The formation of esters was obtained from a study and a sequential list of esters is shown in Table 3 [15].
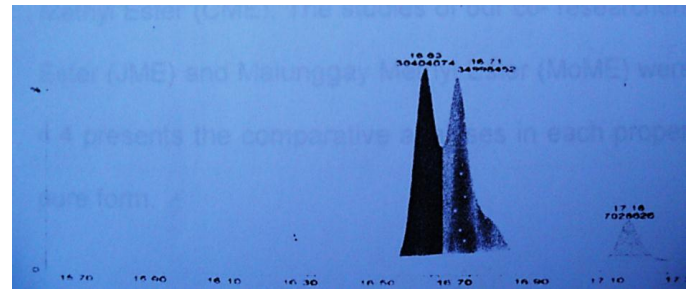

Figure 6 Other esters formed from castor oil [15].

Table 3 Sequential list of ester according to retention time [15]

List of esters
Palmitic acid methyl ester
Linolelaidic acid methyl ester
Elaidic acid methyl ester
(7-Hexadecenoic acid methyl ester) - *Not Applicable*
Stearic acid methyl ester
Ricinoleic acid methyl ester

The two peaks determined by the service provider were studied to achieve the yield of conversion of esters. The GC/MS analysis showed that CasME was composed mostly of ricinoleic acid methyl ester as shown in Table 4. This just proved that the conversion of the ricinoleic acid to its methyl ester was the most abundant in CasME production.

Table 4 Quantitative analyses of the gas chromatography of CasME.

Methyl Ester	Area (mV-s)	Area (%)	Retention Time (min)
Ricinoleic acid methyl ester	15,617,225	97.9925	31.90
7- Methyl (7E)-7-hexadecenoate	319938	2.0075	24.66

D. Physical Property Analysis

The CasME produced was blended into FAME – blended diesel oil with volume percentages of 5 and 10, respectively. It was submitted to DOE for kinematic viscosity property test for biodiesel. The result of 3.82 for B10 blend of CasME passed the Automotive Diesel Oil (ADO) range for kinematic viscosity property. Furthermore, the B10 blend was subjected to other biodiesel fuel property tests and it all passed the PNS range as shown in Table 5 below.

Table 5 Physical Property Analyses

Test Analysis	CasME B10	PNS (B10) 2020-2007 [ADO]	Test Methods
Kinematic Viscosity at 40ºC, mm^2 / sec	3.82	2.0 – 4.5	ASTM D 445
Flash Point (COC), ºC	87	55, min	ASTM D 92/ 93
Copper Strip Corrosion, 3 hrs at 50ºC	1a	No. 1, max	ASTM D 130
Cloud Point, ºC	10	Report	ASTM 2500
Carbon Residue, % mass	0.02	0.15, max	ASTM D 189/ 4530
Total Glycerine, % mass	0.05	0.24, max	AOCS Ca 14-56
Acid Number	0.06	0.50, max	ASTM D 974/ 664
Sulfur, % mass	0.006	0.05, max	ASTM D 4294
Sulfated Ash, % mass	0.04	0.02, max	ASTM D 874
Free Glycerine, % mass	<0.01	0.02, max	ASTM D 6584

IV. CONCLUSIONS AND RECOMMENDATIONS

In this research study, the transesterification parameters were determined having its highest percent yield at 63.29%. The optimum parameters were reported to be at 70°C with the methoxide concentration of 0.7 M and a reaction time of 1.0 hour. The GC/MS analysis of methyl ester in the oil complied with castor property with respect to its acid content. The percent yield in 2.0 hours of reaction time was inconsistent at 70ºC due to possible degradation of methanol at temperature above 64.5ºC.

From the results obtained from the fuel property analyses performed on CasME, it was confirmed that CasME is a potential alternative fuel and if not, a feasible additive to petroleum – based diesel fuels. The CasME showed favorable results of its kinematic viscosity of 3.82 for B10 blend. All fuel properties tested within this blend conformed within the range of PNS standards for biodiesel.

Further study on the cost of production and economic viability of CasME needs to be focused on. Studies could also include engine performance and smoke emission tests that could verify the feasibility of CasME as an effective additive fuel. Moreover, it is recommended to try other blends higher than B10 to further optimize the value of kinematic viscosity.

REFERENCES

[1] Ramezani, K., Rowshanzamir, S. and Eikani, M. (2010). Castor Oil Transesterification Reaction: A Kinetic Study and Optimization of Parameters. Energy, 35 (10), 4142-4148

[2] Demirbas, A. (2009). Progress and Recent Trends in Biodiesel Fuels. Energy Conversion and Management, 50 (1), 14-34

[3] Berman, P., Nizri, S., and Wiesman, Z. (2011). Castor Oil Biodiesel and its Blends as Alternative Fuel. Biomass and Bioenergy, 35 (7), 2861-2866

[4] Hincapie, G., Mondragon, F., and Lopez, D. (2011). Conventional and in Situ Transesterification of Castor Seed Oil for Biodiesel Production. Fuel, 90 (4), 1618 – 1623

[5] El-Mashad, HM., Zhang, R., and Avena-Bustillos RJ. (2008). A Two-Step Process for Biodiesel Production from Salmon Oil. Biosyst Eng, 99 (2), 220–227

[6] Veljkovic´ VB, Lakic´evic´ SH, Stamenkovic´ OS, Todorovic´ ZB, and Lazic´ ML. (2006). Biodiesel Production from Tobacco (Nicotiana tabacum L.) Seed Oil with High Content of Free Fatty Acids. Fuel, 85 (17-18), 2671–2675

[7] Ghadge, SV., and Raheman, H. (2005). Biodiesel Production from Mahua (Madhuca Indica) Oil having High Free Fatty Acids. Biomass and Bioenergy, 28 (6), 601–605

[8] Jose, D.F.M., Raj, R. E., Prasad, B.D., Kennedy, Z. R., and Ibrahim, A.M. (2011). A Multi-Variant Approach to Optimize Process Parameters for Biodiesel Extraction from Rubber Seed Oil. Applied Energy, 88 (6), 2056–2063

[9] Albuquerque, M., Machado, Y., Torres, A., Azevedo, D., Cavalcante, C., Firmiano, L. Jr., and Parente, E. Jr. (2009). Properties of Biodiesel Oils Formulated using Different Biomass Sources and their Blends. Renewable Energy, 34 (3), 857–859

[10] Cesar, A. and Batalha, M. (2010). Biodiesel Production from Castor Oil in Brazil: A Difficult Reality. Energy Policy, 38 (8), 4031–4039

[11] Dias, P., Granato, L., Ramalho, L., de Oliveira. J., and Pretel, H. (2009). *Ricinus Communis* Biocompatibility Histological Study in the Nose of Cebus Apella Monkeys. Brazilian Journal of Otorhinolaryngology (Impresso), 75 (3), 350-355

[12] Kumar, A., and Sharma, S. (2011). Potential Non-Edible Oil Resources as Biodiesel Feedstock: An Indian Perspective. Renewable and Sustainable Energy Reviews, 15 (4), 1791 – 1800

[13] Gaerlan, M., Martin, T. and Magpayo, J. Thesis, University of Santo Tomas, (2011)

[14] Leung, D., Wu, X., and Leung, M. (2010). A Review on Biodiesel Production Using Catalyzed Transesterification. Applied Energy, 87 (4), 1083 – 1095

[15] Aguilar, A., Cotiangson, M. and Paras, L. Thesis, University of Santo Tomas, (2009)

[16] American Society for Testing and Materials