

Investigation of the Parameters Affecting Castor Oil Transesterification Reaction Kinetics for Biodiesel Production.

Aldo Okullo Apita and Abraham K. Temu

Abstract - Kinetic studies are concerned with the quantitative description of how fast chemical reactions take place and factors affecting them. The study is important to a chemist to understand the fundamental aspects of the reaction pathways to achieve the desired product. It enables us to tailor a chemical reaction so as to produce the desired product in a controlled manner. Castor oil was transesterified with methanol using a molar ratio of methanol to oil (6:1) and sodium hydroxide catalyst (1% wt of oil). The product of the reaction is castor methyl ester (CME) and glycerol with diglyceride and monoglyceride as intermediate products. The experiment was set to determine the effect of temperature, stirring rate and residence time on the rate constants and a second order rate law was used. Four different temperatures (35, 45, 55 and 65°C) and four stirring rates (600, 660, 700 and 800 rpm) were used and the reactions were timed. High temperatures (55 and 65°C) were unfavourable for castor transesterification; both temperatures provided yields of 91%. Low temperatures (35 and 45°C) increased rate constants and produced highest yields (98% and 97% respectively). Increasing stirring rate does not favour conversion rates. The optimum reaction time was 60 minutes. Beyond 90 minutes, the reverse reaction was favoured. The close fit of the data indicates that the selected model was adequate. These results agree well with reports from literature.

Key Words: Castor Methyl Ester, Castor Oil, Kinetics, Rate Constants, Second Order Rates, Transesterification.

1 INTRODUCTION

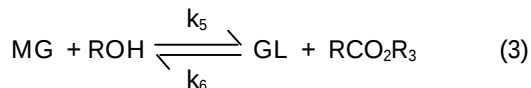
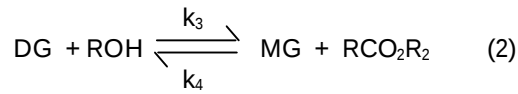
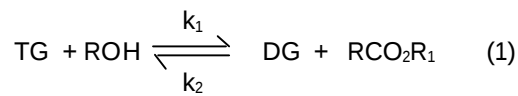
THE use of vegetable oils and derivatives as alternative diesel fuels and blends has become increasingly important over the past few years. The European Union Directive 2003/30/EC mandating the use of 2 and 5.75% biofuels for all petrol and diesel used in transportation by 2005 and 2010 respectively and EU 2005/93/EC allowing exemptions on excise duties on biofuels together with the US Energy policy (EPAct. 1992) all have contributed to the acceleration of the use of alternative fuels for transportation [1].

Biodiesel is a renewable, biodegradable fuel made from vegetable oils and animal fats. A viable commercial method of production that has been used is alkaline transesterification of the oil or fats with alcohol. Methanol has been the most preferred alcohol due to its low cost and short chain that makes it dissolve the catalyst easily. Sodium hydroxide is the commonly used catalyst because it is cheaper and easily available than the other alkaline catalysts. The product of the reaction is methyl ester (biodiesel) and glycerol, with intermediate compounds of monoglyceride and diglyceride.

Castor beans plant (Palma Christi) belongs to the Euphorbiaceae family. It is drought resistant and can grow on marginal lands. It is among the plants with high yield potential though its average yield is 1413 L/ha [2], [3].

Castor has high oil content up to 56% of the seed; however, the oil is not used in food chain due to the toxin known as castor beans allergen (CBA) found in its seeds [2]. Its oil favours transesterification with minimum heating and stirring since it is soluble in alcohol [3].

Varma and Madras [4], among others synthesised methyl ester from castor oil and lindseed oil in supercritical fluids to determine the effects of molar ratio and temperature on the yield. However, data on parameters that affect castor oil transesterification is still scarce. In this study, castor oil was transesterified with methanol and sodium hydroxide as a catalyst. The experiment was set to determine the effect of temperature, mixing intensity and reaction time on rate of reaction of castor oil. Second order rate law was used to determine rate constants from the following consecutive and reversible reaction:



Where: TG = triglycerides; DG = diglyceride; MG = monoglyceride; GL = glycerine; ROH = methanol and RCO_2R_1 , RCO_2R_2 , RCO_2R_3 , are methyl esters; k_1 , k_3 , k_5 are forward rate constants and k_2 , k_4 and k_6 are reverse rate constants.

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2 MATERIALS AND METHODS

2.1 Materials

Castor beans were obtained from Dodoma region in Tanzania. Analytical grade sodium hydroxide, methanol (99% purity) and potassium hydroxide (98% min. assay) were locally obtained from Dar es Salaam. GC calibration standards were obtained from Choice Analytical Pty, Thornig, Australia.

2.2 Methods

Transesterification was carried out in a two-litre round bottom flask immersed in a constant temperature water bath. The flask was fitted with a stirrer, a condenser, a thermometer and a sampling port. A catalyst (1% wt of oil) was dissolved in the required amount of methanol and the solution was added on to the oil in the reactor while stirring started immediately. This was the starting time for the reaction which was allowed to continue for two hours.

Samples were drawn at five minutes interval initially for 20 minutes then changed to 10 minutes intervals. These were quenched in a mixture of two ml tetrahydrofuran and two ml 0.5M sulphuric acid. Samples were shaken and centrifuged at 2000 rpm for 15 minutes to separate the methyl ester from the glycerine. The methyl ester was washed with warm water (50°C) three times and dried using anhydrous sodium sulphate and kept for analysis below minus two degrees celsius. A GC/FID Shimadzu 2010 model A17, AAF V3 was used for the quantification of TG, DG, MG, GL and the fatty acid methyl ester (FAME). Gas Chromatographic analysis was carried out according to the ASTM D 6584/EN14105 standards.

3 RESULTS AND DISCUSSIONS

Figs 1 to 4 show the conversion of castor oil into castor methyl ester (CME) for different temperatures. The results for all these temperatures show that the reaction was complete within 90 minutes instead of 120 minutes as reported for other oils (points indicated by solid arrows in Figs. 1- 4). The highest conversions appeared after 30 and 60 minutes of the reaction (points indicated by dash arrows). Longer reaction time than 90 minutes resulted into the formation of the reactants as indicated by the reversibility of the reaction (1 – 3). This is due to high solubility of castor oil in methanol, in the product CME formed and in glycerine. The curves also show characteristics of consecutive and reversible reactions; whenever there is an increase of methyl ester, there is a subsequent decrease of diglyceride or monoglyceride. This supports the proposed second order model for the reaction and the close fit of the data indicates that the model was adequate.

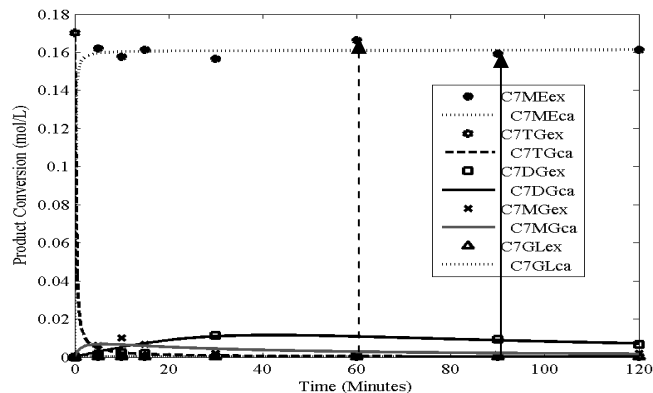


Fig1.eps, Conversion versus time. Temperature = 35°C, stirring rate = 700 rpm; molar ratio = 6:1 and catalyst loading = 1%

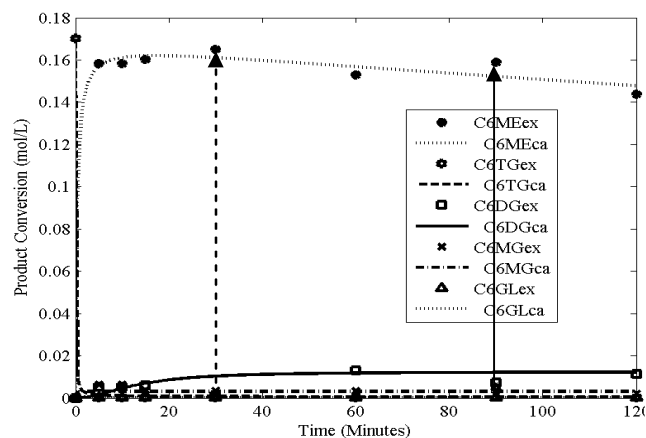


Fig2.eps, Conversion versus time. Temperature = 45°C, stirring rate = 700 rpm; molar ratio = 6:1 and catalyst loading = 1%

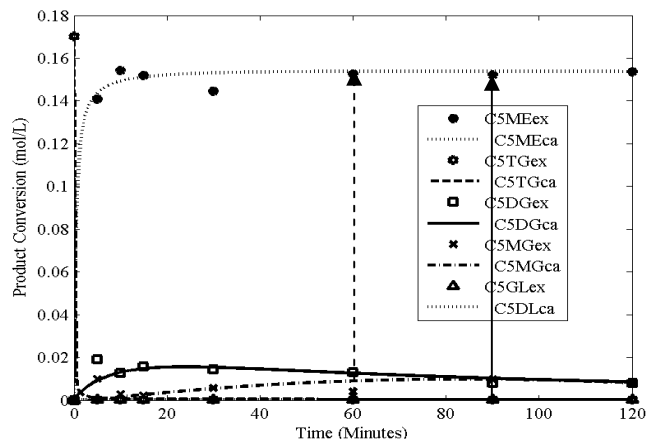


Fig3.eps, Conversion versus time. Temperature = 55°C, stirring rate = 700 rpm; molar ratio = 6:1 and catalyst loading = 1%

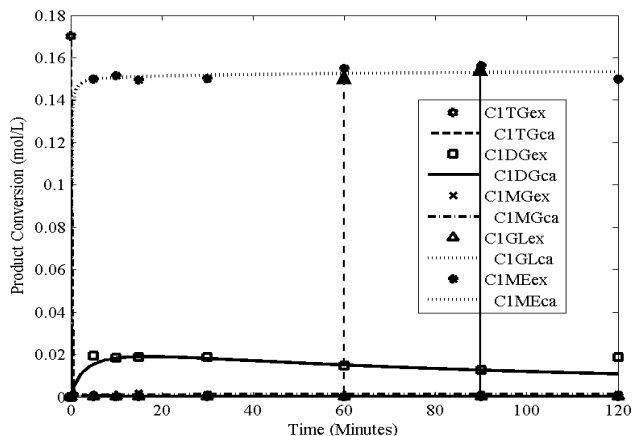


Fig4.eps, Conversion versus time. Temperature = 65°C, stirring rate = 700 rpm; molar ratio = 6:1 and catalyst loading = 1%

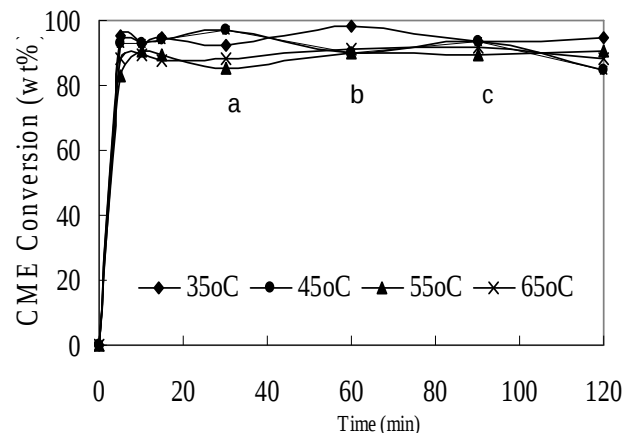


Fig5.ps, Temperature Effect on CME conversion

3.1 Temperature Effect

Figure 5 shows temperature effects on the transesterification of castor oil. It is not easy to see a straight forward trend of the effect of temperature on the conversion of castor oil to methyl ester. However, low temperature favours conversion; the highest conversion of 98% was observed for a temperature of 35°C after 60 minutes of reaction whereas the second highest conversion of 97% was seen for a temperature of 45°C after only 30 minutes. Temperatures of 55 and 65°C gave lower conversions of 90 and 91% respectively compared to the previous ones (Fig 5). Castor oil has a behaviour which is different from other vegetable oils due to the presence of three functional groups in its structure; firstly it has 90% ricinoleic acid with hydroxyl group attached to the 12-carbon atom, secondly it has a double bond on the 9th carbon atom and thirdly it has a carbonyl (carboxylic) group on the first carbon atom. This structure favours solubility and low temperature operability of castor oil. Meneghetti [5], reported maximum yield of CME in one hour after which reversibility became more prominent. Da Silva [6], reported low temperature transesterification of castor oil to the methyl ester while [7] reported optimum transesterification temperature of castor oil as being 40°C and optimum time of reaction of 90 minutes. High solubility of castor oil in methanol was also reported by [2] giving a transesterification period of 30 minutes. The swinging of points at (a), (b) and (c) show the reversible nature of the reaction; point (a) reveals a high conversion after 30 minutes for a reaction at 45°C while point (b) shows a high conversion after 60 minutes for a reaction at 35°C and at point (c), all reactions give almost the same conversion after 90 minutes.

3.2 Stirring Effect

There is no clear trend in mixing intensity effect on the conversion of castor oil. High mixing intensity of 800 rpm tends to favour the reversed reaction with the formation of reactants. The solubility of CME in methanol and in glycerine makes the reverse reaction possible under high temperature (55°C) at this impeller speed, especially after one hour when CME is sufficiently formed (Fig 6). Increasing mixing intensity with castor oil transesterification has no advantage and therefore not necessary. Similarly, the reversible nature of the reaction is shown in Fig 6 by the swinging of points.

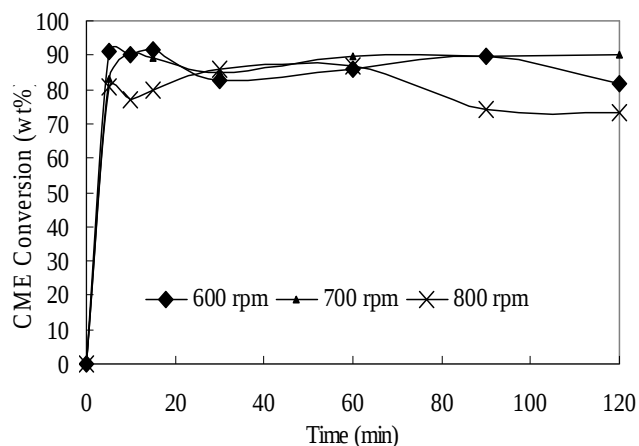


Fig6.ps, Stirring effect on CME conversion

3.3 Rate Constants and Activation Energies

Rate constants and activation energies were determined for castor oil transesterification and the results are given in Table 1. Rates were lower at higher temperatures. Fast forward reactions; (TG→DG), (DG→MG) and (MG→GL) were high at low temperatures. The reactions eventually slowed down at high temperatures. The rate determining step was the conversion of monoglyceride to glycerol (k_5) for the entire period of the reaction. The higher concentrations of DG than MG as seen in the plots were expected since the second reversible reactions (k_4) was faster than the third forward (k_5) at high temperatures (Table 1). This shows that high temperature favours the reversible reaction. The explanation still lies in the structure of the triglycerides with three functional groups that make castor oil operate under low temperatures.

TABLE 1
RATE CONSTANTS AND ACTIVATION ENERGIES
OF CASTOR CME

	35°C	45°C	55°C	65°C	Ea (Jmol ⁻¹)	R ²
k ₁	0.9685	0.0302	0.0020	0.0002	236.2954	0.994
k ₂	0.0048	0.0042	0.0020	0.0017	33.6924	0.912
k ₃	0.2371	0.0187	0.0015	0.0003	190.5803	0.988
k ₄	0.0334	0.0031	0.0005	0.0001	172.5793	0.996
k ₅	0.1075	0.0018	0.0001	0.0000	304.3702	0.997
k ₆	0.1620	0.0082	0.0011	0.0001	209.9125	0.990
SSE	0.00007	0.00003	0.00004	0.00003		

3.4 Castor Methy Ester Quality

The amounts of triglycerides (TG), diglyceride (DG), monoglyceride (MG) and glycerine (GL) remaining in the product methyl ester after purification are out of the range specified in EN14214 standard (Table 2). Since conversions are relatively high, this may indicate an insufficient purification of the methyl ester. However, repeatability is within the range of specification except for DG and hence total glycerides. Washing methyl ester with water alone does not produce sufficient separation of CME from glycerine. CME and glycerol associate through hydrogen bonding. They form a homogeneous phase in methanol which is not easy to separate. A better method of separation for such heat sensitive compounds like CME would have been molecular distillation where a liquid component evaporates without boiling due to high vacuum.

TABLE 2
PRODUCT COMPOSITION SHOWING CME, FREE AND TOTAL
GLYCERINES IN THE MIXTURE

GLS (%m/m)	35°C	45°C	55°C	65°C	EN1421 4
GL	0.14	0.13	0.14	0.16	≤ 0.02
R	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	
MG	1.11	1.23	4.20	0.67	≤ 0.80
R	-0.03±0.05	-0.03±0.02	-0.06±0.05	0.02±0.01	
DG	3.86	13.68	7.75	10.96	≤ 0.20
R	0.52±0.48	0.78±0.46	1.46±0.45	1.94±0.29	
TG	6.35	1.97	1.64	2.66	≤ 0.20
R	0.41±0.06	0.34±0.22	0.20±0.04	0.22±0.04	
T.GL	11.46	17.00	13.73	14.44	≤ 0.25
R	1.92±0.34	2.01±0.29	2.45±0.37	2.39±0.19	

4 CONCLUSIONS

Increasing temperature did not favour the rate of reaction of castor oil; this behaviour was attributed to castor oil's 4. triglyceride structure with three functional groups on the molecule. Increasing mixing intensity is not necessary since the oil is soluble in methanol.

The optimum transesterification conditions for castor oil were: temperature, 35°C; reaction time, 60 minutes; molar ratio of 6:1 methanol to oil and moderate stirring (600 rpm). A product yield of 98% methyl ester was obtained under these conditions. It was observed that a reaction time longer than 90 minutes results in reactants formation due to the reversibility of the reaction.

Separation of castor methyl ester from glycerol requires molecular distillation since the methyl ester is soluble both in methanol and in glycerol. The close fits of the calculated data to the experimental data points in this study showed that the model selected for the study was adequate. Castor oil transesterification can be described by second order rate law.

Castor methyl ester is not suited for use in diesel engine due to its high kinematic viscosity. Alternative method of reducing its viscosity should be looked into; such as blending with petro-diesel or with some other appropriate additives.

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