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The Effect of Reaction Temperature, Catalyst Concentration and Alcohol Ratio in the Production of Biodiesel from Raw and Purified Castor Oil

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Abstract

In this study, a homogeneous alkaline catalyst was used in the production of biodiesel from raw and refined castor oil feedstock. The effect of potassium hydroxide (KOH) as a catalyst between the two feedstocks, raw and refined castor oil was compared. The transesterification technique was utilized in this study, aiming to investigate the effect of different parameters, which include the reaction temperature, methanol-to-oil mole ratio, and catalyst concentration at a constant period of 90 minutes. The result revealed the performance of the KOH catalyst on raw castor oil yielded 98.49% FAME, which was higher than the refined castor oil which yielded 97.9% FAME. The optimal conditions obtained from refined castor oil were applied to raw castor oil because of the same properties. The fuel quality of castor oil and produced biodiesel were tested for physicochemical properties.

Keywords

Biodiesel Fuel, Raw Castor Oil, Refined Castor Oil, Transesterification Process

1. Introduction

Petroleum fuels are crucial to the development of many industries, transportation systems, agriculture, and a range of basic human needs in contemporary civilization. Due to a sharp increase in demand, gasoline supplies are scarcer every day [1]. Furthermore, the usage of petroleum fuel has generated toxic gases,

which have consequently resulted in many environmental issues and problems. As a result, biofuels are considered an environmentally friendly alternative fuel source. The burning of biofuels results in products with lower levels of particulate matter (PM), carbon monoxide (CO), toxic sulfur (SO_x), and nitrogen compounds (NO_x) [2].

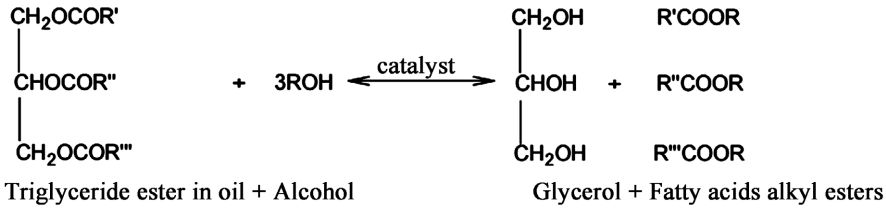
The research done by British Petroleum [3] shows that South Africa is considered among the top countries contributing to the depletion of the ozone layer. It accounts for almost half of the carbon dioxide (CO_2) emissions in Africa. CO_2 contributes about 1.6% of the world's emissions, and South Africa's economy largely depends on energy derived from fossil fuels [3]. To reduce the problem, the alternative fuel extraction of biodiesel needs to be implemented aggressively.

The need to substitute the raw material for the production of diesel with biodiesel, which is extracted from renewable resources such as biomass for bioenergy, is of great importance. Producing biodiesel from renewable energy remains profitable after Rudolf Diesel's test of vegetable oil as an engine fuel [4]. If the policies set in place are implemented, it is anticipated that both production and demand for biodiesel will rise in the upcoming years [3]. The South African government intends to approve the rules requiring mandated biodiesel blends in petroleum-based fuel [4].

One of the non-edible oils that are most frequently utilized in the production of biodiesel is castor [5]. Originally a tree or shrub, the castor plant comes in a number of different varieties that can be cultivated. The average yield of castor oil seed worldwide is about 1.1 hectares, although it may be possible to obtain a maximum of 4.2 hectares. Castor oil seeds typically contain 40% - 55% oil [6]. Castor, hence, has one of the largest potential oil yields among plants [6]. Throughout the world, biodiesel has primarily been produced from edible vegetable oils. This has now had an impact on the global imbalance between market demand and food supply [7]. Additionally, the cost of this type of feedstock accounts for 70% - 80% of the overall cost of the biodiesel process. It is advisable to use non-edible oils more often because they can grow on barren land, and are not used in human nutrition. Non-edible oil plants can be cultivated for significantly less cost and without having an impact on the food market [8].

Biodiesel is described as a fuel for diesel engines produced from chemically converted animal fats and vegetable oils [9]. Under normal conditions, low molecular weight alcohol interacts with triglyceride esters of oil or fat, forming the corresponding fatty acid alkyl ester (FAAE) and glycerol (GL) as the only reaction products shown in **Reaction 1**. Further, the reaction of alcohol (ethanol/methanol) in the presence of catalysts, potassium hydroxide (KOH) produces glycerol as a by-product and fatty acids alkyl esters [10].

The transesterification reaction is the most commonly practiced process by many researchers using the primary alcohol, which is methanol. Methanol is preferred because it is less expensive and has a short hydrocarbon chain. The transesterification reaction of methanol has a shorter reaction time compared to that of ethanol [11] [12].



Reaction 1. Reaction of triglyceride with alcohol to form fatty acids alkyl ester (FAAE) and glycerol (GL).

An alternative to producing biodiesel without producing aqueous waste is heterogeneous catalysis. The catalyst can be recovered, renewed, and reused in this process. High quantities of high-quality biodiesel can be produced in batch or continuous processes without the need for additional purification stages. One major benefit of this catalysis is that it allows simultaneous triglyceride transesterification and free fatty acid esterification, which saves time and energy [13]. Commercially available solid catalysts for heterogeneous esterification include those from the amberlyst and Nafion families. Several solid acids, including mesoporous silica with sulfonic acid, carbon-modified metal oxides, heteropolyacids, metal-incorporated porous oxides, zeolites, ion exchange resins, and inorganic-oxide solid acids. The supported noble metal oxides have been synthesized to be used as catalysts in the production of biodiesel from low-quality oils [13]. According to Du *et al.* [14], heterogeneous catalysts have been used for biodiesel production from various vegetable oils. Sun *et al.* [15] conducted a study on heterogeneous catalysts, showing that prepared with supported potassium oxide (K_2O_3) loaded to AL-Ca hydrotalcite has an effect on reaction temperature, reaction time, and catalyst concentration. The biodiesel yield was 87.4%, with optimal operating conditions: methanol:oil mole 13:1 ratio, reaction temperature 65˚C, catalyst concentration 2 wt%, and reaction time of 2 hours.

A process for producing biodiesel from canola oil was developed using sodium methoxide (CH_3Ona) crystallized from dimethyl carbonate (DMC) as a catalyst. Except for producing glycerol as a byproduct, this process helps to achieve conversions above 95%; however, the catalyst's efficiency declines with each reaction. Some vegetal-derived materials have also been proposed as catalysts. In the study conducted by Li *et al.* [16] experimented with concentrated sulfuric acid while using a solid acid catalyst (RHC-SO_3H) obtained from rice husk activated carbon (RHC). This catalyst presented high catalytic performance and high stability in the biodiesel production process using waste cooking oil. Low reaction rates are one of the main disadvantages of heterogeneous catalysts, which are caused mainly by the use of a large amount of catalyst and conditions that affect the stability of the catalyst [17]. The primary factors that affect chemical transesterification are reaction temperature, alcohol-triglyceride ratio, reaction time, catalyst concentration, moisture content, and the amount of free fatty acids [18]. To produce biodiesel from castor oil, they optimized several ultrasound-assisted transesterification reactions. Under optimal conditions, they obtained a reaction yield of 87% with a wave ultrasonic amplitude of 64%, 0.73% of

an ultrasonic cycle, and a 1:8.15 methanol:oil ratio [18].

The transesterification was carried out using a simple and high-catalytic method, which is a homogenous alkaline transesterification reaction. The reaction conditions were reviewed from previous studies. The optimal operating conditions were: time (2 - 8 h), reaction temperature (55˚C - 65˚C), methanol to oil molar ratio (6:1) and 1 KOH % (w/w), product yield range (43.3% - 74.1% w/w biodiesel) [18] [19]. Keera *et al.* [6] studied the castor oil biodiesel production and optimization using a heterogeneous alkaline transesterification reaction process, methanol as an alcohol, and KOH pellets as a catalyst. A yield of 95 wt% biodiesel using a 9:1 methanol:oil mole ratio, 1 wt% KOH catalyst, a 60˚C reaction temperature, and a 30-minute reaction time. Jiyane *et al.* [20] studied the optimization of esterification and transesterification in the production of biodiesel from raw *Croton gratissimus* oil using sulfated zirconia and KOH pellets as catalysts, 84.51% FAME yield and 90.66% FAME purity using 1.439 mass% KOH catalyst concentration, 7.472 methanol:oil mole ratio, and 63.50˚C reaction temperature. The research done by Sabzimaleki *et al.* [21] is an example of biodiesel production from castor oil.

In this study, the objective is to investigate the effects of reaction temperature, catalyst, reaction time, and alcohol-oil molar ratio. KOH was selected to be used as a catalyst based on the performance of previous investigations. **Table 1** presents the initially investigated parameters for this study. This study aims to present a comparison between refined and raw castor oil in producing biodiesel to determine the kinetics of the product. The aim is to find optimum operating conditions for refined castor oil, which will then be applied to raw castor oil. The optimum operating conditions of the study that were assessed are methano:oil ratio, reaction temperature and catalyst concentration under, which can yield high biodiesel conversion in raw castor oil feedstock. If there is high free fatty in raw castor oil it will result in a two-step process, which involves esterification to transeterification reactions carried out over homogeneous KOH alkaline catalysis.

2. Materials and Methods

2.1. Materials

Commercial castor oil (CCO), methanol with a purity of 99%, and 0.1 molar N potassium hydroxide pellet (KOH) were purchased from LabCare suppliers. The raw castor oil produced by Mkhize [22] at Durban University of Technology

Table 1. Measured parameters in this study.

Parameters	Value Range	Units
Catalyst Concentration	0.625 - 3.125	% wt KOH
Alcohol Ratio	3:1 - 9:1	Methano:oil
Reaction Temperature	45 - 70	˚C
Reaction Time	90	Minutes

Chemical Engineering laboratory was used.

2.1.1. Oil Characterization

The acid value of raw and refined castor oil was determined by titration. The acid value obtained is presented in Table 2. Equation (1) was used evaluate AV:

$$\text{Acid Value}\left(\text{AV}\right)=\frac{40\times N\times V}{m} \tag{1}$$

where 40.0 is the constant in the molar mass of NaOH, N is the normality of the standardized NaOH solution, V is the volume of the NaOH solution, and m (g) is the castor oil. The acid value for refined castor oil was found to be 1.65, which is within the limit of 1 - 4 accepted the required AV for direct transesterification. To ensure the accuracy of the feedstock characterization absolute relative error was calculated.

$$\text{AE}=\left|\text{AV}_{\text{lit}}-\text{AV}_{\text{Cal}}\right| \tag{2}$$

2.1.2. Transesterification Experimental Method

The design expert software was used to determine the number of experimental runs base on the mentioned parameters. Prior conducting experiments, the jacketed reactor was cleaned with warm deionized water and rinsed with acetone 5 times then dried in the oven at the temperature of 60˚C. This was done to ensure that there are no contaminants with the reactor to cause side reactions.

Transesterification reactions were performed in a 500-ml batch jacketed reactor equipped with a Graham condenser and a magnetic stirrer. A weighed sample of (± 40 g) of oil was placed in a 250-ml glass beaker to be heated up to (45 −70˚C) in a heat plate. A weighed sample of alcohol according to the ratio of methanol:oil (3:1 - 9:1) and a weighed sample of KOH catalyst according to oil percentage (0.625% - 3.125% wt KOH) were placed into the orbital shaker and shaken to dissolve the KOH catalyst into methanol to form potassium methoxide ($KOCH_3$). A known mass was transferred into a 500-ml jacketed reactor and brought to the reaction temperature (45˚C - 70˚C) by circulating water from a hot water bath filled with water and an immersion temperature regulator-circulator. A potassium methoxide ($KOCH_3$) solution prepared in a 100-ml beaker was poured into the beaker and agitated using a magnetic stirrer at 580 rpm. A Graham condenser, connected to the jacketed beaker, was used to capture methoxide escaping from the reaction at a higher temperature as shown in Figure 1 and Figure 2.

Table 2. Acid Value (AV) absolute error AE.

	AV (raw castor oil) literature	AV obtained (raw castor oil)	Ref	AV (commercial castor oil) literature	AV obtained (commercial castor oil)	Ref
Acid Value	0.25	0.4	[17]	1 - 2	1.65	[22]
Relative Error		0.15			0.97	

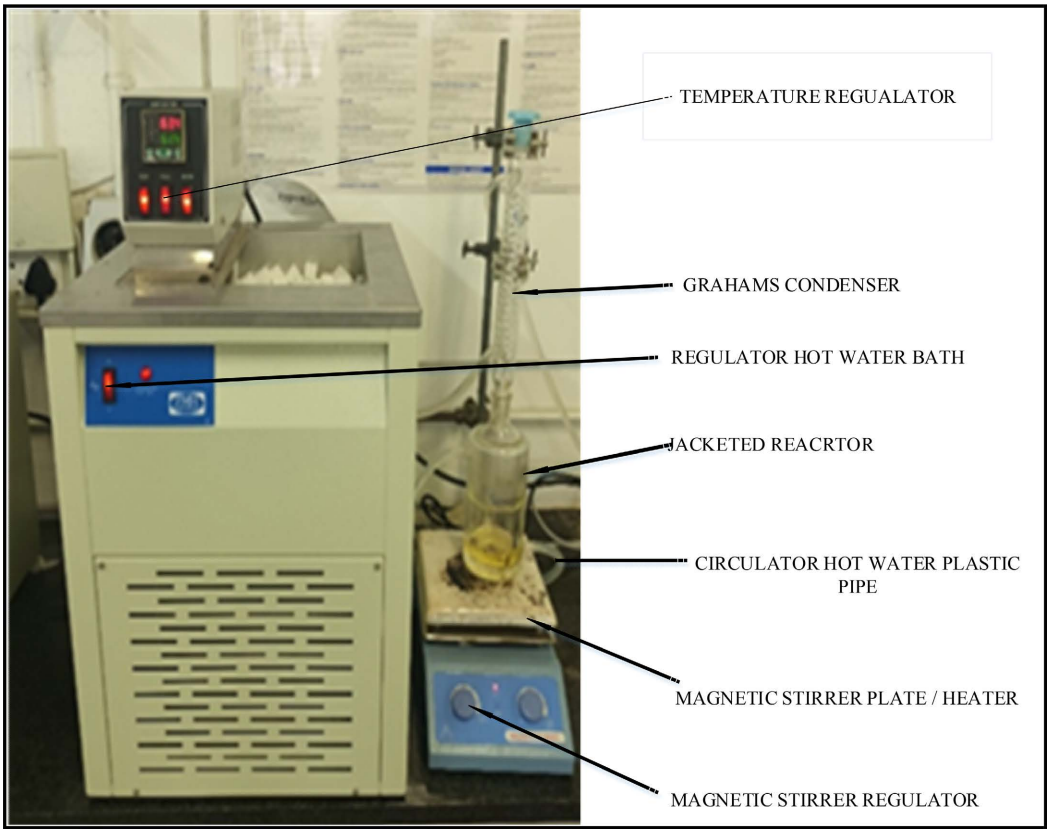


Figure 1. Transesterification equipment setup.

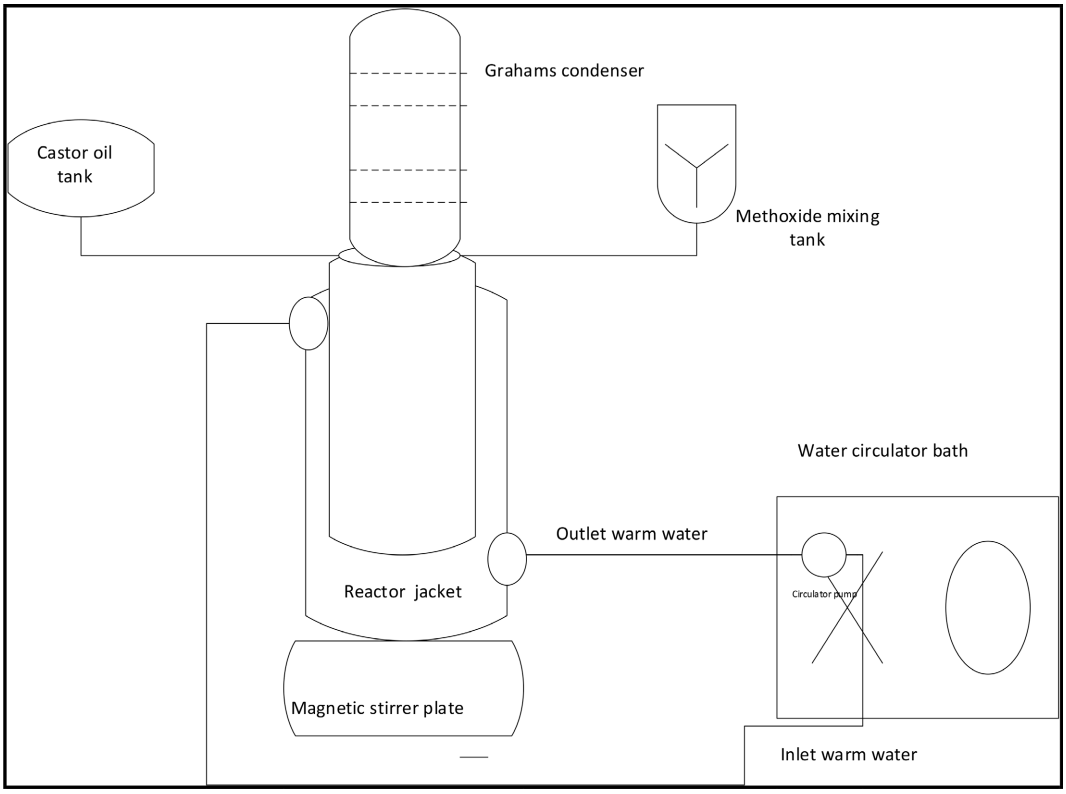


Figure 2. Transesterification reaction laboratory scale.

After 1.5 hours of reaction time, the mixture was transferred into a separating funnel. The product in the separating funnel consisted of a biodiesel layer, a methanol, a water layer, and a glycerol layer. The bottom glycerol layer was decanted. The remaining biodiesel, methanol, and water layers were cleansed with warm deionized water. **Figure 3** shows three distinct layers in a conical flask, and after the first washing of methyl ester, it was transferred to a separating funnel and settled. After several washes, the final wash shown in **Figure 4** product of fatty acid methyl esters (FAME) was weighed in the weighing balance to find the co0.version percentage of methyl ester from castor oil.

The product samples of biodiesel were characterized. The most important characteristics of biodiesel are the ones that directly affect the engine's performance such as viscosity, flash point, density, calorific value, and so on. All of these characteristics help the engine last longer, provide better lubrication, and enable complete combustion so that the engine can generate more energy.

2.1.3. Kinetic Models of Transesterification Reaction

The transesterification reaction's kinetics has been studied theoretically. The process of making biodiesel involves mixing triglycerides and free fatty acids (FFA) from vegetable oils and animal fats with alcohol while an enzyme, an acid, or an alkaline catalyst is present by [16] [23] [24] [25]. According to stoichiometry, 1 mol of triglycerides and 3 mol of alcohol react to yield 1 mol of glycerin

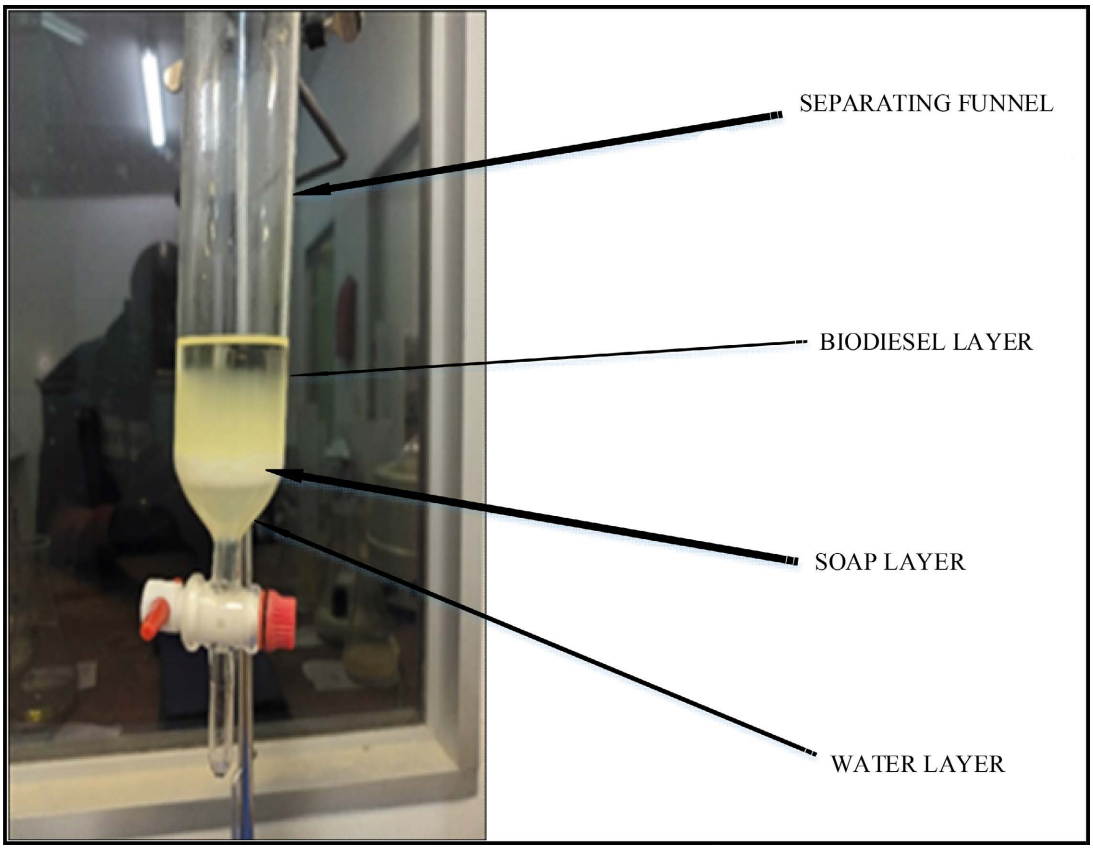


Figure 3. Transesterification product after 1st wash.

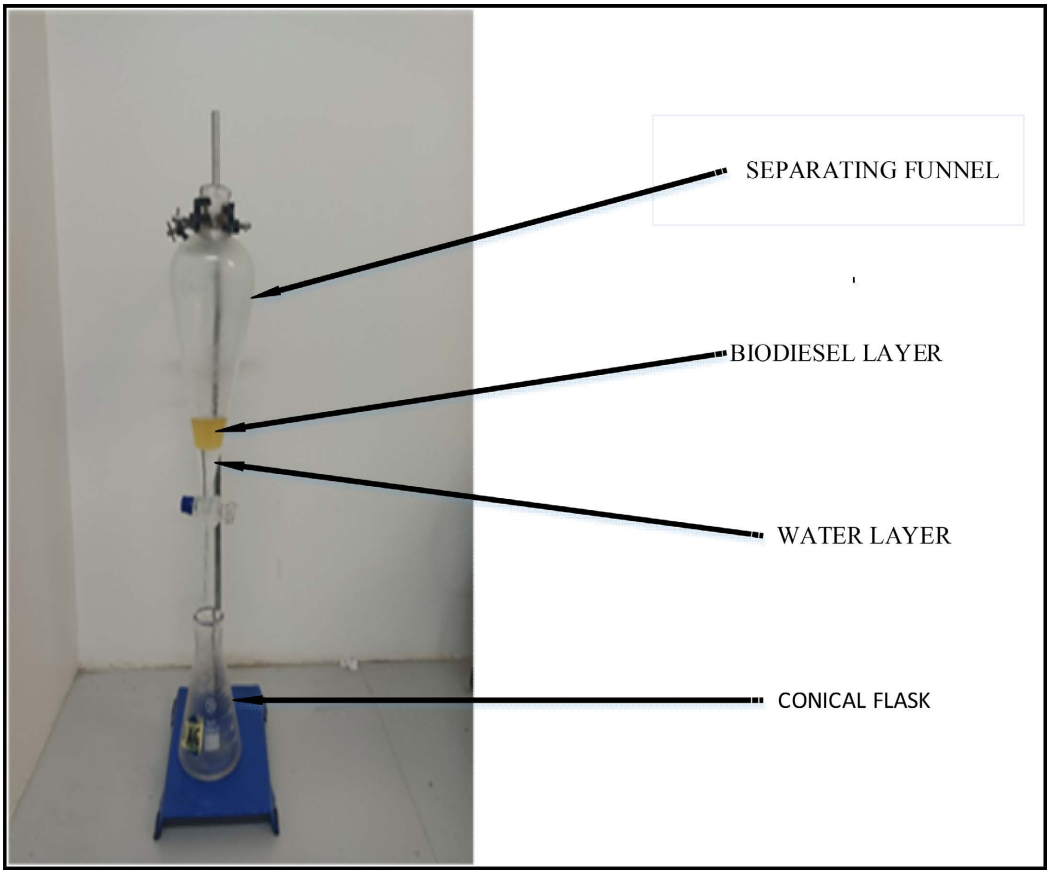


Figure 4. FAME after final wash.

and 3 mol of fatty acid methyl ester (biodiesel). The kinetics of transesterification reactions can be modelled using many kinds of simple empirical kinetic models. Pseudo-First Order (PFO) [25] [26], Second-Order (SO) [24], and Pseudo-Second-Order [27] [28] models are the most fundamental and commonly utilized empirical kinetics modes of this reaction in the literature. These kinetic models were all put forth using empirical data. Additionally, kinetics models integrating reversible Second-Order are typically used because of incomplete triglyceride conversions during the reaction period [29]. It is observed that the reaction kinetics initially follows the pseudo-first-order kinetics model, then transitions to the pseudo-second-order model, particularly in the later phases of the reaction [30] [31] [32]. Furthermore, it has been noted that transesterification reaction kinetics departs from the Second-Order-Model, particularly in the reaction's later phases. Additionally, when the reaction is spontaneous ($\Delta_r G \ll 0$ conditions or at short initial times of reaction), a modified version of the Second-Order model (MSO) is derived [30] [33]. The glycerol effect is the cause of this deviation, according to Ezzati *et al.* [33] studied, this deviation is caused by the glycerin byproduct, which lowers the solubility of triglyceride in methanol and reduces mass transfer of triglyceride into methanol, thereby inhibiting the transesterification reaction rate by preventing the diffusion of triglycerides from the oil phase to the methanol phase [33].

General Rate Equation (GRE)

$$T + A \xleftrightarrow{\text{step 1}} D + ED + A \xleftrightarrow{\text{step 2}} M + EM + A \xleftrightarrow{\text{step 3}} G + E \tag{3}$$

where A, T, D, M, G, and E are alcohol, Triglyceride, Diglyceride, Monoglyceride, Glycerine and Methyl ester respectively in reaction (2) above. Due to the immiscibility of methanol and oil, the transesterification reaction system initially consists of two phases. In this instance, mass transfer regulates the kinetics of the reaction during its initial phases. The chemical reaction stage controls the action stage both in the initial phases of the reaction and throughout the entire reaction time range. This is true for both the transesterification reaction rate and the early stages of the reaction [33]. It is reported that the mass transfer at the initial stage of mass transfer control is negligible when the impeller speed at the transesterification reaction is at least 600 rpm [33]. Consequently, believe that transesterification occurs in one process. It has been reported that the transesterification reaction between triglyceride and methanol is slower than the reaction between diglyceride and monoglyceride with methanol. As a result, step 1 may determine the rate, and the rate equation is based on the assumption. Step 1 states that the rate equation can be expressed as follows:

General Rate Equation

$$r = k_1[T][A] - k_{-1}[D][E] \tag{4}$$

where [T], [A], [D] and [E] are the concentration of triglyceride, alcohol, diglyceride and methyl ester respectively. Also K_1 and K_2 are rate constants for step 1. Assumptions made is the concentration of intermediates in the reaction (diglyceride and monoglyceride) are close to their equilibrium concentration.

$$r = k_1[T][A]\left[1 - \frac{Q}{R}\right] \tag{5}$$

The reaction quotient for overall reaction Q.

$$Q = \frac{[G][E]3}{[T][A]3} \tag{6}$$

The equilibrium constant of the overall reaction. K

$$K = k_1 k_2 k_3 \tag{7}$$

Pseudo-First-Order model (PFO)

Assumptions

- High initial concentration of alcohol.
- Value of Q is close to zero

$$r = k_{PFO}[T] \tag{8}$$

where K_{PFO} is the PFO is rate constant and is defined as:

$$k_{PFO} = k_1[A] \tag{9}$$

The Second-Order model (SO)

Assumptions

- High initial concentration of alcohol.

- Value of Q is close to zero

$$r = k_{SO}[T][A] \tag{10}$$

where K_{SO} is the SO rate constant and is defined as:

$$k_{SO} = k_{\_1} \tag{11}$$

Modified-Second-Order Model (MSO)

$$r = k_{\_1}[T][A]e^{-\frac{Q}{K}} \tag{12}$$

3. Results and Discussion

The transesterification method was chosen for the production of biodiesel. All input raw materials were checked for purity. The raw and purity commercial castor oil were used for the investigated of the effect of the following parameters reaction temperature, methanol-to-oil ratio, and catalyst concentration. The procedure and test system of Tumba *et al.* [34] was used in this study to verified experimental procedure. The results obtained of 93.3% FAME was in agree of Tumba *et al.* [34] for the highest yield of 93.63% FAME.

The acid value of castor oil depends on density. If the density of the feedstock is high, then the acid value will also be high, especially for raw castor oil extracted from castor seeds. Acid value also increases or decreases the yield of biodiesel in a feedstock because it determines the formation of the soap in the product (biodiesel). Soap is easily formed on products when the acid value is greater than 4.

The heat and mass transfer, of the reactants oil and alcohol, have a significant impact on the biodiesel yield. The mass transfer on the transesterification reaction is a concern due to the fact that raw materials which are methanol and vegetable oil are immiscible. The difference in chemical and physical properties and must be taken into account when producing biodiesel with jacketed reactor technology. These additional process parameters, in addition to the typical processing parameters (reaction temperature, methanol-to-oil ratio, and catalyst concentration), need to be taken into account. The crucial process variables must be considered in order to produce biodiesel more sustainably [35]. The methyl ester (FAME) production yield was calculated using Equation (13). **Table 3** presents the methyl ester characterization.

$$\text{Percentage Biodiesel Yield}(\%Y) = \frac{m(\text{biodiesel yield})}{M(\text{feed castor oil})} \times 100 \tag{13}$$

3.1. Effect of Reaction Temperature

Measurements were conducted in the reaction temperature range 45˚C to 70˚C. The range was selected based on Keera *et al.* [6] reaction temperature range (30˚C - 60˚C) which indicates that even at lower temperatures there will be a production of biodiesel from feedstock castor oil. The yield was calculated using Equation (13). **Figure 5** shows the effect of temperature, as temperature increases

Table 3. Physiochemical properties of methyl ester (biodiesel) produced.

Property	Raw castor oil results	Purified/ commercial castor oil results	Standard SANS specification limits	Reference	Test method	AAD Raw castor oil	AAD Refined/ commercial castor oil
Kinematic viscosity (cSt) @ 50˚C	1.98	2.98	1.9 - 6	[28]	ASTM D445	0.003	0.03
Ash (g)	0.003	0.005	-	-	ASTM D874	-	-
Flash point ˚C	114	116	130 max	[5]	ASTM D93	0.70	0.40
Sulphur (ppm)	0.64	0.65	10 max	[4]	ASTM D5453	0.36	0.35
Density kg/m^3 at 25˚C	920	960	860 - 900	[28]	ASTM D1298/4052	0.01	0.032
Water content % vol. at 25˚C	0.05	0.04	0.05 max	[5] [28]	ASTM D2709	0.00	0.20
Calorific Value kJ/kg	44121	44121	44000	[28]		0.003	0.003

$$\text{AAD} = \left| \frac{P_{\text{lit}} - P_{\text{meas}}}{P_{\text{lit}}} \right|.$$

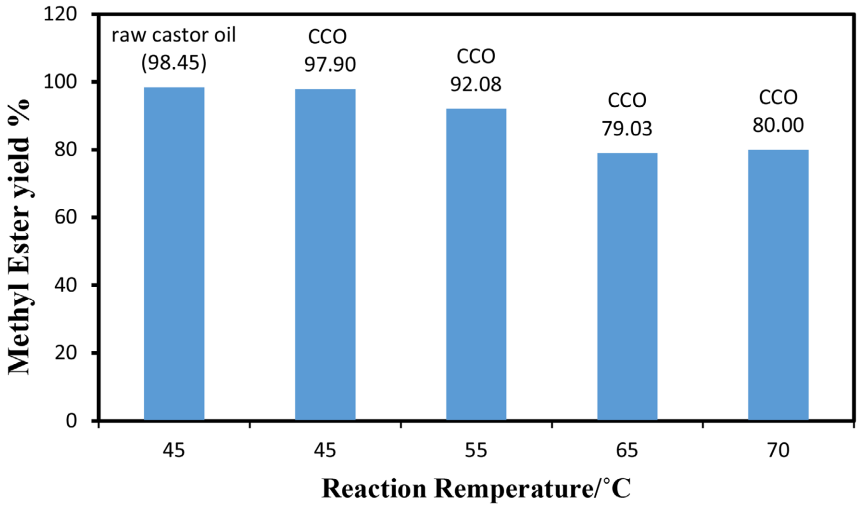


Figure 5. Effect of reaction temperature on methyl ester.

the biodiesel yield decreases this is due to that as the reaction temperature increases methanol reaches the boiling point and start evaporating which favors the reverse reaction. The optimum was found using commercial castor oil. It was found to be 45˚C reaction temperature and yield was 97.9% biodiesel at optimum temperature. The raw castor, which was produced in the lab by Mkhize [22] was measured. The yield obtained was 98.49% biodiesel using the same optimum conditions obtained on commercial castor oil. The biodiesel yield from raw castor oil is higher than that of commercial castor oil the acid value has an impact. The acid value for commercial castor oil is higher than that of raw castor oil which can be the caused by extraction process of raw castor oil.

According to Tabatabaei *et al.* [36] it can be postulated that at least no eco-

nomically profitable reaction could be conducted at a temperature below 32˚C. However, the application of temperatures lower than the melting point of oil, for example, 50˚C, could complete the reaction. However, beyond certain limits, the increase in temperature either has an adverse impact on reactants (degradation, side reactions, and vaporization) or is not cost-efficient. As illustrated in **Figure 4**, an experiment was conducted under an ideal 9:1 methanol:oil molar ratio, and due to the polarity of ricinoleic acid, it was demonstrated that the reaction reached its steady state after 90 min. Castor oil has high miscibility in alcohol due to the presence of acid and methanol. Because of castor oil's high miscibility in methanol at above-room temperature, this occurred. However, this variable loses some significance after 90 minutes of reaction. The ester yield changes by 18.49 wt% between 45 and 70. Therefore, it is ideal for the reaction to occur at 45˚C. Because temperature affects the amount of catalyst concentration, the yield is 97.9% methyl ester at 45˚C and 0.625 wt% KOH with the same molar ratio. The reaction at higher temperatures could favor a reverse reaction. When the reaction temperature is 65, the yield decreases to 79.78% because that is where methanol starts evaporating, which favors the reverse reaction.

3.2. Effect of Methanol to Oil Molar Ratio

One of the most significant factors affecting the conversion efficiency yield of biodiesel is the molar ratio of alcohol to oil [37]. Higher molar ratios are needed to improve miscibility and the contact between alcohol molecules and triglycerides because the stoichiometric molar ratio of alcohol to oil for transesterification is 3:1 and the reaction is reversible. In practice, to shift the reaction toward completion, the molar ratio should be higher than the stoichiometric ratio [36]. Furthermore, to break the glycerin-fatty acid linkages during the transesterification of triglycerides into biodiesel, excess methanol is required [38]. Higher alcohol to oil molar ratios gives rise to great alkyl ester conversion in a shorter time [37]. An increase in the amount of alcohol in the oil increases the biodiesel yield and biodiesel purity. For this study transesterification reaction, the stoichiometric ratio said that 9 mol of methanol was needed to make 1 mol of glycerol and 9 mol of methyl ester. The reaction is reversible, which requires excess methanol to shift the reaction to the right to favor the products. The reaction was performed while varying the methanol:oil ratio from 3:1 to 9:1. The reaction time was 90 minutes in all experiments. The reaction temperature and catalyst were kept constant at 45˚C and 0.5% wt. KOH, respectively. The biodiesel yield for molar ratio 3:1 is 55.50 wt%; however, the amount of methanol concentration did not complete the phase separation. When increasing the methanol ratio to 9:1, the separation between transesterification reaction products was efficient, yielding 97.90 wt% methyl ester. When decreasing the methanol:oil ratio to 3:1, the yield decreases from 55.50 wt% due to the conglomeration of methanol. Reaction towards completion: the molar ratio should be higher than that of the stoichiometric ratio [37]. **Figure 6** present and verify this information.

3.3. Effect of Catalyst Concentration

In this study, it was found that the concentration of the catalyst has a big effect on the yield of methyl esters over a range of 0.625 - 3.125 wt% KOH while keeping the reaction temperature and the ratio of methanol to oil at 45˚C and 9:1, respectively. The reaction time was constant for 90 minutes throughout the experiment. It is observed that the lower catalyst concentration of 0.625 wt% KOH is enough to give a high yield of FAME in an increase in the amount of alcohol in the oil increases the biodiesel yield and biodiesel purity. The reaction time was 90 minutes in all experiments. The reaction temperature 45˚C and methanol:oil ratio 9:1 were kept constant at 45˚C and the catalyst concentration was varied. The biodiesel yield for catalyst concentration of 1.875 wt% KOH is 91.53% however, when the amount of catalyst concentration is 3.125 wt% KOH, the methyl ester yield is 69.60 wt%. Hence, the increase in catalyst concentration decreases the yield and favors the byproduct, which is a high yield of soap and water. The results show that the high concentration of an alkaline catalyst favors the saponification reaction. On the contrary, 0.625 wt% KOH catalyst concentration was considered to be the optimum catalyst concentration for the study. As mentioned in the study of Keera *et al.* [6] when increasing the concentration of catalyst it decreases the biodiesel yield. As presented in Figure 7.

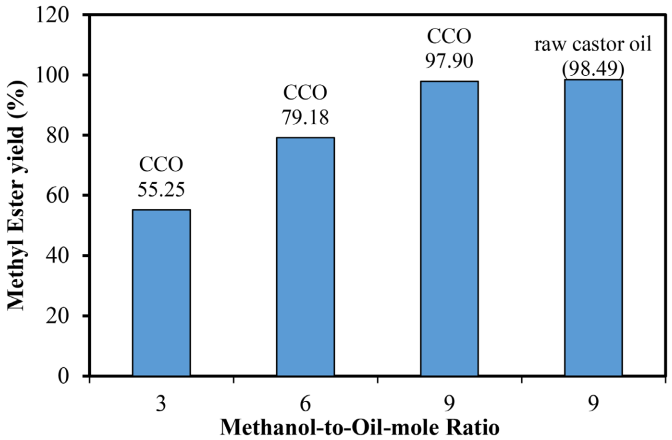


Figure 6. Effect of methanol to oil mole ratio on methyl ester.

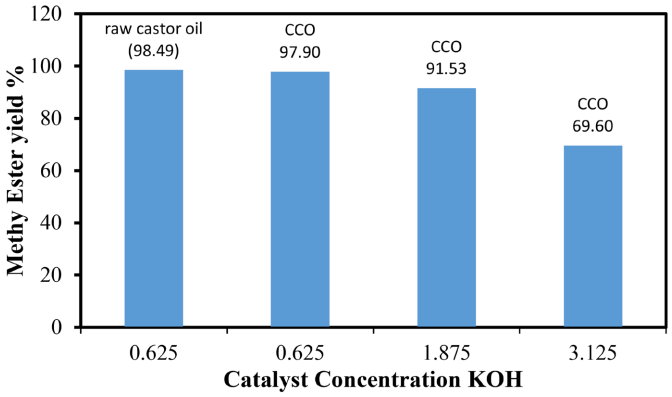


Figure 7. Effect of KOH catalyst concentration on methyl ester.

The outcomes indicate that the methyl ester biodiesel (FAME) produced using a jacketed reactor meets biodiesel specifications and ASTM standards. There are many characteristics of biodiesel, but the ones that directly affect the engine's performance, such as viscosity, flash point, density, etc. are the most crucial. All of these characteristics help the engine last longer, provide better lubrication, and enable complete combustion so that the engine can generate more energy.

3.4. Characterization of Methyl Ester

The physical and chemical properties characterization system was conducted in order to validate the procedures and consistency of the biodiesel data that had already been measured in previous studies [38] [39] [40]. **Table 3** presents the results of the calculation of absolute average deviation (AAD) as shown in Equation (14)

$$\mathrm{AAD} = \left[\frac{P_{\mathrm{lit}} - P_{\mathrm{meas}}}{P_{\mathrm{lit}}} \right] \tag{14}$$

Physiochemical properties were measured to ensure that the produce biodiesel from raw and refined meets the quality standard. These properties were listed in **Table 3**, one of the important property is the calorific value. This property described the quantity of heat energy produced when a unit of fuel burns. The calorific value of produced methyl ester biodiesel is 44121 kJ/kg was compared to the calorific value conventional diesel is 44,000 kJ/kg [28], the average absolute deviation was 0.275%.

Methyl Ester Kinetics

The Pseudo-First-Order model (PFO) and the Second-Order model (SO) were used to evaluated kinetics. Since the transesterification reaction is known to significantly deviate from the SO kinetics model, this equation has been presented to investigate the inhibitory influence of glycerol on the reaction. For both the initial phase and the end of the reaction, GRE and MSO kinetic modelling work effectively [33]. For the accuracy of the calculated reaction rate (r) values using kinetic modeling equation derived from assumptions, the absolute error was measured. **Table 4** presents the results of kinetic transesterification models that

Table 4. Kinetic of transesterification results.

T/K	GRE r (K, mL/mol, min)	PFO r (K, mL/mol, min)	SO r (K, mL/mol, min)	MSO r (K, mL/mol, min)	[a]RE (PFO)	[b]AE (PFO)	RE (SO)	AE (SO)	Ref (PFO)	Ref (SO)
318.15	8.48×10^{-08}	2.80×10^{-08}	3.44×10^{-08}	3.44×10^{-08}	0.997	1.23×10^{-05}	0.999	0.158	[31]	[32]
328.15	1.25×10^{-07}	4.53×10^{-08}	5.57×10^{-08}	5.57×10^{-08}	0.999	3.23×10^{-04}	0.999	0.276	[31]	[32]
338.15	1.59×10^{-07}	5.66×10^{-08}	6.95×10^{-08}	6.95×10^{-08}	0.998	3.11×10^{-05}	0.999	0.325	[31]	[32]
343.15	5.13×10^{-07}	5.49×10^{-09}	6.95×10^{-07}	6.96×10^{-07}	0.999	1.39×10^{-04}	0.999	0.001	[31]	[32]

[a]Relative error; [b]Absolute error.

were investigated for this study. Absolute error and relative error were calculated using Equation (15).

$$AE = Rate_{lit} - Rate_{Cal} \quad (15)$$

4. Conclusions

The characterization of castor oil favours direct transesterification since the acid value is below 4, which is the limit of the acid value. The absolute error ensured the accuracy of the calculated values since it was below 2. The transesterification reaction process approach followed in this study had a significant impact on producing biodiesel with a moderately high FAME yield. The results of this study agree with previous work by Keera *et al.* [6], which used commercial/purified castor oil. Ismail *et al.* [1] and Balamurugan *et al.* [41] used raw castor oil in their work, they obtained a 95% methyl ester biodiesel (FAME) yield in refined castor oil and a 94.9% methyl ester biodiesel (FAME) yield in raw castor oil respectively. In this study, 97.9% methyl ester yield was obtained using refined/commercial castor oil (CCO) and 98.49% methyl ester yield from raw castor oil, although the optimum conditions are not the same as in the literature.

Castor oil, both raw and refined, has been proven to be a good feedstock for the biodiesel production process in the Republic of South Africa and elsewhere according to the data collected and the results obtained in this work. However, competitive crops with superior biodiesel yields will always be preferred. High yields in raw castor oil show superiority over refined/commercial castor oil (CCO). The lower quantity of raw castor oil perhaps limited the study because of scarce availability which remains a matter of concern. The PFO model has less relative error than the SO model and is therefore it is more accurate. PFO and SO kinetics models are suitable for transesterification reactions at short initial times not for the whole range.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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