

Kinetics of Citrus Colocynthis Oil Transesterification

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Summary: Citrus Colocynthis oil and methanol was transesterified in the presence of NaOH as catalyst at five investigated temperatures, whereas the other reaction parameters were kept constant. This study was led to explore the kinetics of temperature and the effect of NaOH concentration on the transesterification reaction, and to assess the reaction constants and activation energies of the three forward reactions. The highest biodiesel yield of 97.8% was obtained at the optimum temperature of 60 °C. The reactions of triglycerides (TG), diglycerides (DG) and monoglycerides (MG) with methanol to produce methyl ester (ME) in the forward reactions appeared to be second order up to 60 min of reaction time. The kinetic constants for TG, DG and MG were found to be in the consecutive of MG>DG>TG. Activation energies were 14.1 kcal/mol, 10.5 kcal/mol, and 6.34 kcal/mol for the TG, DG, and MG hydrolysis reactions respectively.

Keywords: Biodiesel; Citrus Colocynthis oil; Kinetics; Methyl esters; Transesterification.

Introduction

The ASTM D6751-03 describes biodiesel as a fuel containing of long chain mono-alkyl esters derived from vegetable oils or animal fats. Various methods have been applied to convert the oil or fat into biodiesel, such as pyrolysis, microemulsion, catalytic cracking, and transesterification. Among these, the transesterification process has been found to be most suitable. The key of using the transesterification process is to reduce the vegetable oil viscosity, in order to make it suitable for vehicle fuel. The advantages of using biodiesel are to decrease carbon deposition in the engine, and decrease air pollution [1, 2].

Citrus Colocynthis, also termed as bitter apple, is a desert plant of the Cucurbitaceae family which can be found mainly in the gasping areas like the Mediterranean region of Cyprus, India, Sudan and many parts of Northern Africa, and parts of tropical areas in Asia.

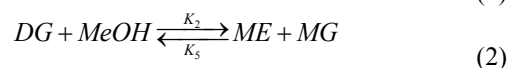
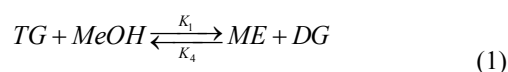
Although the importance of biodiesel as the best substitute for petroleum fuel has grown in the last few years, the chemical kinetics of the alcoholysis reaction is still contentious. A few studies have discussed the kinetics for both acid and alkali-catalyzed alcoholysis of vegetable oils. Those include the kinetics of transesterification of palm oil [3], rapeseed oil [4], soybean oil [5], and sunflower oil [6]. The kinetic study of alkali catalyzed transesterification of Citrus Colocynthis oil (CCO) is a new study and has never been done before. The optimum reaction conditions for the transesterification i.e. methanol to oil molar ratio and agitation rate were selected based on reported literatures. Several researches have reported that the optimum molar ratio of methanol to triglycerides is 6:1; no significant increase in yield was obtained at

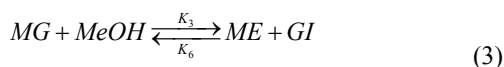
higher molar ratios [7]. The reaction agitation speed of 600 rpm was used in this study as recommended by Elsheikh [8], which was reported as satisfactory agitation speed for overcoming the mass transfer limitation during the transesterification reaction progress. Based on the respective study of transesterification of canola oil and sunflower oil by Leung and Guo [9] and by Rashid *et al.* [10], 1.0 wt% of NaOH was used for the transesterification of the CCO. Wang *et al.* [11] used 340 rpm for the biodiesel production while Issariyakul and Dalai [12] initiated that the reaction steps were reversible and mass transfer effect minimization was reported at an agitation speed of 600 rpm.

The main objective of this work is to investigate the kinetics of NaOH on the transesterification of CCO, keeping the molar ratio methanol/oil and agitation speed constants with the change of temperature and the concentration. This study also aims to explore the reaction constants and the energies of activation for the three forward reactions.

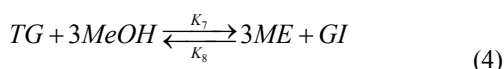
Kinetics Theoretical Background

Ruzich and Bassi [13] and Diasakou *et al.* [14] proposed the division of the overall transesterification reaction into three reversible reactions with intermediate creation of DG in the first reaction and MG produced from the reaction of DG and alcohol. The stepwise reactions are:





In general, the transesterification reaction of TG with methanol (MeOH) in the presence of a suitable catalyst, to form three moles of ME and a mole of Glycerol (GI) [14]. The general equation presented in Equation 4.



The general outline of the main set of equations describing the forward and reversible reactions associated with the transesterification, without the shunt reactions, calculated from the TG and the intermediates differential equations are as follows [15]:

The kinetic study in this work takes the following assumptions:

- (i) The concentration of FFA in the CCO is negligible.
- (ii) The reaction takes place in the oil phase.
- (iii) The use of excess methanol (>3:1) ensures the forward reaction [16].

$$\frac{d[TG]}{dt} = -k_1 [TG][MeOH] + k_4 [DG][MeOH] - k_7 [TG][MeOH]^3 + k_8 [MeOH][GI]^3 \quad (5a)$$

$$\frac{d[DG]}{dt} = k_1 [TG][MeOH] - k_4 [DG][ME] - k_2 [DG][MeOH] + k_5 [MG][ME] \quad (5b)$$

$$\frac{d[MG]}{dt} = k_2 [DG][MeOH] - k_5 [MG][ME] - k_3 [MG][MeOH] + k_6 [GI][ME] \quad (5c)$$

$$\frac{d[ME]}{dt} = k_1 [TG][MeOH] - k_4 [DG][ME] + k_2 [DG][MeOH] - k_5 [MG][ME] + k_3 [MG][MeOH] - k_6 [GI][ME] + k_7 [TG][MeOH]^3 - k_8 [GI][ME]^3 \quad (5d)$$

$$\frac{d[GI]}{dt} = k_3 [MG][MeOH] - k_6 [GI][ME] + k_7 [TG][MeOH]^3 - k_8 [GI][ME]^3 \quad (5e)$$

$$\frac{d[MeOH]}{dt} = -\frac{d[ME]}{dt} \quad (5f)$$

where [TG], [DG], [MG], [ME], [GI] and [MeOH] denote the molar concentration of TG, DG, MG, ME, GI, and methanol and $k_1, k_2, k_3, k_4, k_5,$ and k_6 are reaction rate constants.

- (iv) The backward reaction is neglected due to the usage of high quantity of methanol and the low concentration produced [3]. Thus, the transesterification kinetics was only calculated for the forward reactions.

Results and Discussion

Optimization of NaOH catalyzed transesterification

Alkaline catalyzed transesterification of CCO at five different temperatures (20–60 °C) were investigated. The other parameters, such as the molar ratio of methanol to oil, NaOH concentration, and the agitation speed were retained constant at 6:1, 1.0 wt%, 90 min reaction time and 600 rpm, respectively.

Effect of Reaction Temperature on NaOH Catalyzed Transesterification

Reaction temperature can have a significant effect on the reaction rate and biodiesel yield [17]. Figures 1–5 reveal the curves for the formation of ME and the rate of TG consumption, as well as the formation of intermediate compounds (DG and MG) during the reaction at the selected temperature range from 20 °C to 60 °C. Based on the results shown in Fig. 2, at 20 °C, the conversion rate is slow in the 90 min of reaction, which might be due to the high viscosity of the oil, which prevented it from mixing and solubilizing in methanol. Consequently, after completion of the reaction, the remaining TG was higher than DG and MG concentrations.

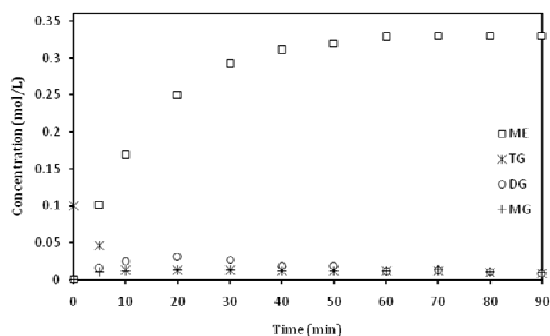


Fig. 1: Change of TG, ME, and intermediates concentrations during the transesterification reaction of CCO at 20 °C

Increasing the reaction temperature from 20 °C to 30 °C, at the same reaction conditions, led to an increase in the ester yield from 83.8% to 89.9% (see Fig. 2). However, the TG concentration, after 30 min of reaction, was lower than the DG and MG.

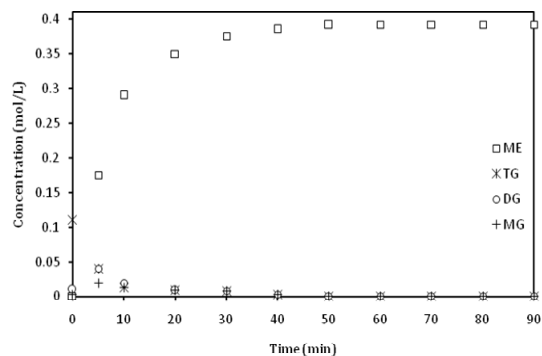


Fig. 2: Change of TG, ME, and intermediates concentrations during the transesterification reaction of CCO at 30 °C

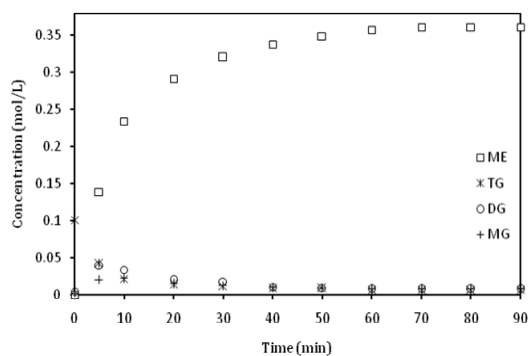


Fig. 3: Change of TG, ME, and intermediates concentrations during the transesterification reaction of CCO at 40 °C.

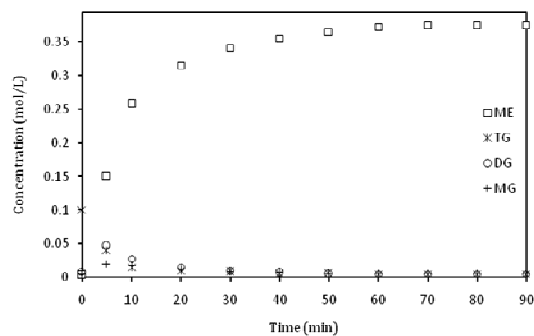


Fig. 4: Change of TG, ME, and intermediates concentrations during the transesterification reaction of CCO at 50 °C.

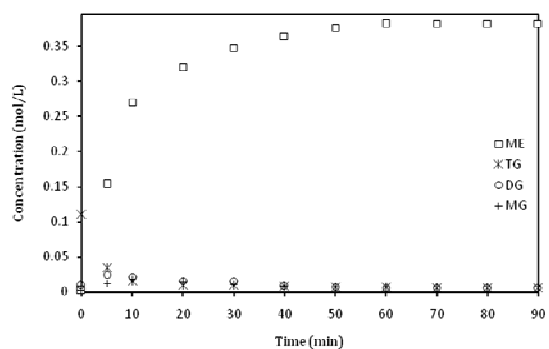


Fig. 5: Change of TG, ME, and intermediates concentrations during the transesterification reaction of CCO at 60 °C.

Fig. 5 shows that the maximum yield of 97.8% was achieved at a higher temperature of 60 °C. In the first 10 min, the ME concentration increased from 0–80.5% while the TG concentration dropped from 95.4% to 5.1%. On the other hand, in the first 10 min, the DG increased and then started to fall meaning that it was converting to MG as soon as it formed. Similarly for the DG, the concentration of MG primarily elevated until it's at a maximum concentration in 20 min, and then it began to drop very slowly. The expected behavior of the homogeneous reaction is that the concentration of TG ultimately falls below the concentration of DG and MG [18].

Generally, in the transesterification reaction the mixture contains three phase system of the two reactants (oil and methanol) and catalyst, in which the diffusion resistance between different phases took place and as a result the reaction would be inhibited. This is may be due to that at high temperatures the solubility of the reactants will be increased and consequently enhance the contact between the

reactants and the catalyst. Therefore, the reaction rates can be prompter at elevated reaction temperature.

Determination of Kinetic Parameters

To correlate the experimental results achieved from the reaction time and five different temperatures, the kinetics analysis came out with the set of three rate constants for each temperature.

The initial fatty acid composition of CCO was measured and found to be containing 95.4% TG, 4.1% DG, and 0.50% of MG. CCO was found to be containing eleven fatty acids, of these four fatty acids including linoleic acid (C18:2), oleic acid (C18:1), palmitic acid (C16:0), stearic acid (C18:0) are the main components, while the other seven fatty acids which are myristic (C14:0), palmitoleic (C16:1), margaric (C17:0), linolenic (C18:3), arachidic (C20:0) gadoleic (C20:1), and behenic (C22:0), are presented in minor amounts. The average molar weight of ME, TG, DG, and MG were 285, 853, 597, and 345 respectively, detected by gas chromatography, in terms of the oil fatty acid composition, using the official methods and recommended practices of the AOCS of Ce 1-62 [19].

The configuration of DG, MG, and even soaps surface active was found to be forming a very little but stable emulsion. Therefore, the reaction mixture can be deliberated as a pseudo-homogeneous media and the reaction kinetics was controlled by the transesterification reaction. In this work, with the above mentioned assumptions, the reaction order is assumed to be a pseudo second order reaction, thus the TG rate of reaction stated in Equation 2 would conform to the following law [3]:

$$\frac{d[TG]}{dt} = -k_{TG} [TG]^2 \quad (6)$$

By integrating Equation 1:

$$\frac{1}{[TG]} - \frac{1}{[TG^0]} = k_{TG}.t \quad (7)$$

Likewise, integration of Equations 2 and 3 would obtain the reaction constant for DG and MG as given below:

$$\frac{1}{[DG]} - \frac{1}{[DG^0]} = k_{DG}.t \quad (8)$$

$$\frac{1}{[MG]} - \frac{1}{[MG^0]} = k_{MG}.t \quad (9)$$

Where t is the reacted time, [TG⁰] is the TG initial concentration; [DG⁰] and [MG⁰] are the initial highest concentrations of di and monoglycerides.

The forward kinetic constants and their corresponding correlation coefficient values obtained at 5 different temperatures and for 90 min of reaction time are shown in Table 1. The values in the table are average of triplicate runs for each set of conditions. The values of reaction constant are observed to increase at higher temperature. The reaction constant for MG is higher than the reaction constant for DG, which is higher than the reaction constant for TG.

The Svante Arrhenius theory gave quantitative basis for the relationship between the activation energy, temperature and reaction rate constant and the final form of the equation can take a linear form and can be expressed as follows:

$$k = e^{-\frac{E_a}{RT}} \quad (10)$$

Integration of Equation 10 yields:

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad (11)$$

Where E_a is the activation energy (kcal/mol), k is the average overall reaction rate constant, A is an Arrhenius constant, R is the universal ideal gas constant (cal/mol.K) and T is the absolute temperature in Kelvin.

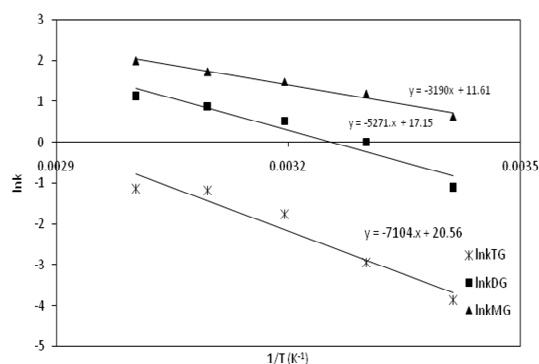


Fig. 6: Plot of $\ln k$ (natural logarithm of the rate constant) versus the inverse of absolute temperature ($1/T$) in Kelvin for the transesterification reaction.

Table-1: Reaction rates for TG, DG and MG at different investigated temperatures

Temperature (°C)	TG → DG		DG → MG		MG → GI	
	k _{TG} (1/molar.min)%	R ²	k _{DG} (1/molar.min) %	R ²	k _{MG} (1/molar.min) %	R ²
20	0.021	0.987	0.327	0.957	1.871	0.982
30	0.052	0.991	1.002	0.95	3.256	0.971
40	0.171	0.889	1.697	0.979	4 .429	0.898
50	0.306	95.1	2.424	95.7	5.574	92.4
60	0.319	99.3	3.042	98.6	7.265	97.7

Arrhenius equation and the calculated reaction constants were both used to define the activation energy for MG, DG, and TG from plotting the inverse of absolute temperature (1/T) and the overall reaction rate constant. As can be seen in Fig. 6, a straight line with a slope of $-E_a/R$ was resulted.

Table 2 presents the estimated activation energies for the overall forward reactions. At the end of the transesterification reaction, as expected, at higher temperatures the concentrations of MG were higher than TG and DG. Therefore, the third reaction (equation 4), was found to be having a lower activation energy than the others. These results were in conformity and within the range of results found by Darnoko *et al.* [3] and Nouredini and Zhu [5].

Table-2: Arrhenius activation energy E_a in kcal/mol for TG, DG, and MG during transesterification of CCO

Glyceride	E_a (kcal/mol)	R ²
TG	14.1	0.975
DG	10.5	0.926
MG	6.3	0.935

Fuel Properties of CCOME

The selected fuel properties of the CCOME are presented in Table 3. The results are found to be within the acceptable limit of the American Standards for Testing of Material (ASTM D6751-03) specifications.

Table-3: Fuel properties of CCOME as compared to ASTM D6751-03 biodiesel specifications.

Property	Unit	CCOME quality	Limits	Test methods
Flash point	°C	172	≥130	ASTM D93
Kinematic viscosity, 40°C	mm ² /s	3.8	1.9–6.0	ASTM D445
Density	kg/m ³	879	860–900	ASTM D4052
Cetane no.	–	61.8	≥47	ASTM D613
Sulfated ash	% mass	0.004	≤0.02	ASTM D874
Free glycerine	% mass	0.009	≤0.02	ASTM D6584
Total glycerine	% mass	0.08	≤0.24	ASTM D6584
Acid value	mg KOH/g oil	0.24	≤0.50	ASTM D664
Distillation temperature, 95%	°C	349	≤360	ASTM D1160

Experimental

Materials

Citrus Colocynthis seeds were collected from Atbara market, Sudan. The extraction of CCO was performed according to the AOAC official method 963.15 [19], on a soxhlet in which n-hexane was used as the solvent of oil extraction.

The following chemicals were used in this work: esters reference standards including methyl esters of methyl heptadecanoate, methyl myristate, methyl laurate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, 1,2,4-butanetriol (5 mL, concentration 1 mg/mL in pyridine) assigned as internal standard 1, and internal standard 2 of tricaprins (5 mL, concentration 1 mg/mL in pyridine) were purchased from Supelco (USA). N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA), besides, monolinolein (99%), dilinolein (99%), trilinolein (99%), methanol (>99.8%); and n-heptane (GC grade, >99%) were provided by Sigma-Aldrich Company (Malaysia). All the chemicals require no drying or any further purification.

Characterization of CCO

Some of the oil properties were presented in Table 4. The free fatty acid content of CCO as determined by AOCS titration method [19] was 0.9%, which is lower than the recommended maximum acidity for alkali catalyzed transesterification [7, 10]. The density was examined by an Anton Paar density meter, the kinematic viscosity was analyzed by an Ubbelohde glass viscometer while the iodine value was determined according to the recommended AOCS method of cd 1c-85 [19].

The fatty acid composition was determined using Agilent/HP 6890A technology GC equipped with a FID and Supelco-2340 capillary column with various specifications of 60 m column length, 25 mm internal diameter, and stationary phase film thickness of 0.2 μm at a split injection of 100:1. Before injection, the samples were diluted 100 times in n-

hexane. The oven initial temperature was set at 150 °C for 90 seconds, then the temperature was raised at a ratio of 3 °C/min up to 210 °C, after 30 seconds the temperature was finally raised to 240 °C at the same rate and was held for 8 min. The detector and injector temperatures were set at 240 °C. A constant carrier gas of Ultra highly pure helium at a fixed flow rate was used. A triplicate GC run of the sample was performed.

Table-4: Physicochemical properties of CCO.

Acids	CCO
Density, 20°C (kg/m ³)	925.7
Kinematic viscosity, 38°C (mm ² /s)	35.20
Iodine value (g I/100 g oil)	107.4
Fatty acid composition (wt%)	
Myristic acid (C14:0)	0.70
Palmitic acid (C16:0)	10.53
Palmitoleic acid (C16:1)	0.05
Margaric acid (C17:0)	0.14
Stearic acid (C18:0)	9.57
Oleic acid (C18:1)	14.07
Linoleic acid (C18:2)	64.65
Linolenic acid (C18:3)	0.10
Arachidic acid (C20:0)	0.12
Gadoleic acid (C20:1)	0.06
Behenic acid (C22:0)	0.01

Transesterification Reaction

A 100 g of CCO was placed in the reactor and was heated while stirring up to the desired temperature. After reaching the desired temperature, a pre-calculated amount of freshly prepared NaOH-alcohol mixture was mixed with the oil. At considered time intervals, a sample was taken from the transesterification reactor for kinetic analysis. When the target reaction time was reached, the transesterification reaction was stopped and the mixture was cooled to room temperature.

The reaction product mixture was subjected to settling step to allow the liquid phases to separate by gravity. A glycerol, catalyst residue and excess methanol layer at the bottom, and a top layer holding crude ester phase. The crude ester layer was then collected after being washed repeatedly with water, warmed at 50 °C [10], to remove the spent catalyst from the ester.

Characterization of Biodiesel

The derivatized samples were analyzed to determine the concentration of Citrus Colocynthis methyl esters (CCOME), monoglycerides, diglycerides, and triglycerides in triplicate by gas chromatography.

A Shimadzu Chromatographic analysis equipped with AOC-20i autoinjection and FID was

performed. The capillary column was Supelco SGE HT-5; 10 m length, 0.32 mm inside diameter and coated with a 0.1 µm film thickness of an excellent thermal stability dimethylpolysiloxane phase. After steadying for 1.0 min and 50 °C, the oven temperature was increased to 180 °C, then raised at a ratio of 7 °C/min up to 230 °C, followed by another temperature ramp at a ratio of 10 °C /min and was held at 370 °C for 5 min. The analysis time of the glycerides was approximately half an hour to confirm their complete elution. The carrier gas, helium with a minimum purity of 99.95 mol % with gas flow of 3 mL/min and injector split setting of 100:1, depending on volume injected. The detector temperature was allocated at 380 °C. A 1.0 µL automatic syringe sample was injected into the GC.

Conclusion

The transesterification progress was studied at different temperatures as a function of time in order to determine the optimum temperature. At 60 °C the formation of the methyl ester was very rapid in the first 5 min of reaction, then moderated and reached equilibrium at approximately 50 min.

The best biodiesel yield of 97.8% was obtained under the optimal reaction conditions of 60 °C, 6:1 molar ratio of methanol to CCO, 1.0 wt% catalyst concentration, and stirring rate of 600 rpm. The considerable yield of methyl ester, besides its good properties could make the CCO suitable for industrialization.

The obtained activation energies revealed that highest increasing reaction temperature had a significant effect on ester conversion. The experimental rate constants are well fitted by linear regression of 1/T plotted against ln k for each type of fatty acid.

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