



Kinetic and Thermodynamic Studies of Microwave-Assisted Transesterification of Papaya Oil

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Microwave-assisted transesterification due to drastic reduction in reaction time when compared with conventional method gain the research attention. Present study explores the kinetic and thermodynamic study of microwave-assisted transesterification of non-edible papaya oil. The experiments were performed using pre-optimized process parameters having 9:1 molar ratio of methanol to oil, 1 wt. % NaOH catalyst. The experiments carried out in commercial microwave reactor with infrared temperature controller. Kinetic study of microwave-assisted palm oil methyl ester (POME) conversion was carried out by varying temperature from 50 to 65 °C with an increment of 5 °C. Kinetic study revealed that microwave-assisted homogeneous alkali-catalyzed transesterification follows first order having lower activation energy 27.86 KJ mol⁻¹. Also, higher frequency factor 14764 min⁻¹ and rate constant 0.6703 min⁻¹ at 60 °C revealed the non-thermal and thermal effect of the microwave. Other thermodynamic properties such as ΔG , ΔH and ΔS were found out to be 94.48 KJ/mol, 24.87 KJ/mol and -0.209 KJ/mol K, respectively, which show that reaction is non-spontaneous, endothermic and endergonic in nature.

Keywords: Papaya oil, Biodiesel, Microwave, Transesterification.

INTRODUCTION

Biodiesel is future of fuel, since conventional feedstocks are limited and polluting. The feedstock for biodiesel synthesis is oil based on its availability is further classified as edible, non-edible and waste oil. The use of edible oil is criticized due to food security as well as forest land issue. Various non-edible oils such as neem [1], karanja [2] and jatropha [3] were explored for biodiesel synthesis. However, limited investigation on papaya oil as a feedstock for biodiesel was found in the research literature. India share 35 % of papaya production and placed at 4th position worldwide [4,5]. An estimated papaya oil production is approximately 0.32 lakh tons per annum [6].

In literature, conventional heat source was explored for esterification and transesterification of raw papaya oil [7]. However, kinetic study of microwave-assisted transesterification of papaya oil is not yet reported in literature. Microwave as a heat source has several advantage over conventional heat source in term of energy requirement and time required for conversion. Lin *et al.* [8] reported that energy required is 10

times lower while time required for transesterification is 13 times lower. On the other hand, Patil *et al.* [9] reported 23 times lower energy consumption for given yield in transesterification. Susceptibility of heating under influence of microwave mainly depends upon dielectric constant and dielectric loss of material [10]. Methanol due to its high dielectric loss tangent and high reactivity is used for biodiesel synthesis. Transesterification reaction involved the conversion of triglycerides into monoalkyl esters in presence of methanol. The overall reaction takes place in three steps: (i) conversion of triglycerides into diglycerides, (ii) diglycerides into monoglycerides and fatty acid alkyl ester, (iii) finally monoglycerides to monoalkyl esters and glycerol. Fig. 1 presents overall transesterification reaction. Present study investigates the kinetics and thermodynamic study of microwave-assisted transesterification of papaya oil.

EXPERIMENTAL

Refined papaya oil was purchased from M/s Katyani Exports Pvt, Ltd., New Delhi, India. All chemicals such as NaOH,

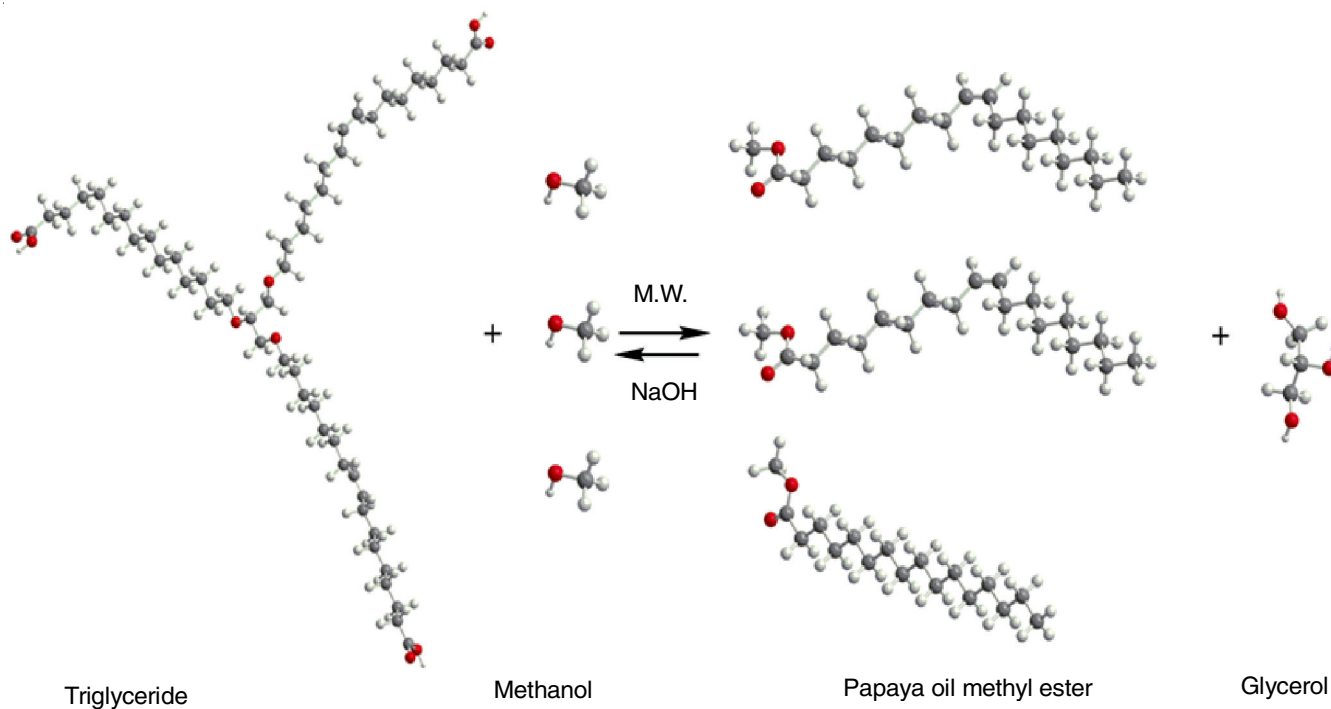


Fig. 1. Microwave-assisted transesterification of triglyceride of papaya oil into papaya oil methyl ester

KOH, and methanol were of AR grade and 99 % pure. Acid value and saponification value of papaya oil were 0.8 and 194 mg g^{-1} , respectively. The fatty acid composition of papaya oil were : oleic acid 80.57 %, palmitic acid 9.33 %, behenic acid 1.96 %, eicosenoic acid 1.46 %, arachidic acid 1.17 %, lignoceric acid 0.99 %, palmitoleic acid 0.73 %, linoleic acid 0.71 % and myristic acid 0.21 %. The degree of unsaturation of papaya oil is found to be 83.47 %. Molecular weight of papaya oil based on fatty acid composition is 866 g mol^{-1} . The physico-chemical properties of papaya oil such as density, viscosity and cloud point were found to be 907 kg m^{-3} , 29.30 cSt and $-0.1\text{ }^\circ\text{C}$, respectively.

General procedure: Microwave-assisted transesterification of papaya oil was carried out in a 250 mL glass flask with a water-cooled condenser at the top. It was charged with 5 mL (4.52 g) of oil, 09:01 molar ratio of alcohol and 1 wt. % of NaOH of catalyst. The reaction temperature was controlled by infrared temperature sensor with a controller. The kinetic evaluation of biodiesel production *via* microwave-assisted transesterification from papaya oil was done at 50, 55, 60 and 65 $^\circ\text{C}$ at a different time interval. The reaction mixture was stirred magnetically and refluxed for the required reaction time. The reaction was carried out at 700 W and the reaction mixture was cooled and allowed to settle down into two layers.

Top layer mainly consists of papaya oil methyl ester and unreacted triglycerides (oil), while bottom aqueous layer mainly having glycerol and methanol. Traces of methanol present in oil phase were removed by heating at 70 $^\circ\text{C}$ for several minutes.

Detection Method: Top layer biodiesel purity was confirmed by 3:27 test [11]. The yield of palm oil methyl ester (POME) is calculated by eqn. 1:

$$\text{Yield of POME} = \frac{\text{Amount of POME produced}}{\text{Theoretical maximum amount of POME produced}} \quad (1)$$

RESULTS AND DISCUSSION

Rate constant and order of reaction: The transesterification reaction kinetics is represented by eqn. 2 [12]:

$$\frac{-d[\text{Ca}]}{dt} = k \times [\text{Ca}]^n \times [\text{MeOH}]^m \quad (2)$$

As per stoichiometry, methanol requirement is 3:1 and during the kinetic study. During the experiment, the excess molar ratio 9:1 was used hence reaction kinetics is pseudo-order with respect to the concentration of methanol. It is expressed as:

$$\frac{-d[\text{Ca}]}{dt} = k \times [\text{Ca}]^n \quad (3)$$

The initial concentration of triglycerides was 0.00075 mol/mL. As the reaction proceeds, the triglyceride converted into palm oil methyl ester (POME). Fig. 2a presents the concentration of POME with time at 50, 55, 60 and 65 $^\circ\text{C}$. The amount of methyl ester formed was determined to calculate the moles of triglyceride unreacted during transesterification. The differential analysis was used to evaluate the rate of reaction and order of the reaction. Fig. 3b shows the differential plot of $\ln d[\text{Ca}]/dt$ vs. $\ln [\text{Ca}]$ for 50, 55, 60 and 65 $^\circ\text{C}$. A straight line is observed with the R^2 values greater than 0.9 indicating that the good agreement with experimental data.

The slope of straight line was used to find the order of the reaction while intercept on Y-axis gave the value of $\ln k$ from which reaction rate constant was evaluated. The microwave-assisted transesterification of papaya oil followed first-order kinetics and the rate of the reaction varies linearly with a yield of methyl ester of palm oil. The order of reaction and rate constants are summarized in Table-1.

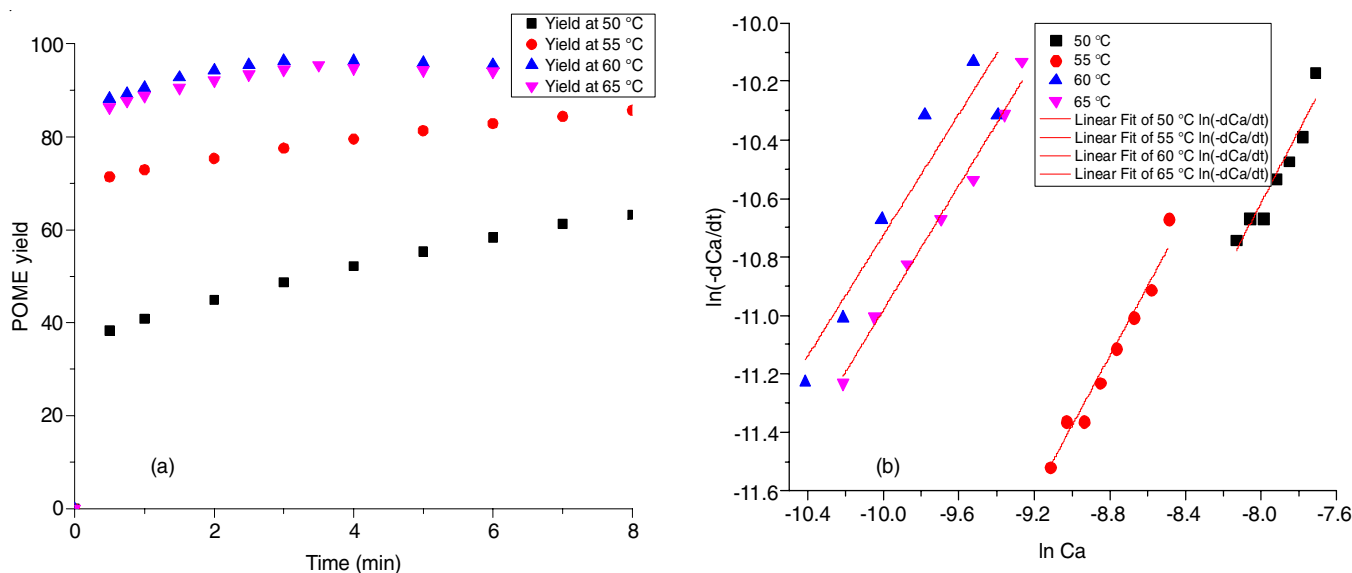


Fig. 2. (a) POME yield with time at a different temperature, (b) Plot of $\ln(-dCa/dt)$ vs. $\ln Ca$ for 50, 55, 60 and 65 °C

TABLE-1
ORDER OF REACTION AND RATE CONSTANT FOR MICROWAVE ASSISTED
TRANSESTERIFICATION OF PAPAYA OIL AND ANOVA OF LINEAR FIT

Temp. (°C)	Order of reaction (n)	ln k	k (min ⁻¹)	R ²	Adj. R ²	F value	P value
50	1.20	-0.77	0.4630	0.99999	0.99997	268463	3.44×10^{-15}
55	1.19	-0.66	0.5168	0.99999	0.99998	387081	0
60	1.03	-0.40	0.6703	0.99992	0.99980	32676	9.83×10^{-11}
65	1.06	-0.35	0.7046	0.99999	0.99998	455520	6.66×10^{-16}

Activation energy: The Arrhenius equation is used to relate the temperature dependency of rate constants. It is expressed by eqn. 4 [13]:

$$K = A_e^{-E_a/RT} \quad (4)$$

where, A is frequency factor (min⁻¹), which measures frequency of collision between reactants. E_a is activation energy (J/mol) for product formation. R is the molar universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K).

By taking the natural logarithm eqn. 4 can be expressed as eqn 5:

$$\ln K = \ln A - E_a/RT \quad (5)$$

The change in the yield of methyl ester of palm oil was studied with the change in temperature from 50 to 65 °C and the results were used to plot the graph between k (rate constant) and temperature. The straight line with the R² value of 0.99 obtained in the graph revealed that reaction follows the first order kinetics. The activation energy and frequency factor for the reaction was determined from the plot of ln k and 1/T. The activation energy and frequency factor found to be 27.86 KJ/mol and 14764 min⁻¹, respectively.

The activation energy of oil depends upon the types of fatty acid as well as degree of unsaturation of fatty acid in the oil. Oil with higher unsaturations is prone to other undesired side reactions. It lower down the reaction rate, hence it has higher activation energy. Apart from nature of oil, other factors, affecting the activation energy are temperature, the source of heating, type of catalyst and catalyst amount. It was reported that, under influence of the nonthermal effect of the microwave,

the active intermediate complex had a lower state of energy which reduced the activation energy [14]. Pre-exponential factor (A) in this study shows high frequency of collision in the microwave-assisted transesterification of papaya oil. It improved the possibility of molecular collision due to the dipolar rotation and ionic movement [15].

Thermodynamic parameters: Eqn. 6 presents the Eyring-Polanyi equation for determine the Gibbs free energy (ΔG) for known value of rate constant (k) [16].

$$k = \frac{K_b T}{h} \times \exp\left(\frac{-\Delta G}{RT}\right) \quad (6)$$

Linear form eqn. 6 can be expressed by eqn. 7 as:

$$\ln k = \ln \frac{K_b T}{h} + \left(\frac{-\Delta G}{RT}\right) \quad (7)$$

Relation of enthalpy and entropy change for Gibbs free energy is written by $\Delta G = \Delta H - T\Delta S$.

Eqn. 7 is written as:

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + \ln \frac{K_b}{h} \quad (8)$$

where, k: rate constant (s⁻¹); T: absolute temperature (K); R: universal gas constant 8.314 J mol⁻¹ K⁻¹; K_b : Boltzmann constant (1.38×10^{-23} J K⁻¹); h: Plancks constants (6.63×10^{-34} Js).

Using eqn. 7 and the values of slope and intercept of the Eyring plot (figure not shown) between 1/T and ln k/T, the values of ΔG , ΔH and ΔS can be calculated. The values of ΔH and ΔS found to be 24.87 KJ/mol and -0.209 KJ/mol K,

TABLE-2
SUMMARY OF COMPARISON OF KINETIC AND THERMODYNAMIC PROPERTIES OF POME

Triglyceride	Source of heating	Reaction condition	n	k (min ⁻¹)	A (min ⁻¹)	E _a (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	Ref.
Papaya oil 0.83 AV U: 83 %	M, Batch	NaOH 1 wt %, 9:1 MeOH:Oil, 60 °C	1	0.6703	14764	27.86	94.48	24.87	-0.209	Present work
Waste cooking oil 2.45 AV U: 96 %	M, Batch	CaDG 1 wt %, 9:1 MeOH:Oil, 70 °C	1	0.139	1650	26.56	N.D.	N.D.	N.D.	[20]
Soybean oil 0.2 AV	C, Batch	CaO/Al ₂ O ₃ 6 wt % 12:1 MeOH:Oil, 60 °C	1	0.004	166	36.34	N.D.	N.D.	N.D.	[21]
Soybean oil 0.5 AV	C, Batch	0.77 wt % NaOH, 1.76 wt % bentonite, 40- 65 °C, 7.47:1 MeOH:oil	1	0.08-0.2	12456	31.03	83.3- 87.69	28.33	-0.18	[17]
Sunflower oil 0.1 AV	C, Batch	3 wt % MgO-La ₂ O ₃ , MeOH:oil 18:1, 65 °C, 700 rpm, 5 h,	2	0.0015	3.5	77.6	-20.7	162	0.54	[22]
Chinese tallow seed	M, Continuous	NaOH 4 wt %, 47.5:39.3:20 MeOH:Heane:Oil(w/w) , 60 °C	1	0.0846	5.5 × 10 ⁷ L mol ⁻¹ min ⁻¹	2.057	85.57	-0.574	-0.267	[14]
Schleichera triguga oil 0.84 AV	US	Ba(OH) ₂ 3 wt %, 9:1 methanol to oil molar ratio	2	0.2678	6.1 × 10 ⁷ L mol ⁻¹ min ⁻¹	53.26	82.44- 85.55	50.62	-0.11	[23]
Spirulina platensis algae biomass U 41 %	C	H ₂ SO ₄ 60 wt % of biomass, 1:4 wt/volume ratio	1	0.001	2.21	14.51	92.71	16.35	-0.23	[18]
Soybean oil	S	CH ₃ ONa 250 °C, 23:1 MeOH:Oil, 1 wt % NaOH	1.5	0.1730	102.07	27.06	137.43	23.15	-0.22	[24]
Leather tanning waste U: 71 %	S	Non catalytic 250-325 °C, 12 MPa, 40:1 MeOH:Oil	1	0.32- 0.96	1176	36.01	153.64- 171.16	31.37	-0.233	[19]

AV = Acid value mg KOH/g of oil, M = microwave, C = Conventional, U = Un-saturation, US = Ultrasound, S = supercritical, n = order of reaction, k = rate constant, A = Pre-exponential factor, E_a = Activation energy, N.D. = Not determined, MeOH = methanol, CaDG = Calcium diglyceride

respectively. Thus, at 333 K, ΔG found to be 94.48 KJ/mol. A positive value of ΔH shows that heat input is required to bring the reactants to the transition state to form the products. A negative value of ΔS indicates that the degree of ordered geometry/alignment of the transition state is better as compared to reactants in ground state. A positive value of ΔG indicates that the reaction is unspontaneous and endergonic in nature. Table-2 summaries the comparison of kinetic and thermodynamic properties of present work with reported work in literature. Thermodynamic parameters such as ΔH and ΔS obtained in the microwave-assisted transesterification of papaya oil differs from soybean oil [17], Spirulina platensis algae [18], leather tanning waste [19] and, Schleichera triguga oil [18]. The variation in a kinetic and thermodynamic parameters is due to the variation in fatty acid composition, degree of unsaturation and difference in methodology adopted for biodiesel production.

TLC analysis: Thin layer chromatography (TLC) test was performed using silica gel fluorescent indicator F254. The solvent hexane, diethyl ether and acetic acid with volume ratio 80:20:1 was used for TLC. The spot observed at retention factor (R_f) 0.74, 0.49 and 0.35 correspond to the position of methyl esters, triglyceride and diglyceride, respectively. The spots at R_f 0.25 and 0.18 represents monoglycerides and free fatty acid, respectively. The spot of triglyceride disappeared with time indicates the conversion of triglyceride into biodiesel.

Conclusion

Kinetic study of microwave-assisted transesterification of papaya oil was carried out by varying temperature from 50 to 65 °C at an increment of 5 °C. The experiments were performed using pre-optimized process parameters having 9:1 molar ratio of methanol to oil, 1 wt. % NaOH catalyst. Kinetic study revealed that microwave-assisted homogeneous alkali-catalyzed trans-

esterification follows first order having lower activation energy 27.86 KJ/mol. Also, higher frequency factor 14764 min⁻¹ and rate constant 0.6703 min⁻¹ at 60 °C revealed the non-thermal and thermal effect of the microwave. Other thermodynamic properties such as ΔG , ΔH and ΔS were found out to be 94.48 KJ/mol, 24.87 KJ/mol and -0.209 KJ/mol K, respectively, which showed that reaction is non-spontaneous, endothermic and endergonic in nature.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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