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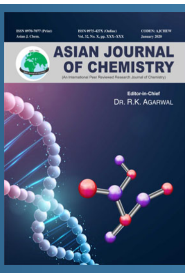

Microwave-Assisted Transesterification of Kusum Oil: Parametric, Kinetic and Thermodynamic Studies

SHEETAL N. NAYAK[1,*], MILAP G. NAYAK and CHANDRAKANT P. BHASIN[1]

[1]Department of Chemistry, Hemchandracharya North Gujarat University, Patan-384265, India
[2]Department of Chemical Engineering, Vishwakarma Government Engineering College (Affliated to Gujarat Technological University, Ahmedabad), Chandkheda-382424, India

*Corresponding author: E-mail: shitalnayak555@gmail.com

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Microwave-assisted transesterification of non-edible oil to produce biodiesel is gaining attention due to lower heat loss as well as rapid conversion. In this study, esterified kusum oil as a feedstock was transesterified in the presence of $Ba(OH)_2$. At 800 W microwave power and constant magnetic stirring the effect of important process parameters such as solvent methanol molar ratio, $Ba(OH)_2$, temperature, and time on biodiesel yield were evaluated. The parametric study suggested that 9:1 M methanol, 65 ºC reaction temperature, 2.5 wt% $Ba(OH)_2$ catalyst and 3.5 min of transesterification time gave close to 96% biodiesel yield. At the above conditions of methanol and catalyst, the reaction kinetics and thermodynamic study were performed using different time intervals. The microwave-assisted transesterification followed pseudo-first-order reaction rate with 34.57 kJ/mol K activation energy and 205664 min^{-1} frequency factor. The reduction in activation energy and increase in the frequency factor reveal the non-thermal effect associated with microwave heating. The thermodynamic properties evaluated using the Eyring equation suggests non-spontaneity and endothermic nature of transesterification.

Keywords: Esterified Kusum oil, Transesterification, Reaction kinetics.

INTRODUCTION

The reduction of oil reserves, growing demand for energy due to technological advancement and population rise, and the increasing environmental concerns about the use of fossil fuels have encouraged the scientific community to develop the novel, non-polluting, and renewable fuel sources [1]. Worldwide new policies are framed to motivate eco-friendly and renewable energy sources [2,3]. The use of solar, wind, tidal and bio-resources are some of the energy sources, which are gaining a lots of attention today [4-6]. Out of which, biodiesel is one of the potential and economical substitutions of fossil fuels [7]. Biodiesel is produced from various feedstock including vegetable oils, animal fats, waste oil and microalgae by transesterification with alcohol in the presence of acid or base catalysts [8]. The physico-chemical properties of biodiesel such as density, viscosity, pour point, flash point, and cetane number are similar or better than the petrodiesel. It enables the use of direct use or blending of biodiesel with petrodiesel without modification in the engine [9]. The edible oils are available readily due to industrial-scale plantation, but their usage for biodiesel is not advisable due to the food crisis and ecological imbalance [10]. It was estimated that biodiesel production cost largely depends upon the cost of feedstock which is around 70-80% [11-13]. The problem associated with the economy of biodiesel can be addressed by the use of abundantly available, low cost non-edible oil plants. In this context, various nonedible oil seeds such as palm [14,15], neem [16,17], jatropha [18-20], mahua [21,22], papaya [11,23], rubber [10,24,25], karanja [26-28], and algae [29-31] have been explored for biodiesel synthesis.

Schleichera oleosa is a non-edible oil tree found in the forest region in central and north-east of India and also in South-eastern Asia [32,33]. It is also known as Kusum tree, which contain more than 50% oil in seed and used for cooking fuel and lighting purpose [34]. The tree grows to 35 to 45 feet and yields fruit in June and July. In India, the estimated oil obtained from Kusum as a feedstock is 25 kiloton per year and it is a potential feedstock for biodiesel [35].

Bhatia *et al.* [36] reviewed Kusum oil potential for biodiesel and other antioxidant properties. Kumar and Tomar [33] investigated Kusum oil methyl ester (KOME) synthesis by esterification *via* *p*-toluene sulfonic acid followed by transesterification with KOH to produce biodiesel. They used a conventional heating system for biodiesel synthesis, which requires more than 100 min of reaction time for conversion. Asri *et al.* [37] synthesized high surface area nano ZnO-CuO/γ-alumina solid catalyst for transesterification of Kusum oil with methanol and obtained 89.71% yield at 80 ºC, 15:1 M methanol to oil ratio in 12 h reaction. The study revealed that the physico-chemical properties of KOME were close to diesel and found to be suitable for the diesel engine. Sharma *et al.* [38] prepared strontium lanthanum mixed metal oxide for the transesterification of Kusum oil and obtained high quality of biodiesel at optimized conditions. Ong *et al.* [32] optimized the KOME production using two-step synthesis and revealed that the physico-chemical properties of obtained KOME were superior to petro diesel. Sharma and Yadav [35] synthesized KOME *via* two-steps chemical processes and optimized the yield of maximum 97.08% conversion of biodiesel.

Most of the reported studies were carried out using conventional heating source for the transesterification of oil. The microwave as a heat source gaining attention in chemical synthesis due to its ability to speed up the chemical synthesis due to the changes in the electron cloud distribution, length and angle of the bond of molecules under the influence of microwave stimulates the reaction to occur [39]. Lin *et al.* [40] and Patil [41] indicates the microwave as a heat source significantly saves time and energy requirements. The reduction of time is largely due to the dipolar polarization, ionic conduction, hot spot generation [42]. Heat absorption by catalyst overcome the barrier for transesterification of oil and reduces time considerably [43]. The non-thermal effect of microwave caused a reduction in energy of activation, improve pre-exponential factor and reduced Gibbs′ free energy change compared to conventional heating [44,45]. The current study deals with the effect of process parameters for microwave-assisted transesterification of Kusum oil. Besides, kinetic and thermodynamic properties of base catal-yzed transesterification were also evaluated.

EXPERIMENTAL

Kusum seeds were collected from the local market of Dahod city, India. It was crushed using a mechanical expeller to obtain brownish-yellow oil. All chemicals such as $Ba(OH)_2$, NaOH, KOH, methanol and ethanol were of AR grade. The acid value and saponification value of Kusum oil were 17.7 and 197 mg g^{-1}, respectively. It was esterified to reduce the acid value less than 2. The major fatty acids composition determined by GC-MS was oleic acid 26.83%, palmitic acid 24.44%, eicosenoic acid 19.03%, arachidic acid 19.37% and stearic acid 8.27% (Fig. 1). The degree of unsaturation of Kusum oil is 45.85 %, while the molecular weight based on fatty acid composition is 901.08 g mol^{-1}. Density, viscosity, and cloud point was found to be 890 kg m^{-3}, 42.05 c St, and 7 ºC, respectively.

Experimental setup: Fig. 2 represents a schematic diagram of the transesterification of Kusum oil. The domestic microwave was modified to carry out the transesterification reaction. The reactor was drilled from the top through which air condenser was passed to connect reaction assembly and a water condenser. The chilled water was supplied in a condenser to prevent the methanol vapour loss. A Pt-100 thermistor with a digital temperature controller was used to monitor the reaction temperature. Constant magnetic stirring was used to provides effective mixing of the oil, methanol and catalyst phase.

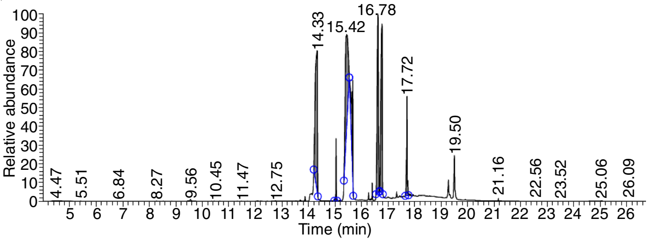

Fig. 1. Graphical presentation of microwave assisted esterification of Kusum oil

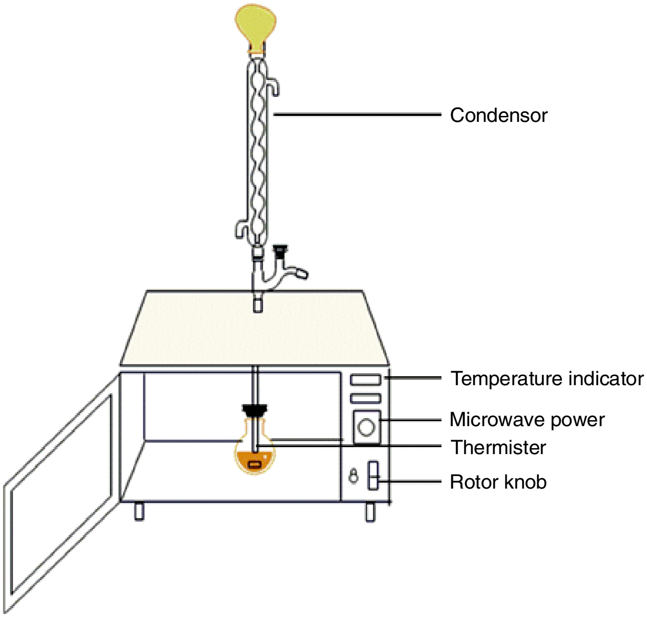

Fig. 2. Microwave reactor setup for the synthesis of KOME

General procedure: The transesterification reaction was carried out using 5 mL (4.45 g) of esterified Kusum oil. The four process parameters and their impact on biodiesel yield were studied by varying one parameter keeping others at constant values. The range used for methanol to oil molar ratio (1:1 to 21:1), $Ba(OH)_2$ catalyst (0.6 to 4.0 wt %), temperature (50 to 80 ºC) and time (1 to 4 min). After completion of every experiment, the product formed was cooled down to stop the further reaction. The product obtained was separated by gravity separation. Biodiesel due to low density separated at the top, while the glycerol and alcohol phase settled at the bottom. The top layer was isolated and heated for several minutes to remove the excess methanol. Unreacted oil, glycerol, and water phase due to their higher density were settled at the bottom. The biodiesel yield was calculated as per eqn. 1 [46].

$$\text{KOME yield} = \frac{\text{Weight of biodiesel}}{\text{Theoritical maximum weight of biodiesel}} \quad (1)$$

From the parametric study, at an optimized molar ratio and catalyst amount the kinetic and thermodynamic parameter evaluations were determined. The kinetic evaluation of microwave assisted transesterification from Kusum oil was carried out at 50 , 55, 60 and 65 ºC at a different time interval. The KOME yield *versus* time study was carried out to find the reaction order and the rate constant. From the linearized form of the Arrhenius equation, the value of activation energy and frequency factor was calculated. Eyring equation was used to calculate the change in enthalpy, entropy and Gibb′s free energy.

RESULTS AND DISCUSSION

Effect of various process parameters such as the molar ratio of methanol to oil, catalyst amount, temperature and reaction time was studied.

Effect of methanol to oil molar ratio on KOME yield: The pre-esterified Kusum oil has an acid value lower than 2, hence transesterification using alkali catalyst doesn't form adverse soap formation. The effect of solvent methanol on Kusum oil methyl ester was studied by varying the concentration of it from 1:1 to 21:1 molar ratio. The constant parameters used were catalyst $Ba(OH)_2$ 1 wt%, 65 ºC and 3 min of reaction time. Fig. 3 shows the effect of the molar ratio on FFA conversion. The transesterification reaction theoretically needs three moles of methanol for a mole of oil [11]. The KOME yield determined by the separating the glycerol phase followed by the removal of methanol was lower at a lower molar ratio.

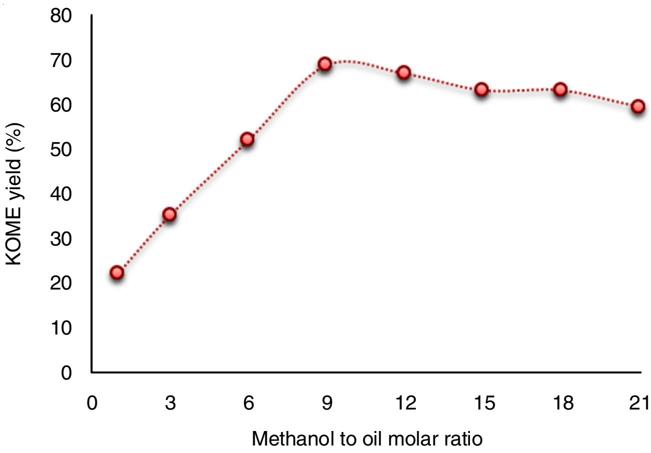

Fig. 3. Effect of molar ratio on KOME yield

At lower molar ratio, the product separation is difficult and also contains unreacted oil. The viscous phase and failure in 3:27 suggest the poor conversion of oil into its biodiesel. Uemura *et al*. [47] postulate the compaction effect in oil molecule at a lower molar ratio, which illicit active ester sites for methanol to react. The transesterification process is reversible by nature and reduction in methanol with the progress of reaction reduces the rate. Hence, to overcome this, it is desired to use the excess molar ratio of methanol. With increasing the molar ratio of methanol to oil, there was an improvement in KOME yield observed. The yield increased from 20% to 70%, with the addition of methanol from 1:1 to 9:1. At excess molar ratio, the increase in the fluidity of reaction mixture and improvement of solubility triggers the KOME formation. Also, the ease in hindrance effect due to a more extended alkyl chain allows the methanol to move toward the reaction site. The results show 9:1 molar ratio is optimum for KOME yield and further increase in methanol lowers the yield. The experimental observation shows that the excess methanol causes the difficulty in final product separation. The excess methanol increases the solubility of KOME in the glycerol phase and reduces the apparent yield [48]. Also, relative dilution of the catalyst and oil is the reason for the reduction in KOME yield at an excess molar ratio. The parametric effect of methanol amount on KOME yield reveals a 9:1 molar ratio is optimal.

Dosage of $Ba(OH)_2$ as catalyst: Due to the presence of basic -OH group, barium hydroxide is soluble in the methanolic phase and absorbs the microwave heat. This ruptures the two-tier structure of methanol and oil and enhanced solubility [49]. Fig. 4 shows the reaction mechanism of microwave-assisted base-catalyzed transesterification.

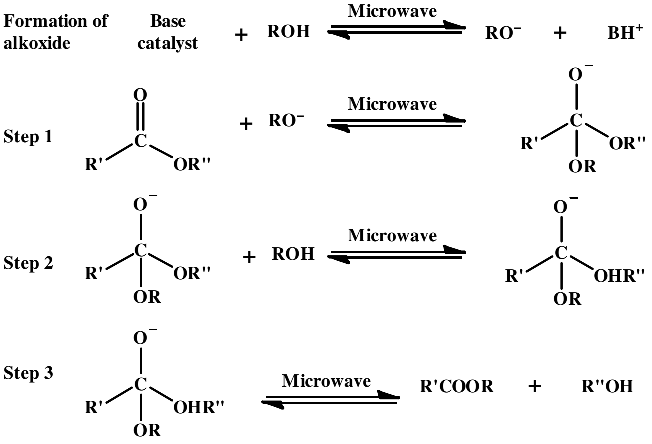

Fig. 4. Reaction mechanism of alkali catalyzed microwave-assisted transesterification reaction

The presence of $Ba(OH)_2$ forms alkoxide CH_3O^- ion from methanol. The methoxy ion combines with carbonyl carbon of Kusum oil and forms a tetrahedral intermediary (step 1). It further reacts to alcohol and forms its alkoxide and intermediate product (step 2). Finally, the rearrangement of the intermediate product gives ester and diglyceride (step 3). Process step 1-3 is repeated for diglyceride to form monoglyceride and ester. Finally, monoglyceride is converted into fatty acid methyl ester and glycerol [50]. The presence of a catalyst triggers the reaction rate. The parametric effect of $Ba(OH)_2$ amount on KOME yield was studied at 9:1 M methanol to oil. The other process parameters were 65 ºC and 3 min of reaction time. Fig. 5 presents the impact of catalyst on KOME yield. The catalyst amount was varied from 0.5 to 4 wt% of Kusum oil.

An improvement in the KOME yield from 60% to 95% was observed when $Ba(OH)_2$ catalyst was increased from 0.6 to 2.5 wt %. The increase in catalyst amount favours the formation of methoxy ions, which triggers the transesterification of oil. At lower catalyst concentration the obtained phases were not separated properly, which suggests the presence of diglycerides and monoglycerides instead of complete conversion into KOME.

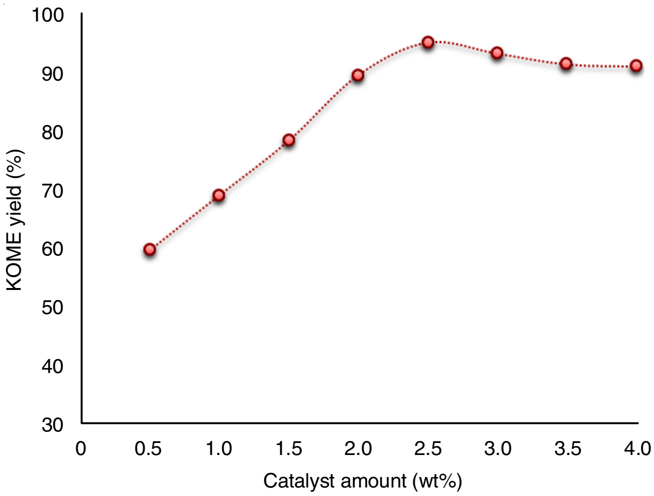

Fig. 5. Effect of catalyst amount on KOME yield

At 2.5 wt% catalyst amount, the phases obtained were easily separable and cleared in the 3:27 test. It indicates a majority of oil is converted into its biodiesel. Nevertheless, a further increase in the catalyst amount is not desirable for KOME yield. The observation suggests the formation of gel at the excess catalyst. It indicates the conversion of oil into its soap, which competes with the desirable transesterification reaction. Also, gel trapped the product in it and caused difficulty in the separation. The effect of catalyst amount revealed that 2.5 wt% of $Ba(OH)_2$ catalyst gives the maximum KOME yield.

Effect of temperature: The transesterification reaction requires the supply of heat to carry out the reaction between the oil and methanol phase. The rate of reaction is enhanced by increasing the reaction temperature. The effect of temperature on KOME yield was carried out at fixed 9:1 M methanol, 2.5 wt % $Ba(OH)_2$ and 3 min of reaction time. The temperature of the reaction was varied from 50 ºC to 80 ºC with an increment of 5 ºC.

The biodiesel yield at a lower temperature was low compared to 65 ºC of the reaction mixture (Fig. 6). At lower temperature, the kinetic energy posses by methanol and oil molecule are also low. Besides, viscous nature oil limits the reaction rate. The rate is governed on contact between oil and methanol phase. The increase in the temperature from 45 ºC to 65°C improves the rate of transesterification (Fig. 6). The increase in the fluidity of reaction mass and rapid movement between immiscible oil and methanol phases, provide the necessary energy for the transesterification of oil. It is evident that at 65 ºC, methanol bubbles within the reaction mass, cause rigorous mixing and turbulence. The KOME yield increased from 79% to 95%, with a rise in the temperature from 45 ºC to 65 ºC. The reaction temperature is an important aspect affecting the transesterification considering both kinetic and thermodynamic aspects. However, the temperature above 65 ºC is not desirable for KOME yield, even though the reaction is endothermic by nature. The KOME yield reduced from 95 to 58%. At temperature above 65 ºC, methanol starts vapourizing from the reaction mass and become limiting compared to the conditions carried out at lower temperature. The formation of bubbles in large amount reduces the methanol and oil contact time. The excess temperature requires the rapid cooling of the generated methanol vapor. It was supported by the finding of Amin *et al.* [51]. The darkening of the product at elevated temperature as well as the formation of other side reactions reduces the KOME yield.

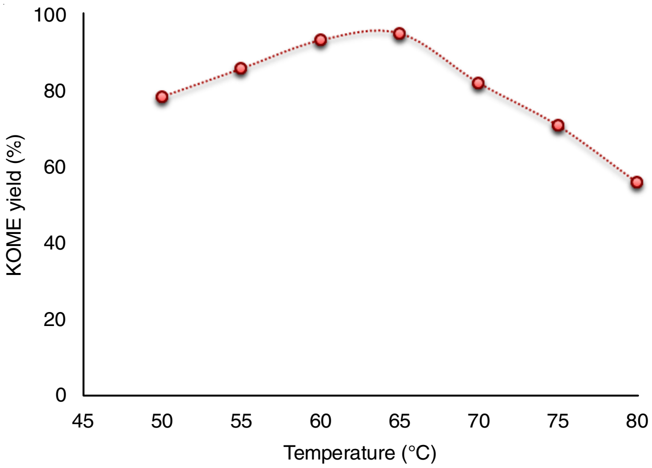

Fig. 6. Effect of Temperature on KOME yield

Reaction time: The effect of reaction time on KOME yield was investigated by varying the reaction time from 0.5 min to 4.5 min. The process parameters were 9:1 M methanol, 2.5 wt % $Ba(OH)_2$ and 65 ºC reaction temperature. The time effect revealed that KOME yield improves with time. At the initial reaction time, the 3:27 test of the top layer shows the trailing of oil, which shows a reaction, is incomplete. With an increase in time the separability of two layers improves and also sample clears in the 3:27 test. The reaction rate is fast compared to conventional heating methods, due to efficient inside out heating associated with microwaves. The electromagnetic waves cause electron excitation, and not change the bond between molecules. The localized superheating and rapid dipole movement overcome the activation energy required for the transesterification reaction [52].

The KOME yield was close to 96% at 3.5 min (Fig. 7). Likozar & Levec [53] and Silva *et al.* [54] concluded that rapid heating in the microwave was due to the thermal and non-thermal effect of a microwave. The time interval above 3.5 min shows a slight decrease in the KOME yield. Hence, the reaction time of 3.5 min is optimum.

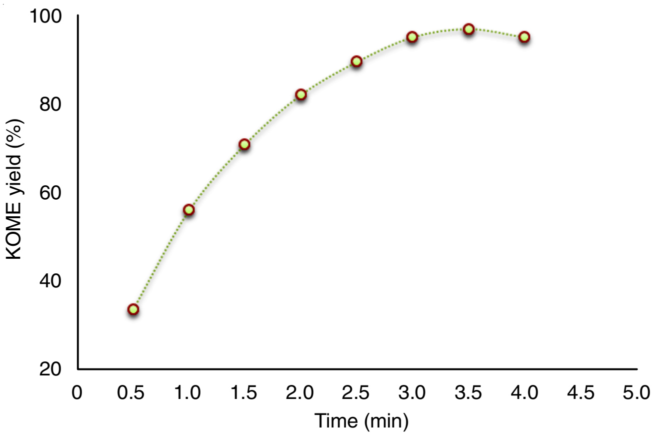

Fig. 7. Effect of time on KOME yield

Rate constant and order of reaction: Transesterification of Kusum oil with methanol in the presence of $Ba(OH)_2$ catalyst is presented by eqn. 2 [55].

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

Theoretically, 1 mol of oil requires 3 mol of methanol for the complete conversion of triglycerides into its ester. The study revealed that 9:1 molar ratio gives the maximum yield. The amount of methanol is almost three times higher than the theoretical requirement. Hence, during the kinetic study, the rate expression presented in an equation can be reduced (eqn 3). This is due to excess molar ratio of methanol to oil, the reaction rate is not governed by the methanol concentration. It is expressed as:

$$\frac{-d[CA]}{dt} = k \times [CA]^n \qquad (3)$$

The above pseudo-order rate expression using variable separation gives

$$\frac{-d[CA]}{[CA]^n} = k \times dt \qquad (4)$$

Upon integration, eqn. 4 gives

$$\frac{[CA]^{-n+1} - [CA0]^{-n+1}}{1-n} = k \times t$$

Case 1: Zero-order kinetics

$$C_A0 - C_A = k \times t \qquad (5)$$

Case 2: First-order kinetics

$$\ln\left(\frac{C_A}{C_A0}\right) = -k \times t \qquad (6)$$

Case 3: Second-order kinetics

$$\frac{1}{CA} - \frac{1}{CA0} = -k \times t \qquad (7)$$

Case 4: Third-order kinetics

$$\frac{1}{CA^2} - \frac{1}{CA_0^2} = 2k \times t \qquad (8)$$

The initial concentration of oil was 0.00047 mol mL^{-1}. As the reaction progress, Kusum oil methyl ester (KOME) and glycerol are generated. Fig. 8 shows the KOME yield as a function of reaction time for 50, 55, 60, 65 and 70 ºC using a microwave heat source. For determination of the reaction rate, the expression for zero, first, second and third-order, eqns 5-8 were used.

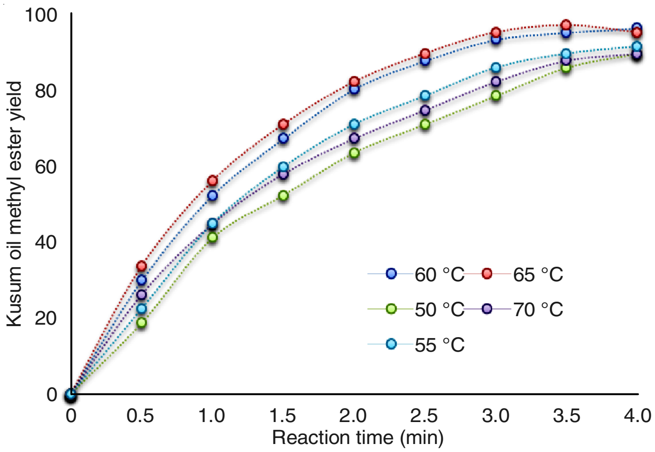

Fig. 8. KOME yield with time for 50° C, 55°C, 60°C and 65°C

The expression for zero-order, first-order, second-order, and third-order kinetics (eqns. 5-8) was used to fit the experimental data. The obtained experimental data are best fitted if the deviation between experimental and theoretical calculations is minimum. The integral expression for all assumed orders with R^2 value close to 1 is desirable. The expression presented in eqns. 5-8 is a straight line passing through the origin (Fig. 9a-d).

In all the assumed rate expression, the first-order kinetics due to higher R^2 is best fitted. The linear fit expression for first-order kinetics (Fig. 9b) is summarized in Table-1. The analysis of variance with high F-value and lower P-value indicates first-order kinetics is suitable for microwave-assisted transesterification of Kusum oil.

Activation energy: Table-1 shows a rise in temperature favours the rate constants, which comply with the van't Hoff law. It suggests the endothermic nature of microwave-assisted transesterification. The activation energy for microwave-assisted transesterification of Kusum oil can be determined by the Arrhenius equation, which has the dependency rate constant on reaction temperature (eqn. 9) [56].

$$k = Ae^{-Ea/RT} \qquad (9)$$

where A is a frequency factor or pre-exponential factor (min^{-1}). It is the measure of collision frequency between reactants. Ea is the activation energy (J/mol) for product formation. R is the molar universal gas constant (8.314 $Jmol^{-1}K^{-1}$), and T is the absolute temperature (K). The equation suggests that the rate constant increases with increasing the pre-exponential factor (A), which is a frequency of the vibrations of molecules at the reaction interface by lessening the activation energy of reaction [45].

TABLE-1
TRANSESTERIFICATION REACTION RATE CONSTANT AT 45, 50, 55, 60 AND 65 °C FOR CONSTANT 09:01 MOLAR RATIO, 2.5 wt% $Ba(OH)_2$ AND ANOVA OF A LINEAR FIT

Temperature (°C)	Order of reaction (n)	Slop (k, min^{-1})	R^2	Adj, R^2	F-value	P-value
45	1	0.4229	0.9826	0.99331	1336	3.4×10^{-10}
50	1	0.5343	0.9899	0.99633	2441	3.1×10^{-11}
55	1	0.6253	0.9968	0.99891	8242	2.4×10^{-13}
60	1	0.8381	0.9927	0.99741	3461	7.7×10^{-12}
65	1	0.8870	0.9536	0.98402	555	1.1×10^{-8}

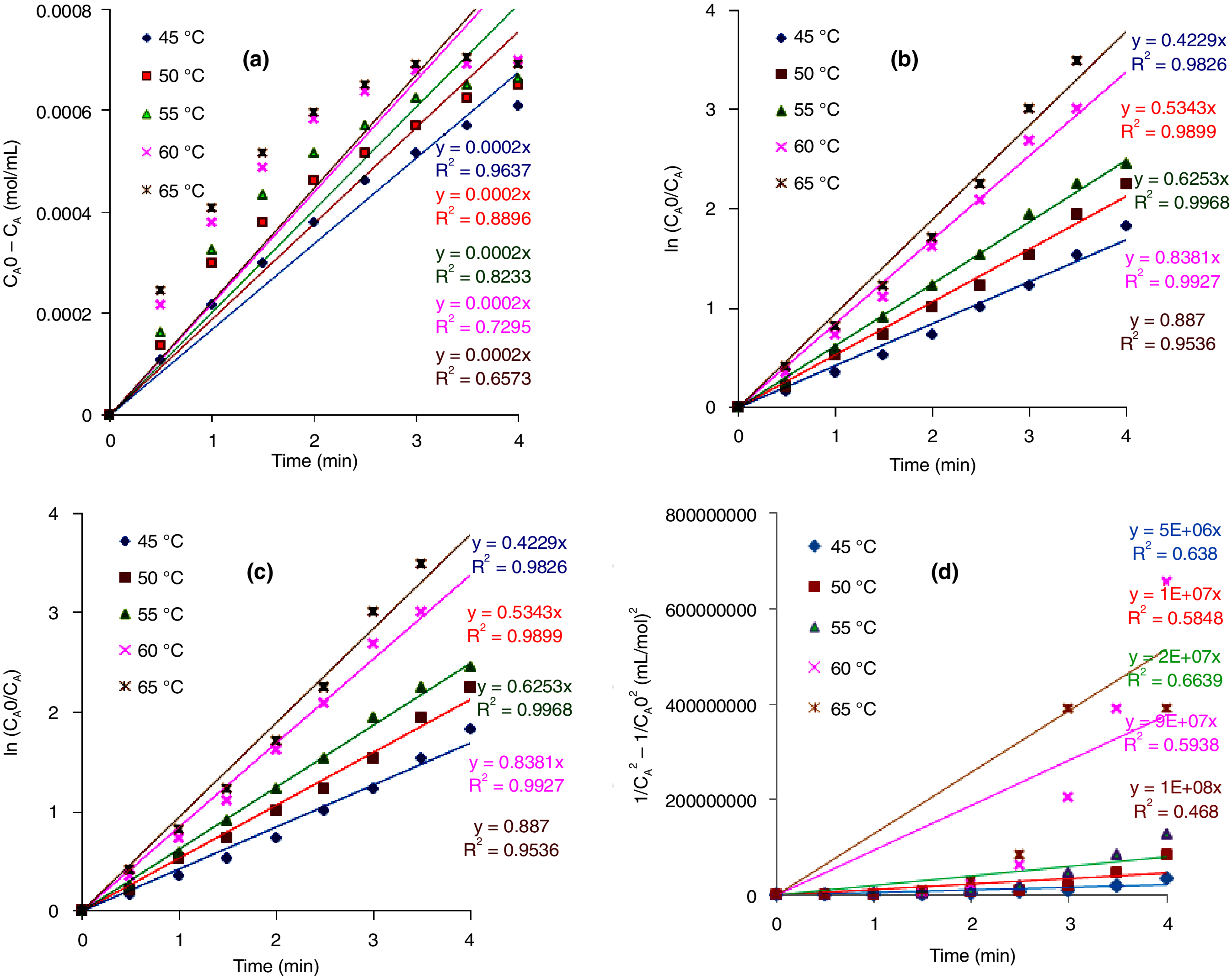

Fig. 9. Kinetic fit of (a) zero-order, (b) first-order, (c) second-order and (d) (d) third-order

To determine the frequency factor and activation energy, the linearized form of eqn 9. becomes as

$$\ln k = \ln A - \frac{Ea}{RT} \tag{10}$$

Fig. 10a presents the rate constant, k *vs*. temperature plot, which slows a linear behaviour for rate constant and temperature. Moreover, the R^2 value of 0.9958 suggested that the reaction rate is first-order. Fig. 10b represents the plot of ln k *vs*. 1/T in which, the slope ($-E_a/R$) and intercept (ln A) give the value of activation energy (34.57 kJ/mol) and frequency factor (205664 min^{-1}).

The reaction rate constant is expressed as

$$k = 205664 e^{\frac{-34.57}{RT}} \tag{11}$$

while the microwave-assisted transesterification is presented as:

$$-r_{FA} = \frac{-dC_{FA}}{dt} = 205664 e^{\frac{-34.57}{RT}} C_{FA} \tag{12}$$

Transesterification involves a reaction of methanol with oil in the presence of catalysts. The catalytic reaction rate is limited by diffusion or by the chemical step. Narkhede and Patel [57] concluded that the diffusion control mechanism has 10-15 kJ mol^{-1} activation energy, while chemical reaction control required 25 kJ mol^{-1}. The activation energy of 34.57 kJ mol^{-1} suggests the chemical step is rate controlling. Since the reaction involves excess solvent methanol, which dissolves catalysts and the reaction mass is homogeneous due to high stirring. There is no diffusion control mechanism.

The activation energy thermodynamically denoted as

$$Ea = \Delta H - T\Delta S \tag{13}$$

Activation energy signifies the lowest energy required for the reaction to occur. The reduction in activation energy in microwave-assisted transesterification was due to higher entropy change at rapid molecular movement at the molecular level [58]. Also superheating due to hotspot generation reduces activation energy in the microwave [59]. The lower value of activation energy for a given system implies that reaction is favorable at a lower temperature. The higher temperature favours the side reaction involving the saponification reaction [60]. The degree of unsaturation also affects the activation energy

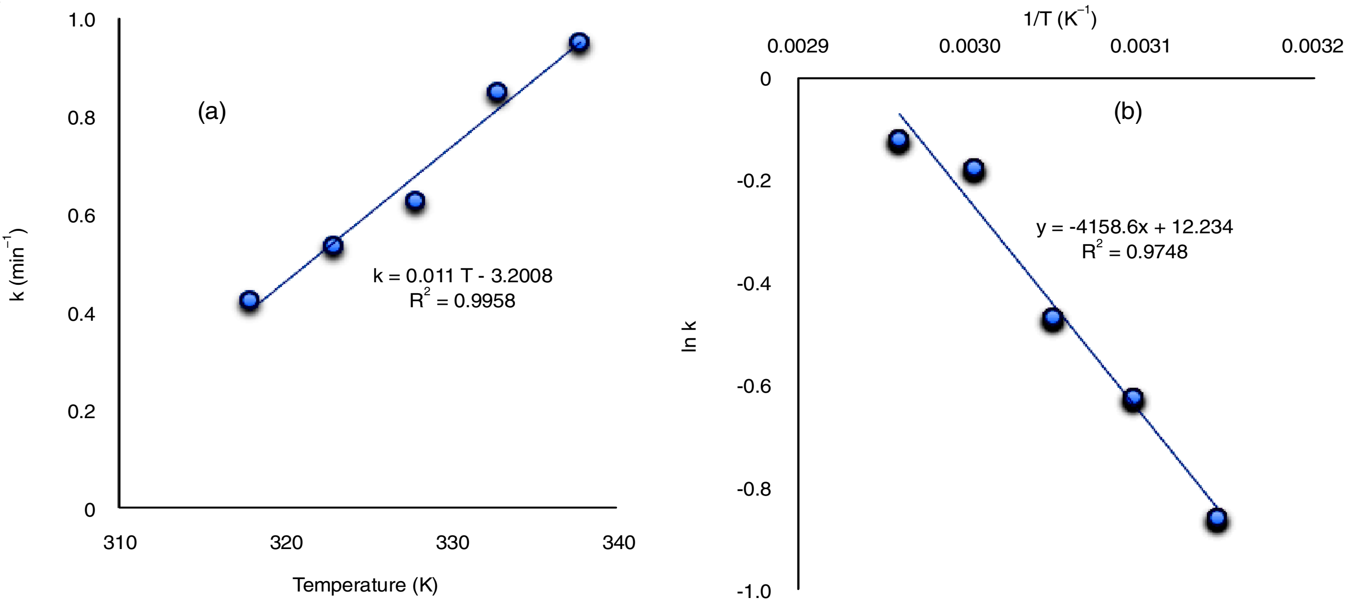

Fig. 10. Plot of (a) rate constant (k) *vs.* temperature (K) and (b) ln k *vs.* 1/T

for transesterification of oil as it causes undesired side reactions. The differences in oil composition also affect the activation energy. The difference in the miscibility of fatty acids in methanol causes variation in activation energy as well as the rate constant. The catalyst type and its amount also affect the activation energy required for the esterification of oil. Moreover, techniques used for transesterification affect the kinetic and thermodynamic parameters. Sharma *et al.* [62] found that activation energy for KOH and CaO catalyzed transesterification in conventional methods was 34.5 and 50.4 k.mol^{-1}. But in case of microwave, the reduction in activation energy up to 62.4% and 42.6% respectively for KOH and CaO catalyzed conditions. The reduction in activation energy compared to conventional heating is due to the presence of dipole molecule and non-thermal effects of the microwave, which enhanced the rate of reaction and reduced the reaction time [63,64]. Fang *et al.* [65] performed the kinetic and thermodynamic study of the transesterification of soybean oil using supercritical methanol and concluded that the reaction order of a kinetic model was 1.5 with 27.06 kJ/mol of activation energy. At a supercritical state, the polarity of methanol decreases and becomes more soluble in the nonpolar oil phase and form a homogeneous phase. This favours the transesterification of oil [66].

The frequency factor in a kinetic study represents the collision frequency of the reactant. The frequency factor with high value enhances the rate constant. Extensive stirring in conventional heating also gives a high reaction rate. However, as presented in Table-2, the frequency factor for microwave-assisted transesterification was very high. It was due to rapid dipole movement [67]. The thermal effect due to a high dielectric constant of methanol and specific thermal effect due to the formation of hotspots increase the reaction rate. The higher value of a frequency factor reveals the presence of non-thermal effects associated with microwave-assisted transesterification. The rapidly changing electric field causes the rotation of dipole to realign [68]. The value of the frequency factor for microwave-assisted transesterification of Kusum oil is 2,05,664 min^{-1}, which indicates effective mixing between oil, alcohol and catalyst, and enables mild operating conditions for transesterification. Hsiao *et al.* [69] concluded that the non-thermal effect of microwave increased in reaction rate by 3.52-7.06. Mazo *et al.* [70] compared the conventional and microwave heating for biodiesel synthesis. The lowering of activation energy up to 10% as well as increase infrequency factor up to 182% confirms the presence of a non-thermal effect.

Thermodynamic studies: The thermodynamic behaviour of microwave-assisted transesterification was predicted by evaluating the change in enthalpy (ΔH), entropy (ΔS) and Gibb′s free energy (ΔG). Eyring [71] proposed the activation complex theory to estimate thermodynamic properties along with temperature-dependent rate constant.

The Eyring-Polanyi equation (eqn. 14) relates the kinetic property and thermodynamic property [72].

$$k = \frac{K_b T}{h} \times \exp\left(\frac{-\Delta G}{RT}\right) \tag{14}$$

The linear form of eqn. 14 becomes as:

$$\ln k = \ln \frac{K_b T}{h} + \left(\frac{-\Delta G}{RT}\right) \tag{15}$$

The Gibbs free energy change for a close system is also articulated by $\Delta G = \Delta H - T\Delta S$.

Thus, eqn. 15 can be presented as

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + \ln \frac{K_b}{h} \tag{16}$$

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

TABLE-2
COMPARISON OF THERMODYNAMIC AND KINETIC PARAMETERS OF MICROWAVE-ASSISTED KOME SYNTHESIS WITH REPORTED RESEARCH

Triglyceride	Heat source	Reaction condition	n	k (min^{-1})	A (min^{-1})	Ea (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	Ref.
Kusum oil, AV 2.3	M, Batch	$Ba(OH)_2$, 2.5 wt%, 9:1 M, 65 °C	1	0.887	205664	34.57	96.48	22.18	-0.22	Present work
Papaya oil, AV 0.8	M, Batch	NaOH, 1 wt%, 9:1 M, 60 °C	1	0.670	14764	27.86	94.48	24.87	-0.209	[74]
Palm oil	C, Batch	KOH 0.4 mol%, 36:1 M, 50 °C	1	2.45	1090	27.2	N.D.	N.D.	N.D.	[47]
Soybean oil AV 6.4	S, Batch	CH_3Ona 1 wt%, 23:1 M, 250 °C	1.5	0.173	102.71	27.06	137.43	23.15	-0.22	[65]
Chinese tallow seed	M, Continuous	NaOH 4 wt%, 47.5:39.3:20 MeOH:Hexane:Oil (w/w), 60 °C	1	0.0846	5.5	20.57	85.57	-0.57	-0.267	[75]
Waste cottonseed oil	M, Batch	KOH 0.65 wt %, 7:1, 50 °C 9.6 min	1	0.3401	N.D.	13.05	82.06	26.3	-0.17	[62]
Microagal oil	M, Batch	CaO 3 wt% 6:1 M, 400 W	1	0.504	N.D.	N.D.	N.D.	N.D.	N.D.	[76]
Coconut oil AV 0.18	M, Batch	CaO 2.5 wt% 9:1 M, 51 °C, 3 min	1	2.969	354000	82.08	N.D.	N.D.	N.D.	[77]
Rice bran oil	M, Cont.	NaOH 0.6 wt% 5:1 M, 50 °C	1	0.068	43.63	6.334	N.D.	N.D.	N.D.	[78]
Cottonseed oil, AV:1.78, U:65	M, Batch	CaO 1.33 wt% 9.6:1 M, 55 °C, 9.7 min	1	0.2532	10600	28.93	82.56	10.4	-0.22	[79]
Jathropha oil AV:22,	M, Batch	BTMAOH 60 °C, 9:1 M	1	0.064	N.D.	21.64	N.D.	N.D.	N.D.	[80]
Oleic acid	M, Batch	H3PW12O40/K10 20 wt%, 160 °C 7.7:1 M	2	0.045	20400	43.69	N.D.	N.D.	N.D.	[81]
Camelina oil AV 3.2	M, Batch	SrO 2 wt%, 9:1 M	2	1.54 g mol^{-1} min^{-1}	N.D.	N.D.	N.D.	N.D.	N.D.	[82]
Dairy scum oil	M, Batch	KOH 1 wt% 7:1 M, 60 °C	1	0.574	212.27×10^7	9.87	N.D.	N.D.	N.D.	[58]
waste cooking oil	C, Batch	$BaSnO_3$ 2.5 wt%, 16:1 M, 65 °C	1	0.113	3.6×10^8	61.57	89.23	59.76	-87.19	[83]
Soybean oil 0.5 AV U : 84.5%	C, Batch	NaOH 0.7 wt%, 7.47:1 M, 58 °C 1.76% bentonite	1	0.1648	12456	31.03	83.30–87.69	28.33	-0.18	[84]
Waste cotton seed oil,	C, Batch	2Sr:Zr 0.7 wt%, 12:1 M, 75 °C 5 wt% 2Sr:Zr	1	0.01	1.33×10^5	48.17	88.23	45.97	-0.12	[85]
Madhuca longifolia oil,	C, Batch	15 wt% H_2SO_4, 55 °C, 35:1 M, 3 h	1	0.003	–	14.84	12.12	96.45	-0.25	[86]
Rapeseed oil 2.29 AV, U: 94.9%	C, Batch	KOH 0.7 wt%, 9:1 M, 60 °C	1	0.1689	461.22	21.88	75.26–79.06	19.59	-0.19	[87]
Schleichera triguga 0.84 AV	U, Batch	Ba(OH)2 3 wt%, 9:1 M	2	0.2678	6.1×10^7*	53.26	82.44–85.55	50.62	-0.11	[88]
Madhuca indica oil,	C, Batch	Strontium titanate 1.3 wt%, 18:1 M, 65 °C	1	0.018	1.78×10^8	65.98	161.56	63.21	-0.29	[89]
Used cooking oil,	C	mesoporous calcium titanate, 100 °C, 3:1 M	1	0.0058384	–	25.25	-24	35.7	-0.16	[60]
Spirulina platensis algae biomass, U 41%	C	H_2SO_4 60 wt% of the biomass, 1:4 wt/volume ratio	1	0.001	2.21	14.51	92.71	16.35	-0.23	[90]
Leather tanning waste, U: 71%	S	Non catalytic 250-325 °C, 12 MPa, 40:1 M	1	0.32-0.96	1176	36.01	153.64–171.16	31.37	-0.233	[91]

AV= Acid Value mg KOH/g of oil, M = microwave, C = Conventional, U = Un-saturation, US = Ultrasound, S = supercritical, Su.C. = Subcritical, n = order of reaction, k = rate constant, A = Pre-exponential factor, Ea = Activation energy, N.D. = Not Determined, MeOH = methanol, CaDG = Calcium diglycerides, W.C.O. = Waste cooking oil, * = unit: L mol^{-1} min^{-1}, # = unit L^2 mol^{-2} min^{-1}, ***Bold italic*** **=** calculated using Eyring equation for comparison.

Eqn. 15 when plotted ln(k/T) *versus* 1/T is a straight line (Fig. 11). The slope $\left(\frac{-\Delta H}{RT}\right)$ and the intercept $\left(\frac{\Delta S}{R}+\ln\frac{K_b}{h}\right)$ gives the entropy and enthalpy change for microwave-assisted transesterification of Kusum oil. The calculated values of ΔH and ΔS are 22.18 kJ/mol and -0.22 kJ/mol K, respectively. The Gibb′s free energy varies from 92-96 kJ/mol from 45-65 ºC, respectively. The positive value of enthalpy change indicates heat supply is mandatory for the progress of transesterification. The negative value of entropy change indicates that the transition state is more polar, stable and has a higher structured alignment compared to reactants in the ground state [73]. The positive value of Gibb′s free energy change reveals the non-spontaneity of reaction. Table-2 represents the summary of the kinetic and thermodynamic properties of present work with reported work in the literature. Factors such as oil and its quality, fatty acid composition and mode of operations also affect the thermodynamic and kinetic properties of the oil.

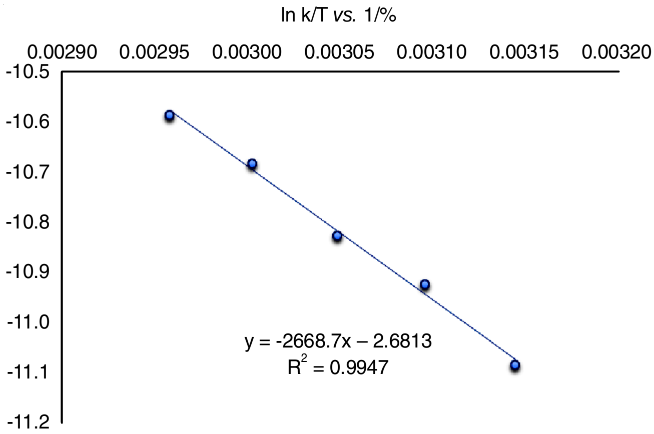

Fig. 11. Plot of ln (k/T) *vs.* 1/T for determination of thermodynamic properties

Conclusion

The parametric study concludes that microwave-assisted transesterification of Kusum oil gave close to 96% KOME yield at 9:1 methanol to oil molar ratio, 65 ºC, 2.5 wt% $Ba(OH)_2$ catalyst, in 3.5 min of reaction time. The use of excess molar ratio, temperature and catalyst amount causes a reduction in the KOME yield. The kinetic study of microwave-assisted esterification of Kusum oil at above optimum conditions revealed that microwave-assisted transesterification is a pseudo-first-order reaction. The 34.57 kJ/mol of activation energy and higher frequency factor 205664 min^{-1} indicates the non-thermal effect associated with the microwave heating. The rate constant 0.887 min^{-1} at 65 ºC revealed that microwave heating significantly reduced the reaction time. Thermodynamic properties such as ΔG, ΔH and ΔS were found out to be 96.48 kJ/mol, 22.18 kJ/mol and -0.22 kJ/mol K, respectively. It shows that reaction is non-spontaneous and endothermic by nature.

CONFLICT OF INTEREST

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

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