

Kinetics of Corn Oil Methanolysis Reaction over Na-Modified Mesoporous Gamma Alumina Catalyst

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The study of chemical kinetics is essential in predicting reaction rates and mechanisms of chemical processes; thus, kinetics study is crucial with the introduction of a new catalyst. In this study, mesoporous gamma-alumina doped NaOH catalyst is employed in the methanolysis of corn oil to evaluate the kinetics parameters. The catalyst is characterized using FTIR, N₂-sorption, FESEM and Basic Back Titration analyses. From the Basic Back Titration result, an increase in basic sites is observed with increasing NaOH doping. The FESEM and FTIR results revealed Na₂O incorporation into the alumina. The high *k*-value of 0.01561 min⁻¹ in the kinetics study is linked to a high level of unsaturated FFA in the corn oil. Similarly, a high level of *E_a* (67.7 kJ mol⁻¹) implies that the methanolysis of corn oil is chemically controlled. Furthermore, the large pre-exponential factor (*A*) (8.6 × 10⁸ min⁻¹) points to a high probability of successful collisions, justifying the high biodiesel yield. From the thermodynamics study, the positive value for the enthalpy implies the methanolysis reaction is endothermic, while the negative value for the entropy proposes an associative mechanism, suggesting a reversible reaction. At the same time, the positive Gibb's free energy suggests a non-spontaneous reaction, signifying the external energy is required for the reaction to progress.

Keywords: Chemical kinetics, Thermodynamics, Na/γ-alumina catalyst, Pre-exponential factor

INTRODUCTION

Price escalation, health standard deterioration and environmental pollution associated with the use of petroleum fuels are issues of concern globally. To curb these menaces, research activities are ongoing for environmentally benign fuel substitute [1-4]. Biodiesel provides an alternative for petroleum-based diesel. It is produced through the transesterification reaction of oil using low molecular weight alcohol in the presence of a catalyst. Both homogeneous and heterogeneous catalysts can be utilized for the transesterification reaction. However, heterogeneous catalysts have several advantages over homogeneous counterparts. Among other benefits of heterogeneous catalysts is the ease of separation from the reaction mixture and catalysts reusability. Apart from that,

biodiesel production is simpler, more economical, and greener with heterogeneous catalysts [5-7].

Chemical kinetics and thermodynamics are the two main principles for the establishment of reaction conditions. Chemical kinetics provides details for chemical reaction rates and mechanisms by which chemical species are converted [8]. It originated in the 17th century derived from the chemical affinity principle of the alchemical concept of the chemical wedding. The chemical affinity principle is based on the opinion that "similar substances will interact so we can categorize them" [9].

To study chemical kinetics, chemical reactions are performed under different reaction conditions such as concentration and temperature. The study of chemical kinetics helps in understanding the mechanisms of chemical processes, including reaction intermediates identification. Even though it is possible to establish the mechanisms of chemical processes through non-kinetic studies, detailed

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kinetics investigations are necessary to authenticate it [8].

In the present work, the kinetics study of Na-modified mesoporous gamma-alumina catalyst in the transesterification of refined corn oil is reported. Given that the mesostructured catalyst has a distinct feature compared to the previously reported modified commercial gamma-alumina, its kinetics study is worthwhile. Furthermore, the thermodynamics study for transesterification especially as related to methanolysis reaction has been rarely reported, despite its significance in providing basic information on the energy requirements and feasibility of a chemical process.

MATERIALS AND METHODS

Materials

The synthesis and characterization of the mesoporous γ -alumina were reported elsewhere [10]. Corn oil was purchased from Giant supermarket, Skudai, Johor, Malaysia. Hydrochloric acid (HCl) with 37% purity, sodium hydroxide (NaOH), and methanol with purity > 99% were supplied by QR&CTM, while 99.8% deuterated chloroform, used for NMR analysis, was supplied by Merck, Germany. All chemicals were of analytical grade and used without further purification.

Catalyst Preparation

The catalysts were prepared by doping 2 g of the mesoporous γ -alumina with 0.1, 0.2, 0.3, 0.4 and 0.5 g NaOH using the wet impregnation method, to obtain 5, 10, 15, 20 and 25 wt% Na/ γ -alumina catalyst, respectively. The catalysts were dried overnight at 120 °C and calcined at 500 °C.

Kinetics Study

The kinetics study was conducted under the following conditions:

Temperature: 40 to 65 °C, reaction time: 30 to 150 mins, catalyst loading: 5 wt%, and oil to methanol molar ratio: 1:15. The reaction was performed in a 500 ml two necked round bottom flask under reflux, with a total reaction mixture of 200 ml. At a specific reaction time, about 0.5 ml of sample was withdrawn from the reaction mixture, and immediately 2 drops of 0.1 M HCl were added to quench

the reaction. After cooling, the sample was centrifuged to remove catalyst and the biodiesel yield was computed using ^1H NMR spectroscopy (Bruker 400 USA) employing the relationship in Eq. (1);

$$\text{Percentage yield} = \frac{2A_1}{3A_2} \times 100 \quad (1)$$

where A_1 and A_2 are the peak areas of the methoxy protons from methyl esters (singlet) at 3.7 ppm and that of the α -carbonyl methylene groups from fatty ester at 2.3 ppm (triplet), respectively [11,12].

Catalyst Characterization

Perkin Elmer 1650 Infra-Red Spectrometer (USA) was used for FTIR analysis of the catalysts in the range of 4000-400 cm^{-1} . The surface area was obtained based on the principle of nitrogen gas adsorption-desorption on the porous surfaces of the sample using Micromeritics Pulse ChemiSorb 2705 (USA). The basic strength of the catalysts was assessed using the basic back titration method. The morphology was established using a field emission scanning electron microscope (FESEM) (SupraTM 35 VP operating at 10 kV) (Germany).

Determination of Process Kinetics

Transesterification reactions are often reported as pseudo-first or second-order and sometimes zeroth-order, depending on the nature of the relationship observed. By and large, methanolysis reaction progresses in three successive reversible reactions as in Eqs. (2) to (4).



where M, TG, DG, MG and GLY refer to methanol, triglyceride, diglyceride, monoglyceride, and glycerol, respectively. However, as DG and MG are consumed at the moment they are formed, their concentrations are presumed to be negligible. Therefore, the reactions above can be condensed into Eq. (5).

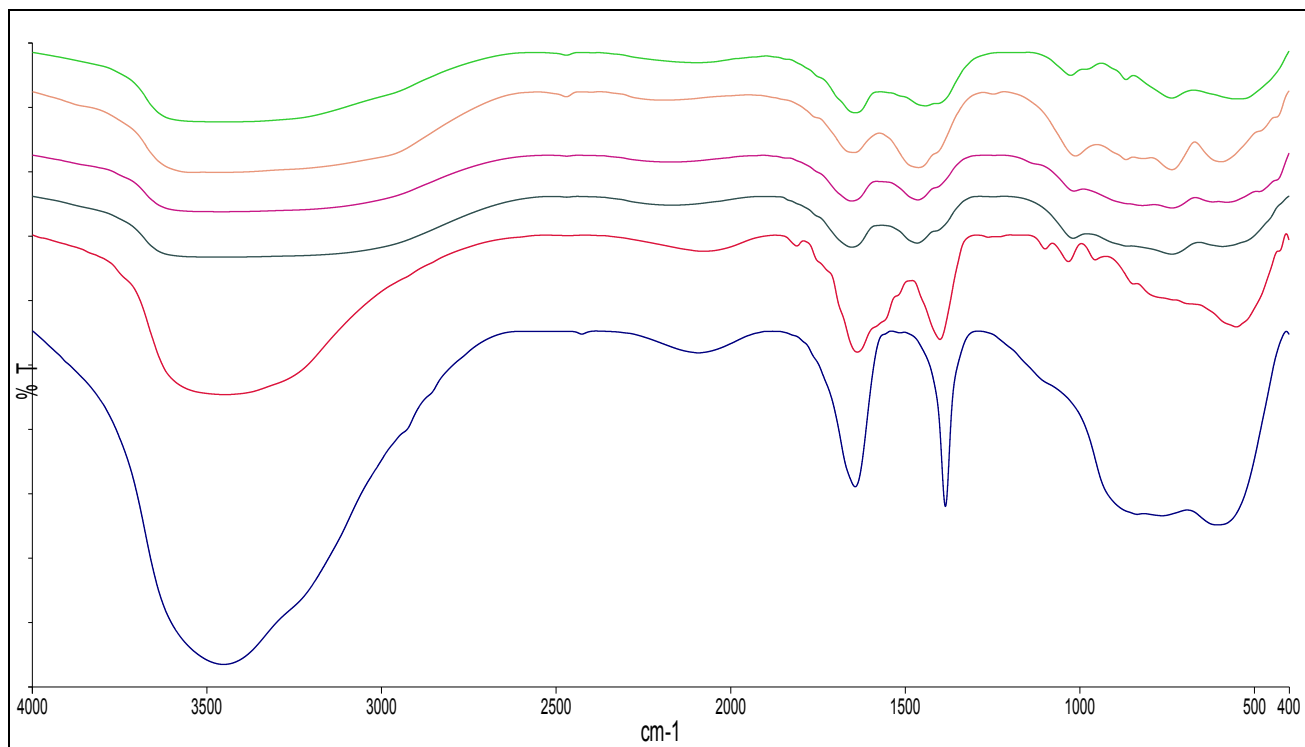
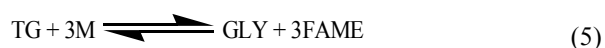


Fig. 1. FTIR spectra of 0% Na/ γ -alumina, 5% Na/ γ -alumina, 10% Na/ γ -alumina, 15% Na/ γ -alumina, 20% Na/ γ -alumina and 25% Na/ γ -alumina, respectively from bottom to top.



Consequently, the overall rate law can be expressed as fourth-order according to E. (6).

$$-r = \frac{d[\text{TG}]}{dt} = k[\text{TG}][\text{M}]^3 \quad (6)$$

However, for the transesterification reaction to proceed appreciably, excess methanol is necessary. For this reason, the methanol concentration is assumed to be constant, and the rate is expressed as a function of TG concentration as shown in Eq. (7).

$$-r = k[\text{TG}] \quad (7)$$

Accordingly, the reaction is regarded as pseudo-first-order kinetics [13,14]. Several reports in the literature concurred with this assumption [6,12,10-13].

RESULTS AND DISCUSSION

Fourier Transform Infra-Red (FTIR)

The FTIR spectra of the catalysts, presented in Fig. 1, revealed that peaks around 3455, 2074, 1642, 1401, 767 and 579 cm^{-1} , allotted to alumina, are preserved even after modification. Nevertheless, a new peak around 1408 cm^{-1} appeared in the spectra of the catalysts. This peak is ascribed to the anti-symmetric vibration of CO_3^{2-} indicating basic site creation [19]. The intensity of the peak increased with an increasing amount of NaOH, demonstrating basic site enhancement. This observation is justifiable since the absorption of CO_2 by oxide anion leads to the formation of surface carbonate, and chemisorption of an acidic probe molecule is a phenomenon for the basic site assessment. Furthermore, a peak around 1044 cm^{-1} is observed for all the samples, it became more intense with increasing NaOH loading, this may be due to Na_2O formation. Additionally, a small peak around 2477 cm^{-1} , assigned to the asymmetric

vibration of CO₂, is observed for 20 and 25% Na/γ-alumina catalysts [20]. These observations indicated enhancement of the basic sites of the mesoporous alumina with modification.

BET Surface Area

The surface area of the catalysts, portrayed in Fig. 2, decreases with increasing the amount of NaOH doping. This may be attributed to the coverage of the surface and pores of the alumina by the sodium compound [21-23]. Furthermore, some NaOH species may enter the mesoporous channels and decreased both the pore volume and the surface area [24].

Basic Back Titration Analysis

The basic strengths of the catalysts are depicted in Fig. 3. An improvement is observed in basic sites with increasing the amount of NaOH loading. This result concurred with the FTIR result that as well points to the same trend in basicity.

FESEM Analysis

The FESEM images of the catalysts are compared in Fig. 4. It is clear that the flaky like morphology of the alumina has transformed into a worm-like structure and the particles have been agglomerated after modification. The particles become more aggregated with increasing the amount of NaOH. This observation indicated the integration of Na into the alumina, further supporting the FTIR and BET results. Besides, the particle agglomeration after doping the alumina with NaOH may be the reason for the surface area lowering as revealed by the BET result.

Kinetics of Methanolysis Reaction

Preliminary methanolysis reactions were performed to select the best catalyst for the kinetics study and the biodiesel yields are presented in Table 1. As can be seen, the highest biodiesel yield was achieved with the 15% Na/γ-alumina catalyst, consequently, it is employed for the kinetics study.

To establish the best kinetics model, zeroth, first, and second-order integrated rate equations were plotted. Despite a straight-line plot, the first-order kinetics model has the highest R² value, thus it was adopted. This is in agreement

with the literature reports indicating that the pseudo-first-order kinetics model is adopted for transesterification reaction [12,15-18]. Hence, in this study, the kinetics calculations are performed employing the pseudo-first-order reaction model presented in Eq. (8).

$$-\ln(1-x) = kt \quad (8)$$

where x is the biodiesel yield, k is the reaction rate constant and t is the reaction time [6,14].

Reaction Rate Constant

From the slope of the plot of $-\ln(1-x)$ vs. t in Fig. 5, the rate constants (k) at different temperatures are acquired. The linear nature of these plots buttressed the fact that the reaction is followed by the pseudo-first-order rate law [12]. It can be observed that as the temperature increases the line slope becomes larger, giving rise to a higher rate constant. This signifies the temperature dependence of the process [25].

The raw data for the kinetics study, the rate constant, and Adj. R² values are presented in Table 2. As can be observed, the rate constant (k) with the highest R² is obtained at 60 °C, thus the kinetics parameters are computed at this temperature. The k value at this temperature is 0.01561 min⁻¹, in agreement with the reported rate constants for heterogeneous catalysts [12-15, 18,26]. The high k -value obtained in this study aligns with the fact that the rate constant for transesterification reaction depends on the fatty acid structures and presence or absence of antioxidants. Whereas a high amount of unsaturated FFAs and/or the absence of antioxidants results in a high rate constant, the reverse is true for a high amount of saturated FFAs and/or the presence of antioxidant [27]. Accordingly, the high amount of unsaturated FFAs in the corn oil, viz. linoleic acid (18:2), and oleic acid (18:1) accounting, respectively for 34.0 to 65.5% and 20.0 to 42.2% of the total FFAs justified the high k value.

Activation Energy

The Arrhenius model in Eq. (9) was utilized for the estimation of activation energy (E_a) and pre-exponential factor (A).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

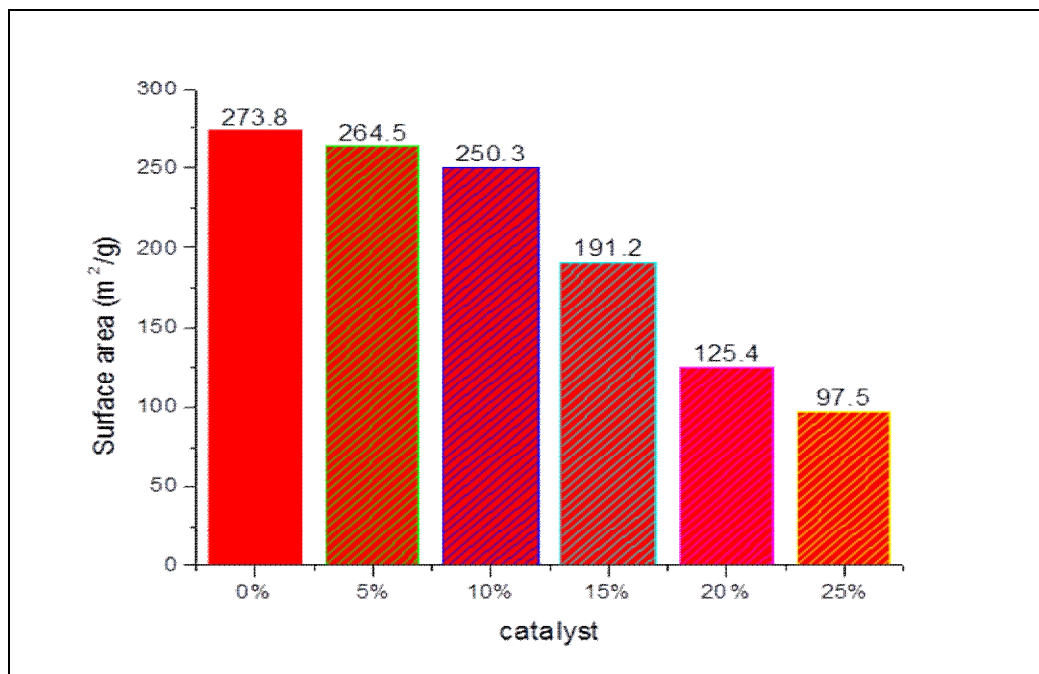


Fig. 2. Surface area of 0% Na/ γ -alumina, 5% Na/ γ -alumina, 10% Na/ γ -alumina, 15% Na/ γ -alumina, 20% Na/ γ -alumina and 25% Na/ γ -alumina catalysts.

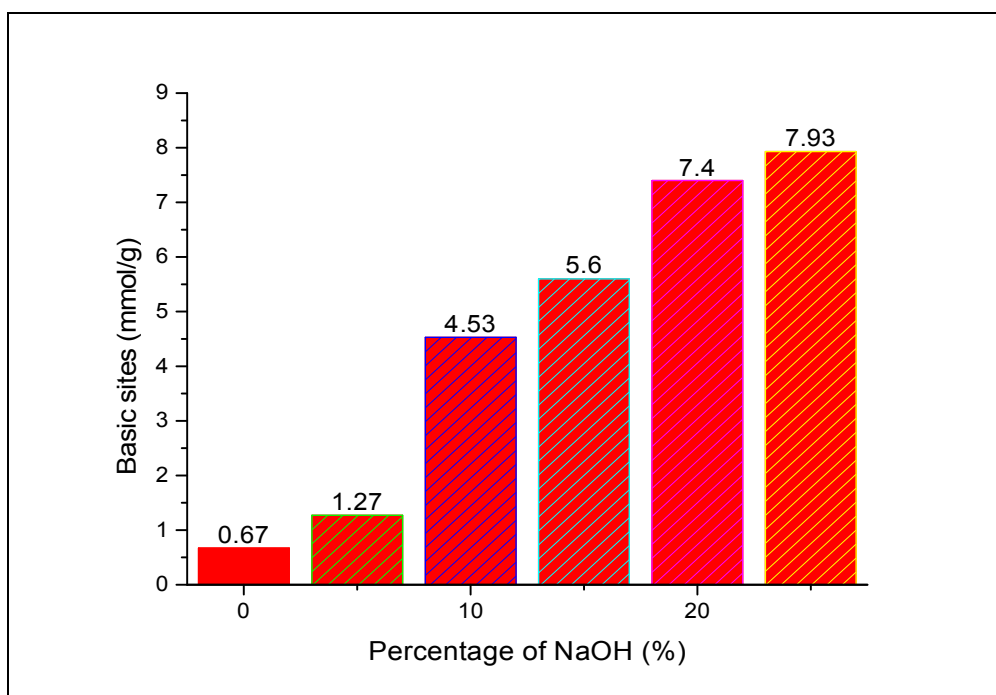


Fig. 3. Basic sites of 0% Na/ γ -alumina, 5% Na/ γ -alumina, 10% Na/ γ -alumina, 15% Na/ γ -alumina, 20% Na/ γ -alumina and 25% Na/ γ -alumina catalysts.

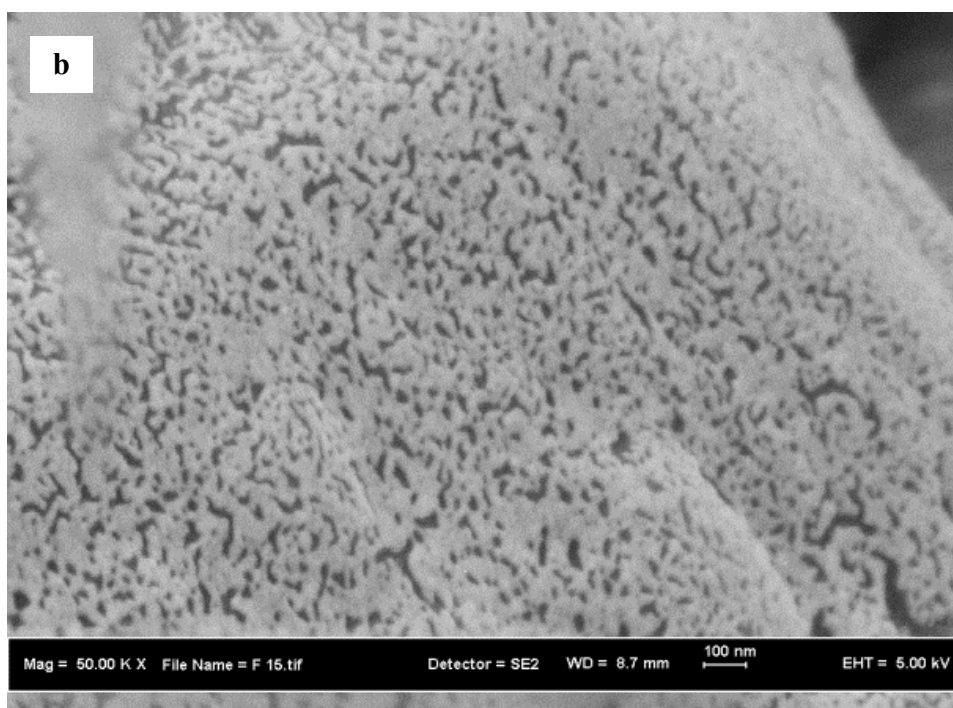
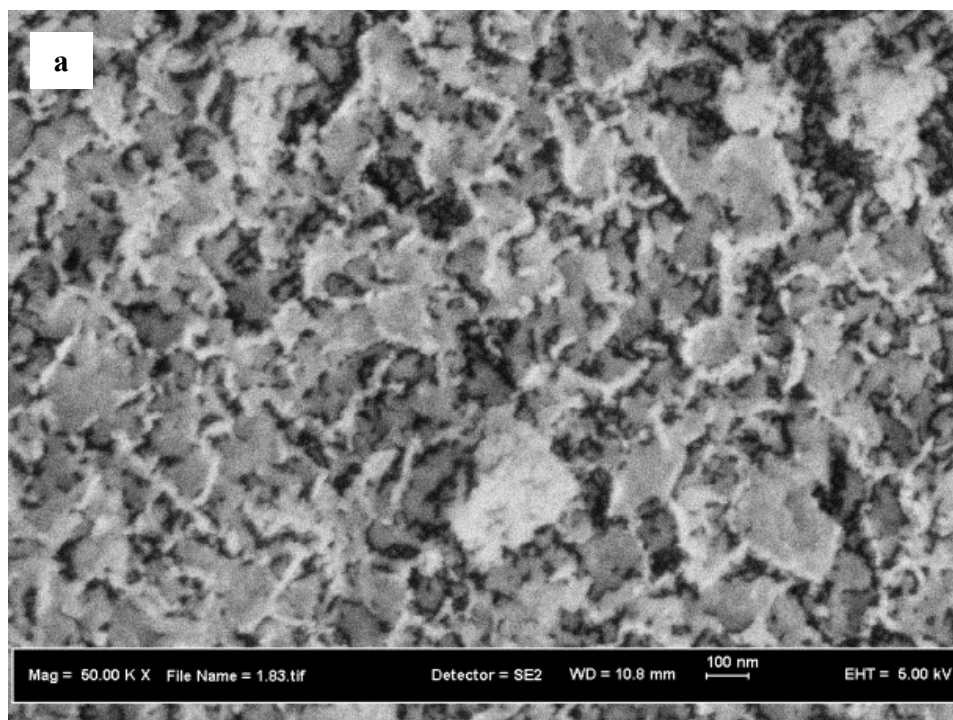


Fig. 4. FESEM image of a) 0% Na/ γ -alumina, b) 10% Na/ γ -alumina, c) 15% Na/ γ -alumina and d) 20% Na/ γ -alumina.

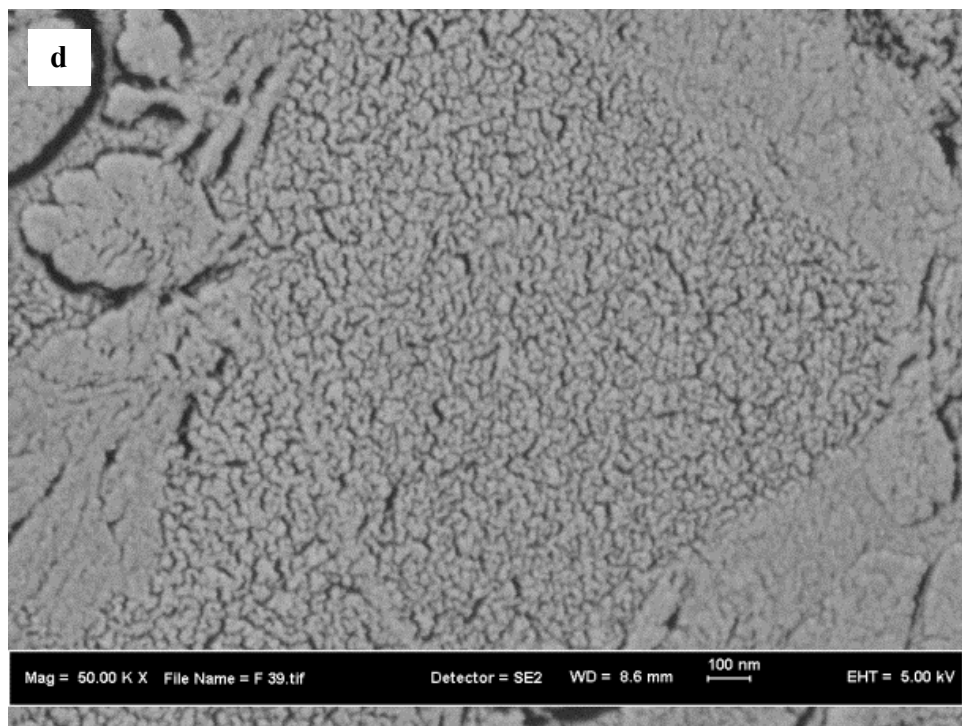
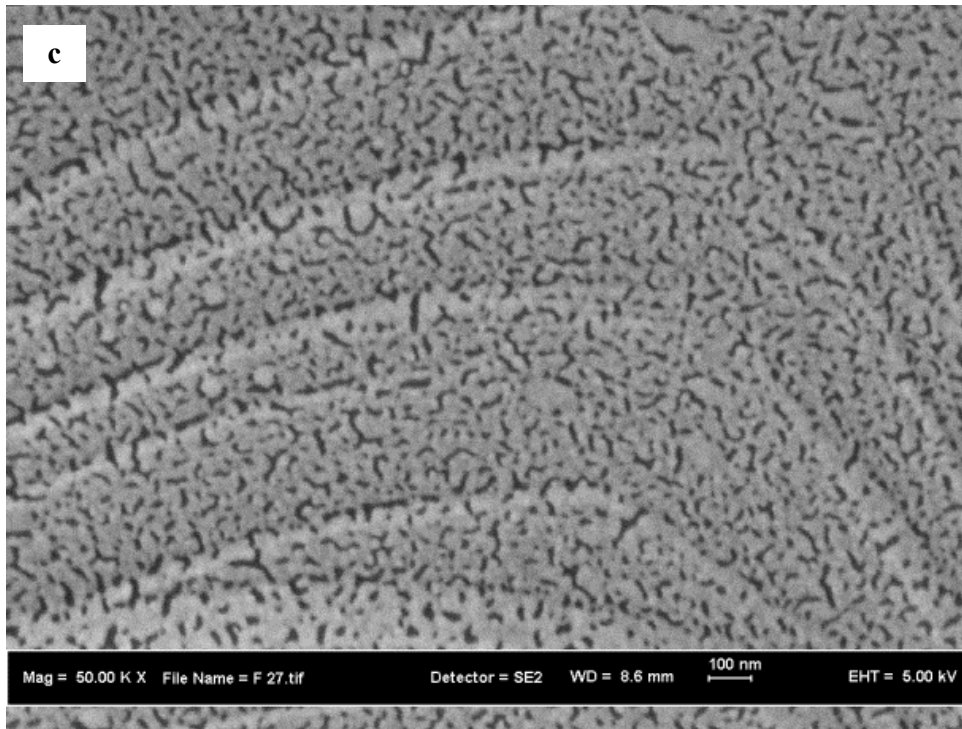
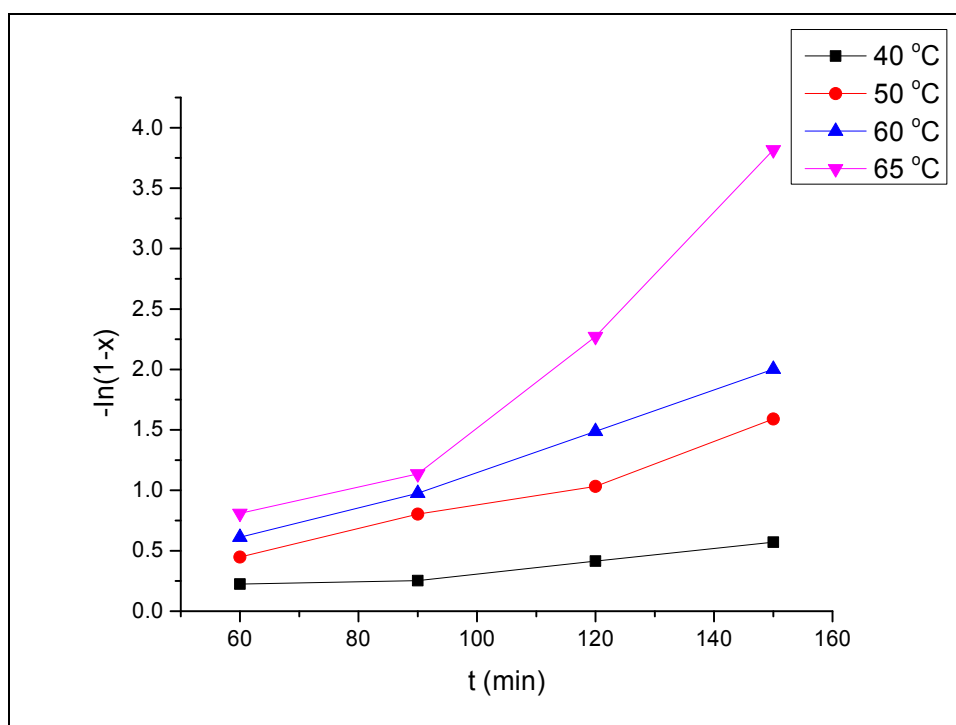


Fig. 4. Continued.

Table 1. Yields Percentage of Biodiesel

Catalyst	Reaction time (Hr)	Catalyst loading (%)	Oil: Methanol (Molar)	Yield (%)
0% Na/ γ -alumina	3	5	1:15	4.1
5% Na/ γ -alumina	-	-	-	50.7
10% Na/ γ -alumina	-	-	-	86.5
15% Na/ γ -alumina	-	-	-	98.9
20% Na/ γ -alumina	-	-	-	96.1
25% Na/ γ -alumina	-	-	-	75.4

**Fig. Error! No text of specified style in document..** Plots of $-\ln(1-x)$ vs. time at 40, 50, 60 and 65 °C,

From the plot of $\ln k$ vs. $1/T$ in Fig. 6, values of activation energy (E_a) and pre-exponential factor (A) are computed with respective values of 67.7 kJ mol^{-1} and $8.6 \times 10^8 \text{ min}^{-1}$. The E_a is within the range of $26\text{--}84 \text{ kJ mol}^{-1}$ reported for heterogeneous catalysts. Furthermore, the activation energy

being greater than 25 kJ mol^{-1} implies the methanolysis reaction is chemically controlled [12]. Conversely, diffusion/mass transfer controlled reactions have E_a value between $10\text{--}15 \text{ kJ mol}^{-1}$ [24]. Additionally, reactions with high E_a values are more temperature-dependent [27]. This

Table 2. Raw Data for the Kinetics Study, k and Adj. R^2 Values

Temp. (°C)	Time (min)	Yield (%)	x	$-\ln(1 - x)$	k	Adj. R^2
40	30	19.5	0.195	0.216913	0.004	0.90061
	60	20.1	0.201	0.224394		
	90	22.3	0.223	0.252315		
	120	33.9	0.339	0.414001		
	150	43.5	0.435	0.57093		
50	30	27.2	0.272	0.317454	0.0122	0.95556
	60	36.1	0.361	0.447851		
	90	55.2	0.552	0.802962		
	120	64.4	0.644	1.032825		
	150	79.6	0.796	1.589635		
60	30	33.5	0.335	0.407968	0.01561	0.99069
	60	45.8	0.458	0.612489		
	90	62.3	0.623	0.97551		
	120	77.4	0.774	1.48722		
	150	86.5	0.865	2.002481		
65	30	42.2	0.422	0.548181	0.03386	0.89749
	60	55.5	0.555	0.809681		
	90	67.9	0.679	1.136314		
	120	89.7	0.897	2.273026		
	150	97.8	0.978	3.816713		

affirmed the temperature dependence of the corn oil methanolysis.

Given that the activation energy is inversely proportional to the rate constant, the high value of the activation energy in this study implies a slow rate of biodiesel formation. This is credited to greater steric interactions (intra- and inter-molecular Van der Waals repulsion) that retard nucleophilic attack on the carbocation

of triglyceride by methoxide radicals. Another possible reason is the structural conformation of the transition state involving the changes in bond lengths and angles. Since triglycerides have a complex molecular structure, both steric interactions and structural conformation are in play [17]. The inverse relation of activation energy with rate constant is noticeable in Fig. 6. The steeper slope of the regression line of the Arrhenius plot indicated greater temperature

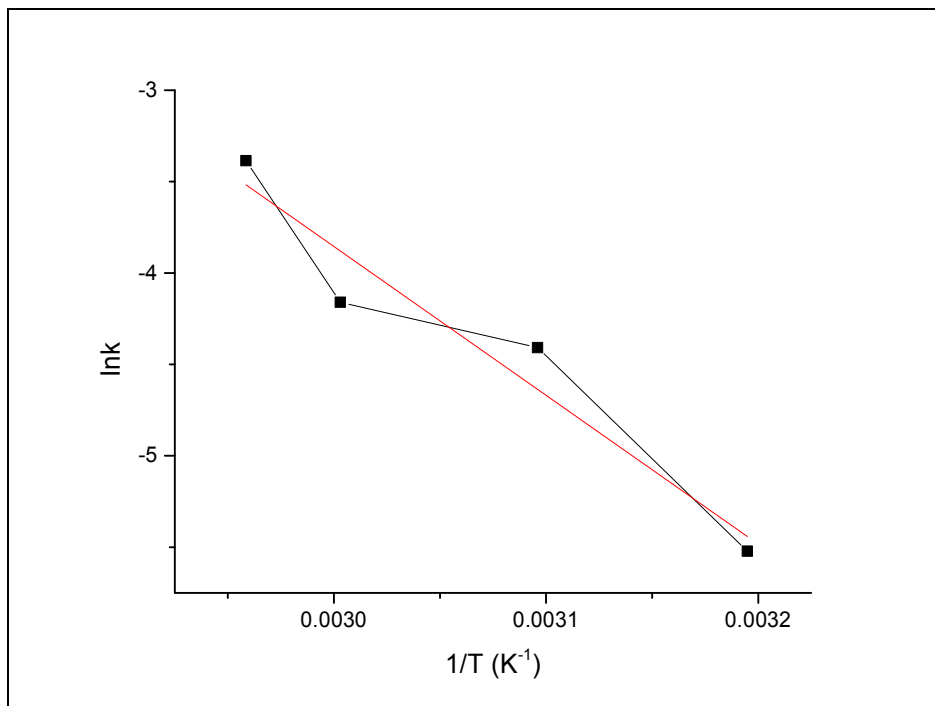


Fig. 6. Arrhenius plot of $\ln k$ vs. $1/T$.

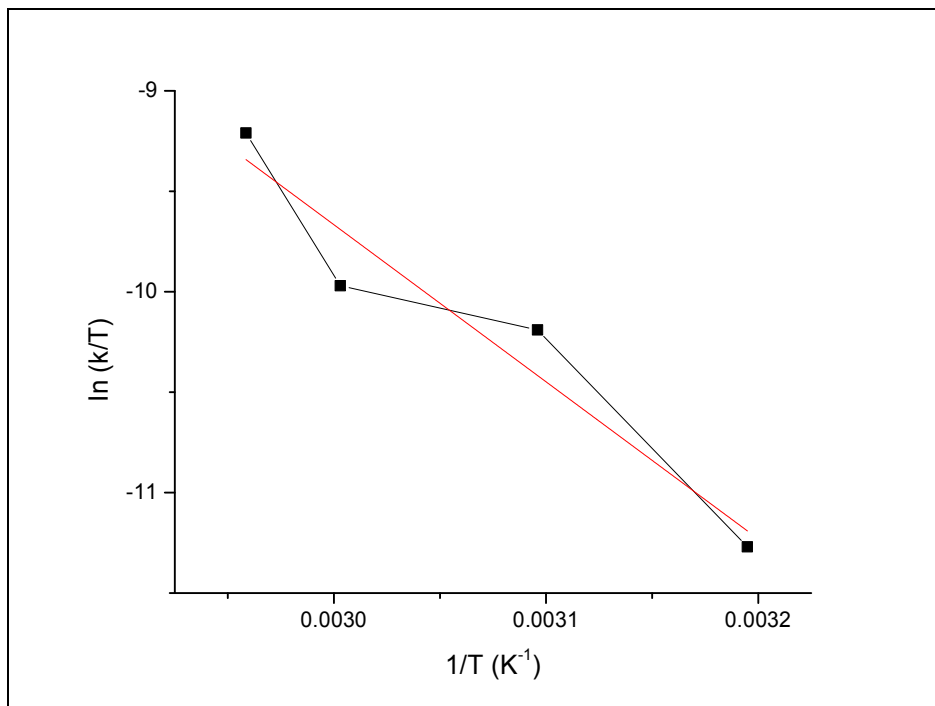


Fig. 7. Plot of Eyring's equation for methanolysis of corn oil.

sensitivity of the rate constants.

Another important parameter in chemical kinetics is the pre-exponential factor (A) which elucidates the fraction of collisions with sufficient kinetic energy for the reaction to progress. It measures the speed of collisions as well as the orientation of the molecules during collisions. The high value of the pre-exponential factor in this study indicates a high probability of successful collisions, thus the reason for the high biodiesel yield. A small change in E_a value results in a significant alteration in the pre-exponential factor [17,27].

Thermodynamics Evaluation

Thermodynamics study is fundamental in chemical reactions since it enables the determination of intrinsic properties; enthalpy, entropy, and free energy. These parameters reveal the energy requirements and feasibility of a reaction.

Enthalpy The total heat change of chemical reactions can be deduced from the enthalpy of the reaction. Eyring's equation presented as Eq. (10) was used to determine both enthalpy and entropy [26].

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{R}\left(\frac{1}{T}\right) + \left[\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R}\right] \quad (10)$$

where ΔH^\ddagger is enthalpy, k is the rate constant, T is the temperature in Kelvin, k_B is the Boltzmann's constant, h is the Planck's constant, ΔS^\ddagger is entropy and R is the gas constant. From a plot of $\ln k/T$ vs. $1/T$ in Fig. 7, the enthalpy of the reaction was found to be $65.03 \text{ kJ mol}^{-1}$. The positive value for the enthalpy signifies that the methanolysis reaction is endothermic, consequently, external heat energy is required for the process [26,27].

Entropy

Similarly, from the same plot in Fig. 7, the entropy (ΔS^\ddagger) was found to be $-82.82 \text{ J mol}^{-1} \text{ K}^{-1}$. The negative value proposes an associative mechanism for the methanolysis reaction, demonstrating that the reactant species join together to form a more ordered transition state along the reaction pathway. This suggests that the transition state has a more ordered structure than the reactants in the ground state [17,26]. Additionally, the negative entropy value

signifies a reversible reaction [28].

Gibb's Free Energy

Gibb's free energy (ΔG^\ddagger) can disclose the degree and spontaneity of chemical reactions. The fundamental thermodynamics expression in Eq. (11) is used to calculate Gibb's free energy and was found to be $93.02 \text{ kJ mol}^{-1}$.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (11)$$

This positive value of ΔG^\ddagger proposes a non-spontaneous reaction. It also indicated that the reactant species are at a lower energy level than the transition state, signifying that external energy is necessary for the reaction to progress [17,26,27].

Turnover Frequency (TOF)

Turnover frequency (TOF) is defined as the number of product molecules formed per catalytic site per unit of time. TOF measures the efficiency of a catalyst and evaluates its capability. It is a chemical reaction rate and not a rate constant. Despite its significance, TOF is seldom reported due to the difficulties associated with the number of active sites evaluation [18]. The relationship in Eq. (12) is used for calculating the TOF of a catalytic process, where m_{cat} is the mass of catalyst used, f_w is catalyst's surface basic sites in mol g^{-1} and t is the reaction time.

The TOF of the catalyst was examined under the assumption that its basic sites was the active sites [18], and was found to be 0.041 s^{-1} . The high value for the TOF implies the 15% Na/ γ -alumina catalyst is an efficient catalyst for industry-level production [6].

CONCLUSIONS

The kinetics and thermodynamics parameters of the novel Na-modified mesoporous gamma-alumina catalyst are evaluated. A high k value of 0.01561 min^{-1} obtained in this study is attributed to the high level of unsaturated FFA in the corn oil. Similarly, the high activation energy (E_a) of 67.7 kJ mol^{-1} signifies the methanolysis of corn oil is chemically controlled, while the pre-exponential factor (A) of $8.6 \times 10^8 \text{ min}^{-1}$ implies a high probability of successful collisions, justifying the high biodiesel yield.

The thermodynamics parameters, enthalpy, entropy, and Gibb's free energy values are respectively $98.91 \text{ kJ mol}^{-1}$, $-247.96 \text{ J mol}^{-1}$, and $182.72 \text{ kJ mol}^{-1}$. The positive value of enthalpy implies that the methanolysis reaction is endothermic, thus the external energy input is required. The negative entropy proposes an associative mechanism for corn oil methanolysis, implying a reversible reaction. Whereas the positive value of Gibb's free energy suggests a non-spontaneous reaction, further asserting external energy requirement for the progress of the reaction.

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