

## Research Article

# Kinetics of Transesterification of *Croton megalocarpus* Oil Using Alkaline Earth Catalysts with Conventional and Microwave Heating

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Transesterification kinetics of *Croton megalocarpus* oil to produce fatty acid methyl esters (FAME) was studied using homogeneous NaOH and heterogeneous alkaline earth Nano MgO, MgO, Nano CaO, CaO, Reoxidized CaO, SrO, and BaO catalysts. Characteristic surface, bulk, and chemical properties of the heterogeneous catalysts were obtained which included surface area, pore properties, scanning electron micrography, X-ray diffraction, basic strength, and basicity. The catalyst porosity varied as Nano MgO > Nano CaO > MgO > CaO > CaO-RO > SrO > BaO and basicity as BaO > SrO > Nano CaO > CaO RO > CaO > Nano MgO > MgO. Catalysts NaOH, BaO, SrO, and Nano CaO gave a good FAME yield (>50%), and reaction order and rate constant have been reported for these catalysts, for both conventional heating and microwave irradiation. The overall reaction for NaOH was of 1<sup>st</sup> order for microwave irradiation with respect to triglyceride and of 2<sup>nd</sup> order with respect to triglyceride under conventional heating. For the heterogeneous catalysts, the overall reaction was of 3<sup>rd</sup> order, 2<sup>nd</sup> order with respect to triglyceride and 1<sup>st</sup> order with respect to methanol for both heating methods. Reaction rate constants for microwave irradiation were higher than those for conventional heating due to faster reaction rates under such heating. BaO was the most active heterogeneous catalyst, followed by SrO and Nano CaO, which was in accordance with their basicity.

## 1. Introduction

Biodiesel is a biofuel obtained from renewable sources having the potential to replace petrodiesel. It is considered to be a green fuel being carbon neutral and free from N and S [1]. *Croton megalocarpus* tree is indigenous to East Africa, with large scale plantations and no adverse ecological farming effects [2]. *Croton megalocarpus* oil is nonedible and has been shown to have the highest potential as a biodiesel feedstock in East Africa [3, 4]. Biodiesel is usually produced by reacting an alcohol with an oil/fat (triglyceride) in the presence of a catalyst, the reaction called transesterification. The overall reversible reaction (Equation 1) is given in Figure 1 [5]. When the reactant alcohol is methanol, the product is fatty acid methyl esters (FAME).

Catalysts used in transesterification are homogeneous (Brønsted acids and bases, biocatalysts, and nonionic organics) and heterogeneous (acidic and basic). Homogenous catalysts are easy to use and economical and in many instances give better conversion. However, they are miscible in reaction media, are not recovered, and require complex postreaction treatment that has environmental issues. Heterogeneous catalysts do not dissolve in the reacting system and can be recovered and recycled, but they are highly selective and activity depends upon their surface properties [6]. Heterogeneous catalysts are acid type and base type. Solid acid catalysts are suited to oils with high free fatty acid (FFA) contents as they catalyze both esterification (converts free fatty acid into corresponding ester) and transesterification reactions [7, 8]. Such catalysts show weak catalytic activity, usually requiring a long reaction time and a

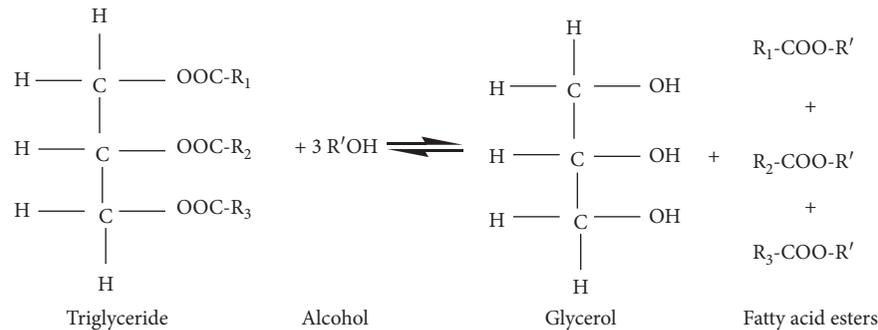


FIGURE 1: Transesterification reaction for biodiesel.

high reaction temperature, and are sensitive to the presence of water [9, 10]. Heterogeneous basic catalysts have a higher reaction rate [11], due to the formation of a highly active alkoxide ion ( $\text{RO}^-$ ) which catalyzes the reaction [12]. Heterogeneous basic catalysts give a lower yield when used with oils with high FFA (>2%) due to soap formation [13]. Basic catalysts have been categorized as single-component metal oxides, zeolites, supported alkali metal, clay minerals, and nonoxides [14]. Alkaline earth catalysts BaO, SrO, CaO, and MgO belong to single-component metal oxides. Alkaline earth oxides have been used to transesterify a variety of oils and fats. CaO and MgO were used to transesterify *J curcas* [15], sunflower oil using MgO and CaO [16], soybean oil using MgO, CaO, SrO, and BaO [17–19], soybean oil over CaO catalyst [20–22], rapeseed oil using MgO and CaO [23, 24], *Camelina sativa* using MgO, CaO, SrO, and BaO [9], palm oil using MgO, CaO, SrO, and BaO [25], waste cooking oil using CaO [20], poultry fat using CaO [26, 27], and palm olein using CaO [28]. These studies have used conventional heating and pressure being atmospheric and above. Khemthong et al. [29] and Patil et al. [30] used microwave irradiation for transesterification of Palm olein using CaO and *Camelina sativa* oil using MgO, SrO, and BaO catalysts, respectively. Waste cooking oil was transesterified using BaO under simultaneous microwave and ultrasound irradiations [31]. This paper reports reaction kinetics for transesterification of *Croton megalocarpus* oil with methanol to produce FAME using alkaline earth oxides, BaO, SrO, CaO, Nano CaO, Reoxidized CaO ( $\text{CaO RO}$ ), MgO, and Nano MgO, by conventional heating and microwave heating.

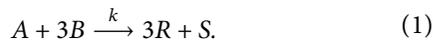
Reactions with homogeneous catalysts have been studied extensively and the observed reaction rates show a lot of variance. Complications arise due to mass transfer limitations in the two-phase reacting system. One of the earliest pioneering work on homogeneous reaction kinetics is that of Nouredini and Zhu [32] for transesterification of soybean oil using NaOH catalyst. Differential reaction rates for the three-step reactions were correlated with experimental data and reaction rate constants, and activation energies, for forward and reverse reactions obtained. Initial reaction rates were slow and it was due to mass transfer limitations. The reaction rate increased with mixing intensity (Reynolds number) in this region of slow reaction. A second phase was when the reaction becomes fast and was kinetics controlled.

Kinetics was of second order and mixing Reynolds number had little effect in this region. A third phase was when the reactions slow down once again which was attributed to an equilibrium state where reverse reactions come into play. Darnoko and Cheryan [33] observed a pseudo-second-order reaction in the first 30 minutes, and first- or zero-order in the later part for transesterification of palm oil using KOH catalyst. An integrated form of rate equations based on triglyceride, diglyceride, and monoglyceride concentrations was used for data analysis and forward reaction rate constants and activation energies for the three-step reactions have been reported. In a similar study of palm oil transesterification [34], it was observed that reverse reactions were insignificant, and, at high mixing intensity (Reynolds number = 2000), the mass transfer controlled region was negligible. A second-order reaction was observed, and forward and reverse reaction rate constants for the three-step reaction were obtained. Transesterification kinetics of sunflower with methanol was studied by Vicente et al. [35] and Bambase et al. [36] and with ethanol by Marjanović et al. [37]. Vicente et al. [35] included the catalyst (KOH) concentration in the reaction rate by defining an effective rate constant which was a multiple of catalyst concentration and the rate constant. This unconventional approach to kinetics resulted in a second-order reaction kinetics. Reaction rate constants and energies of activation were reported. Bambase et al. [36] used NaOH catalyst and observed a second-order rate. Mass transfer limitations were minimal for stirring speeds of 400–600 rpm. Reaction rate constants for forward and reverse three-step reactions were reported. Marjanović et al. [37] used NaOH catalyst and reported reaction kinetics for the overall reaction. Mass transfer limitations were neglected. Initial reaction phase was modelled as irreversible second order and the later phase as a reversible second order. Similar results are reported for the methanolysis of sunflower oil using KOH catalyst by Stamenković et al. [38] at low temperatures of 283–303K, using the overall reaction. Jain and Sharma [39] studied the two-stage esterification/transesterification of *Jatropha curcas* oil with methanol using  $\text{H}_2\text{SO}_4/\text{NaOH}$  catalysts. They used the overall reaction and obtained a first-order reaction rate for both stages. Reaction rate constants for both the stages are reported. Jain et al. [40] studied the two-stage esterification/transesterification of waste cooking oil with methanol using  $\text{H}_2\text{SO}_4/\text{NaOH}$  catalysts. They used the overall reaction and observed a first-

order reaction rate for both stages. Reaction rate constants for both the stages were reported. A supercritical non-catalytic and homogeneous catalytic using KOH, transesterification of *Croton megalocarpus* oil with methanol, gave a first-order reaction for the overall reaction [41]. These kinetic studies on soybean oil, sunflower oil, palm oil, *Jatropha curcas* oil, waste cooking oil, and *Croton megalocarpus* oil show that the observed reaction order varied from zero to two. Initially, the reaction system consists of two phases and mass transfer controls, but very soon the reaction system becomes pseudo-homogeneous and chemical reaction becomes rate controlling. Initial studies focussed on detailed reaction kinetics for the three reaction steps which yields reaction rate constants for forward and reaction rates and activation energies for the three reactions. Heterogeneous catalysts form a three-phase system. Studies of reaction kinetics using alkaline earth catalysts have been limited. Dossin et al. [42, 43] studied kinetics of transesterification of ethyl acetate with methanol over MgO catalyst. Transesterification kinetics of soybean oil over MgO, CaO, and BaO catalysts was studied by Singh and Fernando [44]. Veljković et al. [19] studied the methanolysis kinetics of sunflower oil catalyzed by CaO. Patil et al. [30] studied transesterification kinetics of *Camelina sativa* oil over BaO, CaO, MgO, and SrO catalysts, using conventional and microwave heating. Microwave heating is an energy-efficient, quick heating process for transesterification as compared to conventional convectional heating [45].

A general rate equation has been developed [30, 44] which can take care of varying reaction orders with respect to methanol and triglyceride. This rate equation is applicable to both homogeneous and heterogeneous catalyst systems since it is based on the overall reaction. Overall stoichiometry is written for a forward reaction, assuming a negligible reverse reaction, where A, B, R, and S represent triglyceride, alcohol, fatty acid ester, and glycerol, respectively.

Overall reaction:



For the rate of reaction, written as the rate of disappearance of triglyceride, A is

$$-r_A = -\frac{d[A]}{dt} = k[A]^m[B]^n. \quad (2)$$

In equation (2),  $m$  and  $n$  are the reaction orders with respect to triglyceride and methanol, respectively,  $k$  is the reaction rate constant, and  $t$  is the time. By taking mass balance on triglyceride:

$$[A] = [A]_o(1 - x_A). \quad (3)$$

In equation (3),  $[A]_o$  is the initial triglyceride concentration and  $x_A$  is the conversion.

Similar mass balance on methanol gives

$$[B] = [B]_o - 3x_A[A]_o = [A]_o(\alpha_B - 3x_A). \quad (4)$$

Here,  $\alpha_B = [B]_o/[A]_o$ .

Equations (3) and (4), when substituted in equation (2), give

$$\frac{dx_A}{dt} = k[A]_o^{(m+n-1)}(1 - x_A)^m(\alpha_B - 3x_A)^n. \quad (5)$$

Or,

$$\int \frac{dx_A}{(1 - x_A)^m(\alpha_B - 3x_A)^n} = k[A]_o^{(m+n-1)} \int dt. \quad (6)$$

Limits for the integral are  $x_A = 0$  at  $t = 0$  and  $x_A = x_A$  at  $t$ .

Integral has been evaluated for overall order varying from 0 to 3, for different combinations of  $m$  and  $n$ , and the integrated form of rate equation is given in Table 1.

In equations 8 to 17, a plot of left-hand-side, a function of conversion  $x_A$  versus time  $t$  would be a straight line for the appropriate  $m$  and  $n$ , with reaction rate constant  $k$  given by the slope. The temperature dependency of  $k$  is well represented by Arrhenius' law,  $k = A e^{-E/RT}$ , where  $E$  is the activation energy,  $A$  is preexponential factor,  $T$  is temperature, and  $R$  is universal gas constant [46].

## 2. Materials and Methods

**2.1. Chemicals and Catalysts.** *Croton megalocarpus* oil was obtained from nuts from local trees (Kesses, Uasin Gishu, and Kenya) through solvent extraction. Analytical grade sodium hydroxide, benzoic acid, benzene, phenolphthalein, and universal indicator (maximum pK = 11) were obtained from Gelsup, Nairobi. Analytical grade methanol, GC standards methyl heptadecanoate, Hammett indicators (4-chloroaniline, 4-nitroaniline, 2,4-dinitroaniline, bromothymol blue) were from Sigma-Aldrich. Alkaline earth catalysts, MgO (99%), Nano MgO (99.8%), CaO (96%), Nano CaO (98%), SrO (99.9%), BaO (97%), of analytical grade were from Sigma-Aldrich.

**2.2. Characterization of Croton Megalocarpus Oil.** Characteristic physical properties, density, viscosity, refractive index, sulphur content, moisture content, ash, acid value, saponification value, iodine value, peroxide value, and calorific value were obtained by standard methods, and fatty acid composition was obtained by GC [5].

**2.3. Characterization of Alkaline Earth Catalysts.** Rehydrated CaO (CaO RO) was prepared by first hydrating CaO with water to obtain calcium hydroxide, which was later calcined (at 700°C) back to CaO.

Microscopy: TEM analysis was conducted on a JEOL 2100 F TEM instrument, operated at 200 kV. The powder sample was sonicated in ethanol for 5 min, followed by depositing the solution on a Cu-grid with holey carbon film. The material is dispersed in ethanol using a bath sonicator to form a suspension. One or two droplets were dropped onto a holey carbon-supported copper grid and allowed to dry. TEM imaging was performed on a dry sample.

X-ray diffraction: PAnalytical XPERT-PRO diffractometer was used for X-ray diffraction.

TABLE 1: Integrated form of rate equation (equation (7)).

Case	Overall order	$m$	$n$	Rate equation	Equation number
1	0	0	0	$[A]_0 x_A = k t$	8
2	1	1	0	$\ln(1/(1-x_A)) = k t$	9
3	1	0	1	$-(1/3)\ln((\alpha_B-3x_A)/\alpha_B) = k t$	10
4	2	1	1	$(1/(\alpha_B-3))\ln((\alpha_B-3x_A)/(1-x_A)\alpha_B) = k [A]_0 t$	11
5	2	2	0	$x_{A1}/(1-x_A) = k [A]_0 t$	12
6	2	0	2	$x_A/((\alpha_B-3x_A)\alpha_B) = k [A]_0 t$	13
7	3	2	1	$(1/(\alpha_B-3))[(x_A/(1-x_A))-(3/(\alpha_B-3))\ln((\alpha_B-3x_A)/(1-x_A)\alpha_B)] = k [A]_0^2 t$	14
8	3	1	2	$(1/(3-\alpha_B))[(3x_A/((\alpha_B-3x_A)\alpha_B))-(1/(3-\alpha_B))\ln((1-x_A)\alpha_B/(\alpha_B-3x_A))] = k [A]_0^2 t$	15
9	3	3	0	$(2-x_A)x_A/(1-x_A)^2 = 2 k [A]_0^2 t$	16
10	3	0	3	$1/(\alpha_B-3x_A)^2 - 1/\alpha_B^2 = 6 k [A]_0^2 t$	17

**2.4. Transesterification of Croton Megalocarpus Oil Using Conventional Heating.** A 3-neck round bottom flask (250 ml) fitted with a water-cooled condenser was used as a reactor. It was fitted with a mechanical stirrer and a thermometer and placed in a constant temperature water bath (WB) for studies with conventional heating. Mixing speed was 800 rpm, sufficient to eliminate mass transfer resistances. Alkaline earth catalyst samples were activated by heating under reflux with a weighed amount of methanol for one hour at the desired temperature, before the addition of *Croton megalocarpus* oil. The reaction was timed at this point and samples were drawn from time to time. Studies were also made using NaOH homogeneous catalyst for the sake of comparison between the relative yields between the two catalyst systems. The product drawn was quenched in ice to stop the reaction and made to stand to separate the oil and aqueous fractions. Oil fraction was then centrifuged for 30 min to remove any solid catalysts, heated at 90°C to remove any dissolved methanol, and analyzed by GC for total FAME [5].

**2.5. Transesterification of Croton Megalocarpus Oil Using Microwave Irradiation.** Round bottom flask reactor was placed in a modified domestic microwave (MW) oven (Shivaki, SMW-103, 1300W) fitted with an external magnetic stirrer (Hanna) and a Teflon® shielded thermocouple (Hanna HI9055) as a temperature sensor. Stirring was vigorous to rule out mass transfer resistances. The other procedure was similar to the one described in Section 2.4.

**2.6. Study of Transesterification Kinetics.** In order to study the reaction kinetics at conventional heating, studies were made at temperatures of 40, 50, 60, and 70°C, at methanol to oil molar ratio of 9 : 1, catalyst at 1 mass%, and reaction lasting 3 h; and samples were drawn at time intervals of 15, 30, 45, 60, 90, 120, 150, and 180 min. For microwave irradiation, reactions were carried out at 50, 60, and 70°C, at methanol-to-oil ratio 9 : 1 and catalyst concentration of 1 mass%; and samples were drawn at 30, 45, 60, and 90 s. Gas chromatography was used to estimate FAME yield as given by Kumar and Kiriamiti [5]. Regression analysis was used to identify the reaction order, and the regression coefficients were used to obtain the reaction rate constant.

### 3. Results and Discussion

**3.1. Croton Megalocarpus Oil Characteristics.** Characteristic physical properties obtained by standard methods were as follows [5]: density (293 K) 929.2 kg m<sup>-3</sup>; kinematic viscosity (313 K) 28.52 mm<sup>2</sup> s<sup>-1</sup>; refractive index (293 K) 1.4737; sulphur 0.001 wt%; moisture 0.007 wt%; ash 0.087 wt%; acid value 2.00 mg KOH/g; saponification value 192.1; iodine value 139.2 mg/g; peroxide value 8.66; and gross calorific value 41.0 MJ/kg. Fatty acid composition (mass%) was as follows: caprylic 0.09, caproic 0.08, lauric 0.09, myristic 0.26, palmitic 8.39, stearic 3.15, oleic 12.16, linoleic 70.97, and  $\alpha$ -linolenic 3.89.

**3.2. Alkaline Earth Catalysts Characteristics.** Pore structure, surface area, and basic strength and basicity: these properties have been reproduced in Table 2 from earlier publication [5].

Results show that alkaline earth oxides had low porosity with exception of Nano MgO. Nano MgO had the highest porosity and barium oxide the least. The porosity varied as Nano MgO > Nano CaO > MgO > CaO > CaO-RO > SrO > BaO. Catalysts arranged according to basicity were BaO > SrO > Nano CaO > CaO RO > CaO > Nano MgO > MgO.

Microscopy: Figure 2 gives the TEM images of the catalysts.

X-ray diffraction patterns of calcined catalysts confirmed the purity of catalyst samples.

**3.3. FAME Yield.** The highest yields of FAME (%) for conventional heating for various catalysts were as follows: NaOH 98, BaO 82, SrO 75, Nano CaO 74, CaO RO 42, CaO 30, Nano MgO 25, and MgO 20. Similar yields (%) for microwave irradiation were NaOH 96, BaO 72, SrO 68, Nano CaO 55, CaO RO 20, CaO 14, Nano MgO 2, and MgO 2. Results indicate that the promising catalysts giving good (>50%) yield were NaOH, BaO, SrO, and Nano CaO. Reaction data of these catalysts are been presented here. Figure 3 gives FAME yield as a function of time and temperature for NaOH, BaO, SrO, and Nano CaO catalysts for water bath (WB) and microwave (MW) heating.

**3.4. Reaction Order and Rate Constant.** Kinetic data for Figure 3 were fitted into integrated forms of reaction rate equations (Table 1) to get the reaction order. For all the ten

TABLE 2: Surface properties, basic strength, and basicity of catalysts ( $S_{\text{BET}}$  = BET surface area) [5].

Catalyst	Pore radius (BJH desorp) $m$	$S_{\text{BET}}$ ( $m^2 \text{ kg}^{-1}$ )	Solid density ( $\text{kg m}^{-3}$ )	Porosity ( $\epsilon_p$ )	Basic strength ( $H_-$ )	Basicity (mmol/g)
BaO	9.88E-09	1981.6	5720	0.03	15 < $H_-$ < 18.4	0.0961
SrO	2.50E-08	1361.1	4700	0.04	15 < $H_-$ < 18.4	0.0841
Nano CaO	1.13E-08	24149	3300	0.18	11 < $H_-$ < 15	0.0625
CaO-RO	1.63E-08	4470	3100	0.05	11 < $H_-$ < 15	0.0535
CaO	1.71E-08	6960	3300	0.09	11 < $H_-$ < 15	0.0441
Nano MgO	1.16E-08	40830	3600	0.30	11 < $H_-$ < 15	0.0361
MgO	1.07E-08	19545.5	3600	0.16	11 < $H_-$ < 15	0.0289

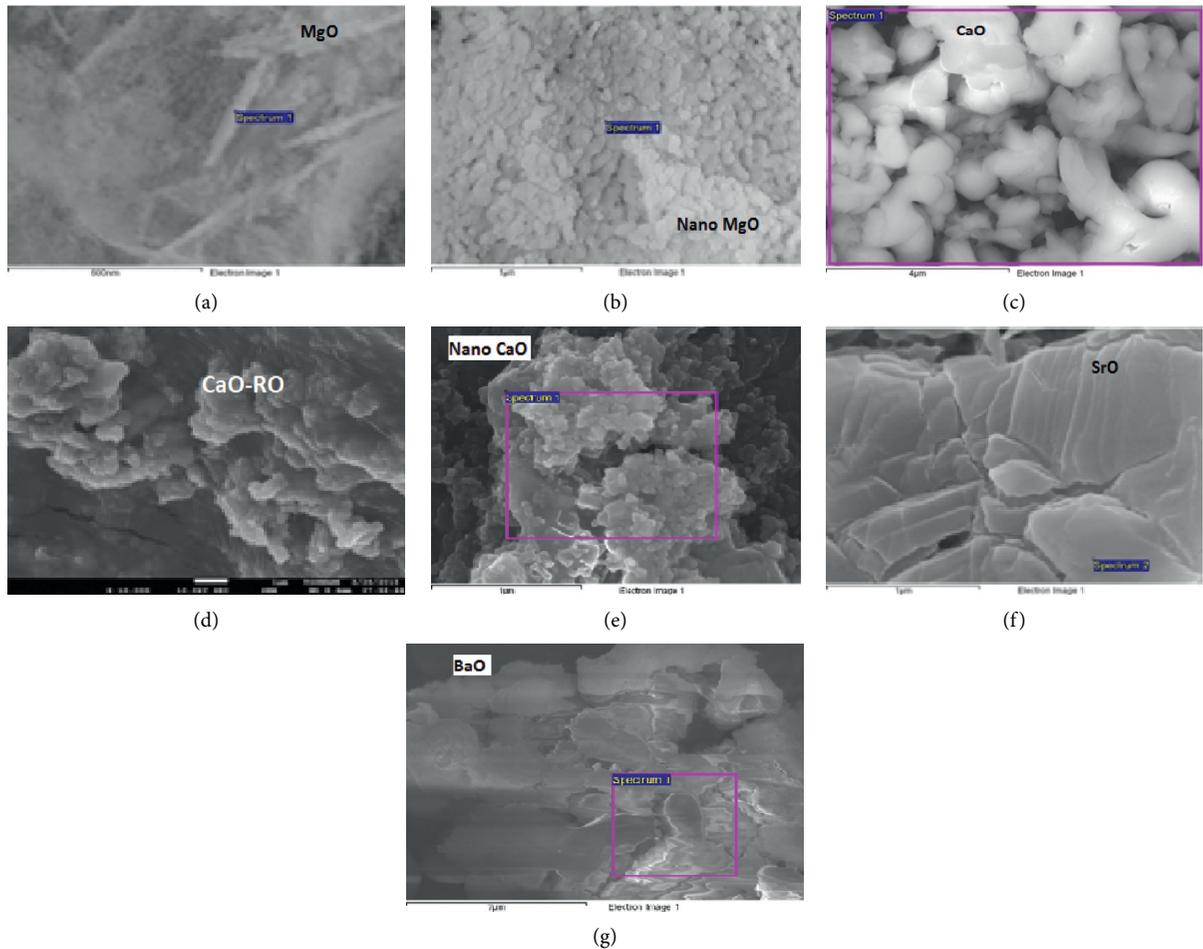


FIGURE 2: TEM images of catalysts (a MgO, b Nano MgO, c CaO, d CaO RO, e Nano CaO, f SrO, g BaO).

cases,  $F(x_A)$  correlated with time  $t$  and the coefficient-of-determination ( $R^2$ ) and normalized root mean square deviation (NRMSD), obtained for a linear regression passing through the origin. Equation with the highest  $R^2$  and lowest NRMSD at a given temperature was taken to be representing the most likely reaction order. Table 3 gives the  $R^2$  and NRMSD for the reaction orders from zero to three, and the largest coefficient  $R^2$  and lowest NRMSD (in bold). Table 4 gives the reaction order with respect to the two reacting species, the overall order, the reaction rate constant ( $k$ ), activation energy ( $E$ ), and preexponential factor ( $A$ ). For any heating mode, rates were the highest for homogeneous

NaOH, followed by heterogeneous BaO, SrO, and Nano CaO catalysts. A comparison of the magnitudes of  $k$  for WB to MW shows that microwave irradiation rates were higher than conventional heating, being 5 times for NaOH, 44 for BaO, 47 for Nano CaO, and 78 for SrO. Hence, for solid catalysts, the most active was BaO, followed by SrO and Nano CaO. Microwave irradiation is a superior heating method due to higher rates, leading to shorter reaction times; and, for alkaline earth metals, the catalyst activity follows the order of basicity and is not related to specific surface area.

Overall observed reaction order ranged from first to third. For NaOH catalyst with microwave irradiation, the

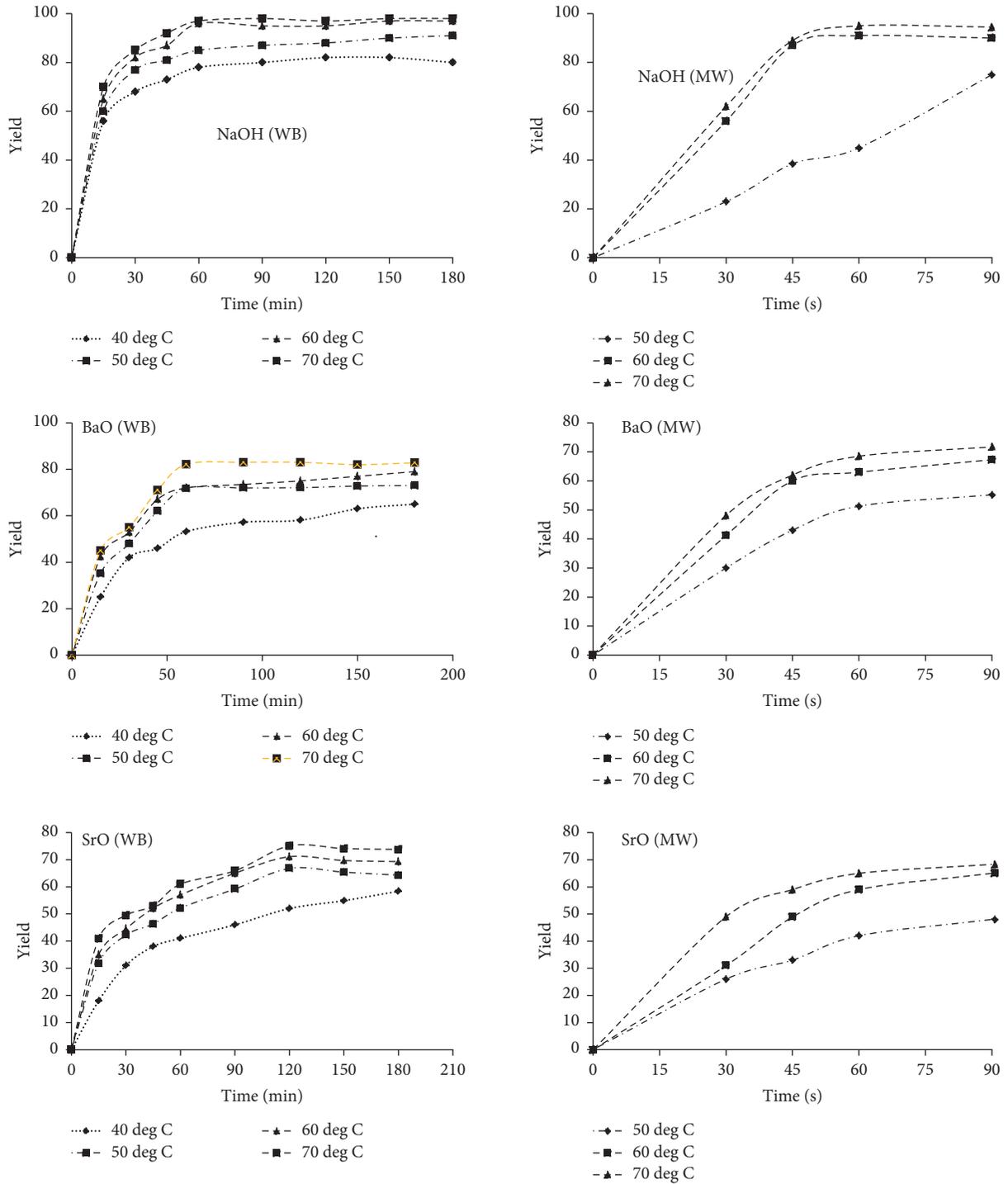


FIGURE 3: Continued.

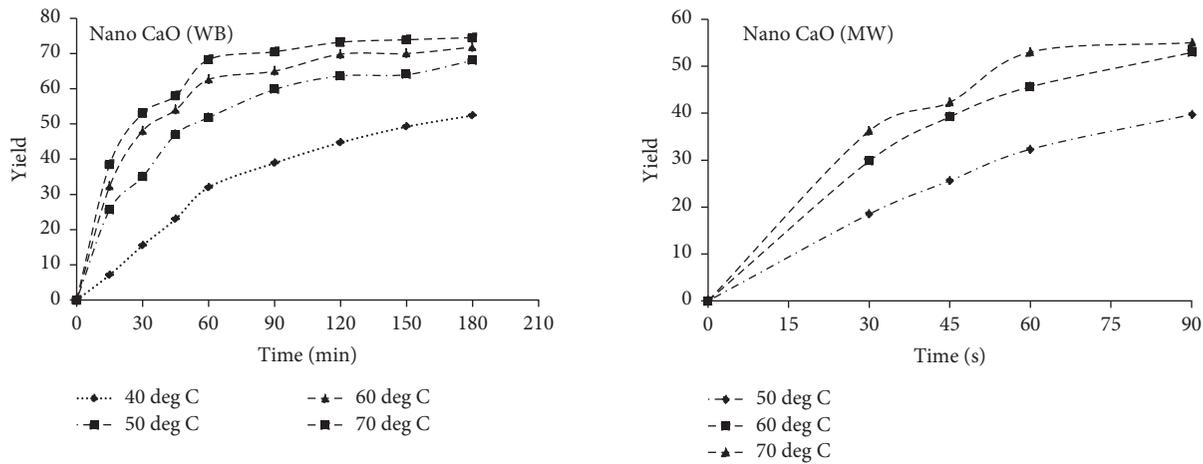


FIGURE 3: FAME yield as a function of time and temperature for NaOH, BaO, SrO, Nano CaO catalysts for the water bath (WB) and microwave (MW) heating.

TABLE 3:  $R^2$  and NRMSD (in brackets) for various catalysts and reaction orders for WB and MW heating at 70°C (numbers in bold refer to largest  $R^2$  and lowest NRMSD).

Case ( $m, n$ )	NaOH (WB)	NaOH (MW)	BaO (WB)	BaO (MW)	SrO (WB)	SrO (MW)	Nano CaO (WB)	Nano CaO (MW)
1 (0,0)	0.3728 (0.1429)	0.7618 (0.0982)	0.5041 (0.1211)	0.7923 (0.0892)	0.5921 (0.1041)	0.7714 (0.0944)	0.5434 (0.1127)	0.8256 (0.0796)
2 (1,0)	0.6763 (0.0892)	<b>0.8533</b> <b>(0.0683)</b>	0.6346 (0.0981)	0.8851 (0.0617)	0.7589 (0.0741)	0.8618 (0.0688)	0.6906 (0.0862)	0.8843 (0.0618)
3 (0,1)	0.4175 (0.1354)	0.7803 (0.0932)	0.5299 (0.1167)	0.8120 (0.0837)	0.6270 (0.0981)	0.7905 (0.0892)	0.5727 (0.1075)	0.8490 (0.0752)
4 (1,1)	0.7175 (0.0818)	0.8483 (0.0785)	0.6528 (0.0947)	0.9017 (0.0562)	0.7900 (0.0681)	0.8803 (0.0630)	0.7196 (0.0598)	0.8969 (0.0577)
5 (2,0)	<b>0.7946</b> <b>(0.0609)</b>	0.6973 (0.0865)	0.7062 (0.0888)	0.9517 (0.0469)	0.8811 (0.0494)	0.9402 (0.0419)	0.8261 (0.0595)	0.9277 (0.0465)
6 (0,2)	0.4650 (0.1274)	0.7969 (0.0884)	0.5550 (0.1123)	0.8315 (0.0781)	0.6620 (0.0919)	0.8098 (0.0839)	0.6024 (0.1023)	0.8557 (0.0708)
7 (2,1)	0.7555 (0.0694)	0.6736 (0.8915)	<b>0.9629</b> <b>(0.0828)</b>	<b>0.9580</b> <b>(0.0338)</b>	<b>0.8940</b> <b>(0.0452)</b>	<b>0.9517</b> <b>(0.0371)</b>	<b>0.8465</b> <b>(0.0551)</b>	<b>0.9444</b> <b>(0.0437)</b>
8 (1,2)	0.7286 (0.0791)	0.8412 (0.0695)	0.7778 (0.0921)	0.9161 (0.0511)	0.8179 0.0625)	0.8977 (0.0574)	0.7463 (0.0757)	0.9093 (0.0534)
9 (3,0)	0.6925 (0.0692)	0.4220 (0.1108)	0.7067 (0.0892)	0.9514 (0.0394)	0.8520 (0.0523)	0.8775 (0.0438)	0.8144 (0.0987)	0.9439 (0.0490)
10 (0,3)	0.5129 (0.1192)	0.8109 (0.0842)	0.5790 (0.1082)	0.9505 (0.0726)	0.6966 (0.0857)	0.8291 (0.0785)	0.6320 (0.0970)	0.8700 (0.0664)

reaction was of first order and that with water bath was of second order. All reactions with heterogeneous catalyst indicated an overall third order, second order with respect to triglyceride, and first order with respect to methanol. For WB, a second-order kinetics has been reported for homogeneous NaOH/KOH catalysts for transesterification of palm oil and methanol [34], sunflower oil with methanol [35, 36, 38], sunflower oil with ethanol [37], and soybean oil with methanol [32]. For MW, literature supporting a first-order reaction for NaOH catalyst is from Jain and Sharma for *Jatropha curcas* oil [39] and Jain et al. [40] for waste cooking oil. Singh and Fernando [19] used BaO for soybean

oil transesterification in a high-pressure reactor and conventional heating and have reported overall third-order kinetics, second-order with respect to triglyceride, and first-order with respect to methanol. For microwave irradiation, Patil et al. [30] report a similar order for transesterification of *Camelina sativa* oil on BaO and SrO catalyst. The present work is in agreement with the published work on BaO and SrO kinetics. No kinetic study involving Nano CaO has been reported. Activation energy and preexponential factor data do not show any trend. A catalyst lowers the activation energy of a reaction, but the magnitude of activation energy for a heterogeneously catalyzed reaction is not automatically

TABLE 4: Reaction orders, rate constants, activation energy, and preexponential factor.

SN	Catalyst	Heating mode	Order w. r. t triglyceride	Order w. r. t methanol	Overall order	Rate constant $k$ at 70°C	Units of $k$	E (kJ/mol)	A
1	NaOH	WB	2	0	2	$4.75E-01$	$\text{cm}^3 \text{mol}^{-1} \text{min}^{-1}$	71.3	$3.73 \text{E} + 10$
		MW	1	0	1	$2.45E+00$	$\text{min}^{-1}$	51.0	$2.68 \text{E} + 06$
2	BaO	WB	2	1	3	$1.27E-02$	$\text{cm}^6 \text{mol}^{-2} \text{min}^{-1}$	35.4	$3.07 \text{E} + 03$
		MW	2	1	3	$5.69E-01$	$\text{cm}^6 \text{mol}^{-2} \text{min}^{-1}$	36.8	$2.38 \text{E} + 05$
3	SrO	WB	2	1	3	$6.19E-03$	$\text{cm}^6 \text{mol}^{-2} \text{min}^{-1}$	26.6	$7.37 \text{E} + 01$
		MW	2	1	3	$4.88E-01$	$\text{cm}^6 \text{mol}^{-2} \text{min}^{-1}$	46.2	$5.67 \text{E} + 06$
4	Nano CaO	WB	2	1	3	$5.65E-03$	$\text{cm}^6 \text{mol}^{-2} \text{min}^{-1}$	33.7	$8.80 \text{E} + 02$
		MW	2	1	3	$2.68E-01$	$\text{cm}^6 \text{mol}^{-2} \text{min}^{-1}$	36.6	$1.79 \text{E} + 03$

accepted to be a quantitative measure of the catalytic activity. The reason for not adopting this criterion is the widespread occurrence of compensation effects [47, 48]. Transesterification reaction consisting of three consecutive reactions falls under this category. Reaction velocity constant in this case is a sum of several reaction steps, and activation energy is termed “apparent activation energy” and the preexponential factor is termed “apparent preexponential factor.” In some cases, the changes in apparent preexponential factor and apparent activation energy display a linear dependency according to the Cremer–Constable relation [49].

#### 4. Conclusions

Transesterification reaction kinetics of *croton megalocarpus* oil depends on the catalyst employed and the heating method. Observed reaction orders ranged between 1<sup>st</sup> (for NaOH, MW), 2<sup>nd</sup> (for NaOH, WB), and 3<sup>rd</sup> (for BaO, SrO, Nano CaO, MW, and WB). For microwave irradiation reaction, rate constants were higher by several orders as compared to those for conventional heating, due to faster reaction rates under the former. Heterogeneous catalyst activity depended on its basicity, with little relationship to the surface area. Among the catalysts studied, homogeneous NaOH gave the highest yield, followed by heterogeneous BaO, SrO, and Nano CaO. Activation energy and preexponential factor data for the catalysts did not show any trend, and the compensation effect is speculated.

#### Data Availability

The reaction kinetics and any other data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

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

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