

# Alkaline Earth Metal Oxide Catalysts for Biodiesel Production from Palm Oil: Elucidation of Process Behaviors and Modeling Using Response Surface Methodology

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**ABSTRACT:** Four different alkaline earth metal oxides i.e. MgO, CaO, SrO and BaO were used as heterogeneous catalysts for biodiesel production from palm oil. Effects of critical process variables i.e. reaction time, methanol to oil ratio and temperature were investigated. The results were then fitted to a historical design to study the Analysis of Variance (ANOVA), to characterize interactions between variables and to simulate the process. MgO did not show good catalytic activity while CaO produced undesired products at longer reaction time. BaO showed the best biodiesel result with a yield of up to 95 %, followed by SrO with a yield of 91 %. A methanol to oil ratio of 9:1 and 60 °C were found to be the optimum conditions. The experimental data were satisfactorily predicted at 99 % confidence level under various conditions with  $R^2$  values higher than 0.92. Characterizations of the catalysts before and after the transesterification process were also performed using a surface analyzer, scanning electron microscopy, Hammett indicator and Atomic Absorption Spectrophotometric (AAS) methods. The catalytic activity was in the order of BaO > SrO > CaO. However, due to lixiviation of BaO in the product, SrO was found to be the most potential catalyst

**KEY WORDS:** Biodiesel, Alkaline earth metal oxides, Process behavior, Historical design, Simulation, Lixiviation.

## INTRODUCTION

Recently, international attention is directed towards biomass as the source of renewable energy. This topic is gaining interest because of global warming and the depletion

of resources caused by high consumption of conventional fossil fuels [1]. Problems such as ring sticking, injector coking and eventual engine failure that are generally

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associated with the direct use of vegetable oils in diesel engines can be alleviated by modifying them through transesterification with lower alcohols such as methanol and ethanol [2]. The process is carried out in the presence of a suitable catalyst (acid or alkali) to produce corresponding mixture of fatty acid methyl esters (biodiesel) and glycerin. Due to its physicochemical and fuel properties which are similar to those of petroleum-based diesel fuel, biodiesel can be used in compression-ignition diesel engines with little or no modification [3].

In conventional transesterification process using homogeneous catalysts, large amount of wastewater is generally produced and the removal of catalysts after the reaction is a difficult task [4,5]. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future with heterogeneous catalysts as the latter are relatively non-corrosive, easy to handle and more environmental friendly. As all reactants in the transesterification process are in liquid phase, heterogeneous catalysts are also much easier to be separated from the liquid products through physical means such as filtration and centrifugation [6]. Heterogeneous catalyst can be divided into two groups, i.e. acid catalysts and base catalysts. It has been reported that acid catalysts usually show low activity and require high reaction temperature and longer reaction time as compared to base heterogeneous catalysts [7]. It has been reported that alkaline and alkaline-earth metal compounds are recently used for biodiesel production to replace conventional homogenous catalysts [8-10]. Alkaline and alkaline-earth metals supported on other materials such as alumina and silica can be considered as potential catalysts for the transesterification process. Zeolites are another group of catalysts studied for this process but they usually show poor activity due to small pore sizes [11,12]. Clay minerals such as hydrotalcite, chrysotile and sepiolite are considered to be the next group [13].

Rate of alkali-catalyzed transesterification process is usually much faster than that in an acid-catalyzed one [5]. Different types of heterogeneous basic catalysts have been studied for this application. One main group proposed is single component metal oxides which are further categorized into alkaline earth metal oxides, alkali metal oxides, rare earth oxides and some solid basic materials such as  $\text{ThO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$  and  $\text{TiO}_2$  [2,5]. As these oxides behave differently in the transesterification reaction,

further research works are required to identify the most suitable operating conditions towards the highest possible biodiesel yield. The common goals are always minimizing the catalyst usage, lowering the reaction temperature on energy input consideration and using the lowest possible methanol to oil ratio on technical feasibility and safety considerations. The highest possible biodiesel yield should be achieved at a shortest reaction time for a better productivity and lower overall energy requirement of the process.

Different types of heterogeneous catalysts have been developed to catalyze the transesterification process. Liu *et al.* [14] used solid-based  $\text{SrO}$  catalyst for biodiesel production with a methanol to oil molar ratio of 12:1 and  $\text{SrO}$  catalyst loading of 3 % and at a reaction temperature of 65 °C to reach a yield of 95%. Activated calcium oxide ( $\text{CaO}$ ) has been used as the solid-based heterogeneous catalyst for several times without experiencing significant catalytic activity loss [15]. Dossin *et al.* [8] claimed that 100,000 tonnes of biodiesel production per year could be achieved with 5.7 tonnes of  $\text{MgO}$  as catalyst in a continuous stirred reactor of 25  $\text{m}^3$  capacity at 50 °C. Anion-exchange resin has also been used as heterogeneous catalyst to achieve 98.8 % of biodiesel. However, a three-step regeneration method preceded the reuse of the catalyst [16]. Xie *et al.* [7] used alumina loaded potassium iodide as a solid-based catalyst to catalyze the transesterification process. With a methanol to oil molar ratio of 15:1 and 2.5 % w/w of the catalyst, the highest conversion of soybean oil achieved in 8h by this catalyst was 96 %. Acidic ion-exchange resins were also investigated as catalysts but they led to maximum conversion of 45.7 % under the optimum conditions [17]. Kim *et al.* [2] prepared a solid super base of  $\text{Na}/\text{NaOH}/\gamma\text{-Al}_2\text{O}_3$ , which showed almost the same catalytic activity under the optimized reaction conditions as that of the conventional homogeneous  $\text{NaOH}$  catalyst. This catalyst was used to catalyze the transesterification reaction at a molar ratio of methanol to soybean oil of 15:1, a reaction time of 7 h, and a catalyst amount 6.5 % and the system could achieve the highest conversion of 87 %.

Fig. 1 shows the five step reaction mechanism generally proposed for the role of metal oxide catalyst in the transesterification reaction. Steps 1 and 2 describe the adsorption of alcohol and fatty acid on two neighboring free catalytic sites, respectively. In step 3,

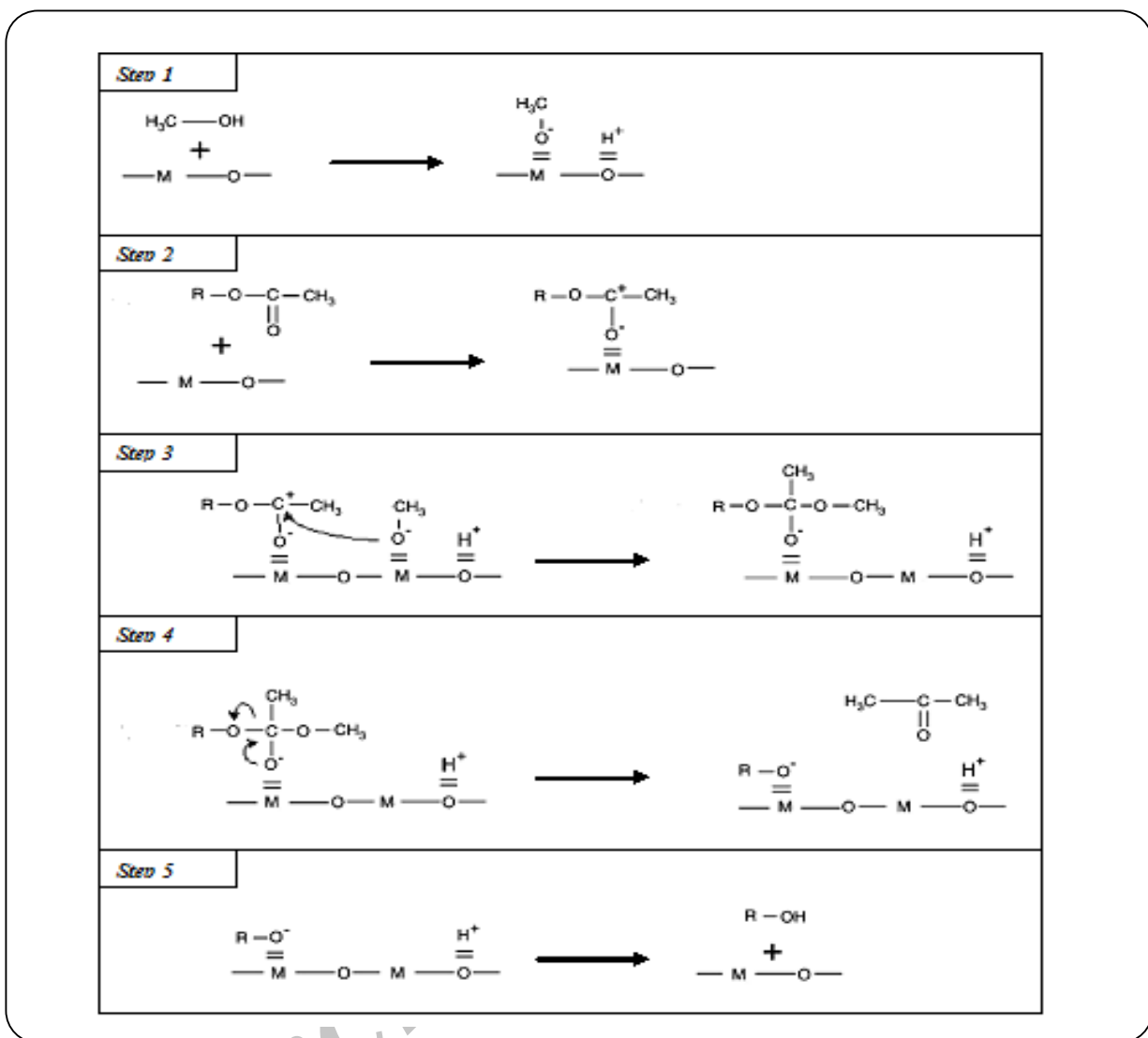


Fig. 1: Schematic representation on the role of metal oxide in the transesterification process of oil with alcohol (adapted from Hattori *et al.* [4]).

the two adsorbed groups react to form surface intermediates. These intermediates will further decompose in step 4 and finally desorb from the surface (step 5). According to Hattori *et al.* [4], the rate-determining step of this mechanism with catalysts having higher basicity such as BaO and SrO is the surface reaction step. Forward reaction generally promotes the formation of esters to result in high biodiesel yield. In this respect, higher alcohol ratios are preferred but amounts exceeding the optimum could dilute the reactants to result in lower reaction rate [18].

In most reported transesterification processes for biodiesel production, vegetable oils particularly sunflower oil [19], rapeseed oil [1,3], soybean oil [14,20] or non-edible oil such as jatropha oil [21] are used. Another alternative i.e. palm oil, receives little attention until very recently despite its high yearly production rate that better justifies its use as feedstock. Also, report on the use of alkaline earth metal oxide catalysts for the transesterification of this vegetable oil is rarely found in the literature. As different catalysts will behave differently with different types of oil, it is of great interest

to characterize the specific behaviors of the process. Thus, this work addresses specific process behaviors of alkaline earth oxides (BaO, CaO, MgO and SrO) catalyzed transesterification of palm oil with methanol. In this respect, effects of different critical process variables i.e. reaction time, oil to alcohol ratio and temperature on biodiesel yield are elucidated. The data obtained are also fitted to a historical design for data prediction study. Besides, lixiviation phenomenon of catalyst into the reaction product during the process is also addressed in this work.

## EXPERIMENTAL SECTION

### Chemicals and catalyst preparation

The alkaline earth metal oxide catalysts used including MgO, CaO, SrO and BaO were supplied by Sigma-Aldrich Corporation (Missouri, USA). The catalysts were initially calcined in a furnace at 500 °C for 3h prior to use and no further modification was made [22]. The calcined catalysts were then kept in an airtight vessel to avoid any physical and chemical changes. Commercial palm oil (Vesawit) was purchased from a local market in Penang and the concentration of free fatty acid was tested to be at 0.11 mg FFA /L.

### Catalyst characterization

#### Scanning Electron Microscopy (SEM)

Scanning Electron Microscopic (SEM) analysis was carried out on the catalysts using a Leo Supra scanning electron microscope (model 50 VP (Germany)) to study their surface morphology. The specific surface area of the alkaline earth metal oxide catalysts was calculated based on BET method using a Micromeritics ASAP 2020 surface analyzer.

#### Hammett indicator method

The basic strength of the catalysts ( $H_-$ ) was determined using Hammett indicators method as reported by Kouzu et al. [23]. About 25mg catalyst was shaken with 5.0 mL of Hammett indicator solutions that had been diluted with methanol and left to equilibrate for 2 h after which no further color change was observed. The color on the catalyst was then noted. The basic strength of the catalyst was reported as being stronger than the weakest indicator which exhibited a color change, but weaker than the strongest indicator that

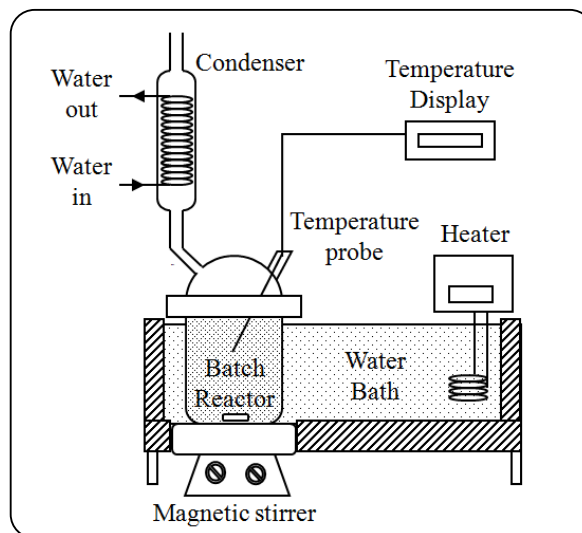


Fig. 2: Schematic diagram of the batch reactor used for biodiesel production.

produced no color change. The following Hammett indicators were used: neutral red ( $H_- = 6.8$ ), bromothymol blue ( $H_- = 7.2$ ), phenolphthalein ( $H_- = 9.3$ ), 2,4-dinitroaniline ( $H_- = 15.0$ ), 4-nitroaniline ( $H_- = 18.4$ ) and 4-chloroaniline ( $H_- = 26.5$ ).

#### Basicity test

The basicity of catalysts was determined using Hammett indicator-benzoic acid titration method [24]. First, 10mg catalyst was shaken in a conical flask with 2.0 mL of Hammett indicator solution that had been diluted with methanol. 0.1 mol/L benzoic acid was then added into the conical flask and the basic catalyst was neutralized by benzoic acid. When the basic color disappeared, the volume of benzoic acid used was recorded.

#### Catalytic activity test

Catalytic activity in the biodiesel production from palm oil was studied using a batch reactor system as schematically shown in Fig. 2. This reactor was placed in a water bath to control the temperature and the system was also equipped with a magnetic stirrer for mixing purposes. The reflux condenser and a thermometer probe were placed in the two-necked flask. The oil and methanol were mixed at desired temperatures ranging between 50 and 65 °C with an interval of 5 °C.

The effects of other variables including reaction time up to 240 min and oil to methanol ratio varying in the range of 1:3 to 1:15 % w/w by an interval of 3 % were studied. Quantitative determinations of the fatty acid methyl esters (biodiesel) yield were performed using a gas chromatograph. Prior to that, excess methanol was removed using an evaporating system. The mixture was then centrifuged at 2500 rpm in an Eppendorf centrifuge for 12 min.

In a typical run, the catalyst was first dispersed in palm oil under stirring and then the mixture was placed in a water bath to reach the desired reaction temperature. Then, pre-heated methanol was added to the mixture and the transesterification process was started. After the desired reaction time, excess methanol was distilled off under vacuum. The mixture was then centrifuged in an Eppendorf centrifuge at 2500 rpm for 20 min. After removing the glycerol layer, the biodiesel layer was collected for chromatographic analysis.

### Product analysis

Reference materials and biodiesel samples were analyzed using a Gas Chromatograph (GC) (Perkin-Elmer Series Clarus 500) that was controlled by a PC with a software package (Perkin-Elmer Turbochrom Navigator). The system was equipped with a capillary column (Nucol, 50m x 50 $\mu$ m) supplied by Supelco-Sigma Aldrich (USA) and helium was used as the carrier gas. The injector port temperature was kept constant at 220 °C and the detector temperature was maintained at 250 °C. The analysis of biodiesel for each reaction mixture was carried out by dissolving 50  $\mu$ L of diluted sample (biodiesel sample in *n*-hexane) into 50  $\mu$ L of internal standard solution at a concentration of 2 g/L and 1  $\mu$ L of this mixture was then injected into the GC. The analytical method used in the analysis was commonly reported in literature [7, 10, 14]. Modification to the ASTM method was done as the sample amount was rather small and accurate measurement of 0.25 g of liquid sample was difficult.

### Lixiviation of catalysts

Chemical stability of the heterogeneous catalysts was investigated by analyzing the presence of free metal in the biodiesel product which could be caused by the occurrence of catalyst lixiviation. After the purification

process of product mixture, the remaining biodiesel solution was analyzed by means of an Atomic Absorption Spectrophotometer (AAS, PerkinElmer 200) in order to determine the metal concentration in the liquid phase. This was done to check the chemical stability of the heterogeneous catalysts. This information was deemed critical to justify the need for any neutralization or purification steps of the produced biodiesel after the reaction.

### Statistical evaluation of data

In order to accomplish the statistical analysis of the transesterification process and to study the specific interactions between the variables, the data were fitted to a historical design based on Response Surface Methodology (RSM) using the Design Expert Software (Version 6.0.7, StatEase, Inc., USA). The quadratic equation model for predicting the behavior of those variables is expressed by in Eq. (1).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where,

$Y$  is the response (dependent variables),

$\beta_0$  is constant coefficient,

$\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are coefficients for the linear, quadratic and interaction effects,

$x_i$  and  $x_j$  are factors (independent variables), while,

$\varepsilon$  is the error.

This software was also used for regression and graphical analyses of the data obtained. The variability in the dependent variables was explained by multiple coefficients of determination ( $R^2$ ) while the model equation was used to predict the optimum values [25].

## RESULT AND DISCUSSION

### Effect of catalyst type and loading

Four different metal oxide catalysts including MgO, CaO, SrO and BaO were investigated. All the used metals are from Group IIA of the periodic table which are known as alkaline earth metals. These metal oxide catalysts were tested under the same conditions in order to compare their performance in the transesterification process. Fig. 3 shows the results of 4 different unsupported catalysts at catalyst loadings of 3 and 5 % w/w. The activity tests were carried out at 60 °C for 90 min under continuous stirring. With two levels of catalyst

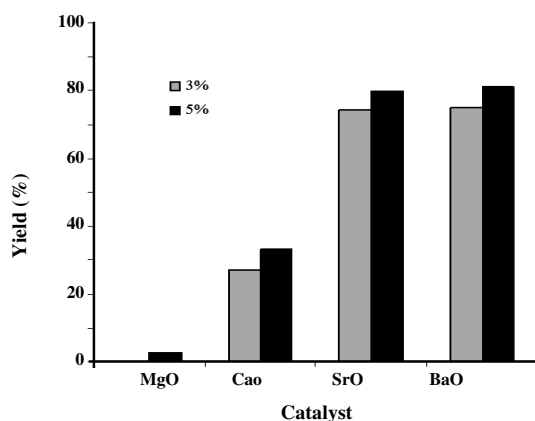


Fig. 3: Biodiesel yield for the unsupported metal oxide catalysts at two different loadings.

loading tested, behaviors in the biodiesel yield with increasing catalytic sites for the reaction could be demonstrated. In the transesterification reaction, increasing methyl ester products during the reaction would affect the equilibrium [2]. This might lead to the change of the reaction direction to the reverse side. A suitable catalyst should be used to favorably result in the production of methyl esters.

As noted in Fig. 3, BaO and SrO showed significantly higher biodiesel yield as compared to MgO and CaO, with a slightly higher yield demonstrated by BaO. The biodiesel conversion with MgO was the lowest and no activity was detected below 5 % of catalyst loading. Increasing catalyst loading of about 67 % from the lower to the higher level (3 % w/w-5 % w/w) merely resulted in a maximum change of about 8 % in the biodiesel yield. The magnitude of increase in the yield was noticeably higher using higher amounts of CaO as the catalyst.

The increase in yield was not necessarily proportional to the catalyst loading. This result was consistent with the observation made by Liu *et al.* [14] who used soybean oil-SrO system and also that reported by Vyas *et al.* [21] for Jatropha oil-KNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system. Thus, it could be concluded that significant improvement in the biodiesel yield with increasing catalyst loading was only achievable when the yield was low. This behavior was therefore concluded to be the common behavior in the reaction, regardless of the types of catalyst or oil used. Higher loading was therefore deemed responsible to promote the reverse reaction, especially when

the equilibrium of the reacting system was reached at high methyl esters concentration.

Chemical properties of the catalysts were deemed the responsible factors for their different behaviors in the transesterification process. This conclusion was based on the fact that their surface areas were low and occurred in a narrow range (10-20 m<sup>2</sup>/g) while showing pore volumes between 0.03 and 0.04 cm<sup>3</sup>/g (Table 1). The narrow ranges of the surface properties were insufficient to pose significant difference in the catalytic behaviors of the heterogeneous catalysts [2,4]. Thus, the catalytic behaviors should be elucidated based on the basicity of the metals.

The ionization energy of an atom or molecule is the amount of energy released when detachment of an electron from it to form a positively charged ion. Correspondingly, the basicity of the metals increases from Mg to Ba. The ionization energy of the alkaline earth metals generally decreases with the increase of the atomic number (descending the same group in the periodic table), while the atomic radius shows a gradual increase [26]. This makes heavier alkaline earth metal oxides to be more readily interacting with the large triglyceride molecules in palm oil and act as better catalysts in the transesterification process. The low conversion with MgO did not justify it to be further used for the transesterification process. Subsequent study was therefore focused on the 3 other catalysts. In this study, BaO showed slightly higher biodiesel yield (74.9 % and 81.3 % for 3 and 5% of catalyst loading, respectively) as compared to SrO (73.4% and 75.6 % for 3 and 5 % of catalyst loading, respectively). The low ionization energy of Ba ion rendered it readily susceptible to interactions with high electron centre in the triglyceride molecule i.e. the -C(=O)-O- group leading to the initiation of the transesterification reaction.

#### Effect of reaction time

Fig. 4 demonstrates the profiles of biodiesel yield with the reaction time for different catalysts while other variables i.e. molar ratio and temperature, were kept constant at 9:1 and 60 °C, respectively. As noted, there is an upward trend, in general, for all the catalysts with the increase in the reaction time until about 180 min after which, the catalysts showed different behaviors. SrO catalyst showed a virtually constant yield at about 84 %

Table 1: Analysis of variance for the quadratic models established for the transesterification of palm oil to biodiesel.

	Source	Sum of squares	DF <sup>a</sup>	Mean square	F value	Prob.> F
Yield <sub>(CaO)</sub> , %	Model	7058.61	6	1176.44	20.636	< 0.0001
	Residual	513.09	9	57.01		
	Lack of Fit	503.47	7	71.92	14.953	0.0641
	Pure Error	9.62	2	4.81		
	Cor Total	7571.70	15			
$R^2 = 0.9322$ , $CV^b = 21.28$ %						
Yield <sub>(SrO)</sub> , %	Source	Sum of squares	DF <sup>a</sup>	Mean square	F value	Prob.> F
	Model	7906.75	6	1317.79	26.741	< 0.0001
	Residual	443.53	9	49.28		
	Lack of Fit	436.38	7	62.34	17.446	0.0553
	Pure Error	7.15	2	3.57		
	Cor Total	8350.28	15			
$R^2 = 0.9469$ , $CV^b = 11.48$ %						
Yield <sub>(BaO)</sub> , %	Source	Sum of squares	DF <sup>a</sup>	Mean square	F value	Prob.> F
	Model	7912.02	5	1582.405	59.808	< 0.0001
	Residual	264.58	10	26.458		
	Lack of fit	245.53	8	30.692	3.223	0.2583
	Pure error	19.05	2	9.523		
	Total	8176.60	15			
$R^2 = 0.9676$ , $CV^b = 7.74$ %						
<sup>a</sup> DF = Degree of freedom <sup>b</sup> CV=Coefficient of variation						

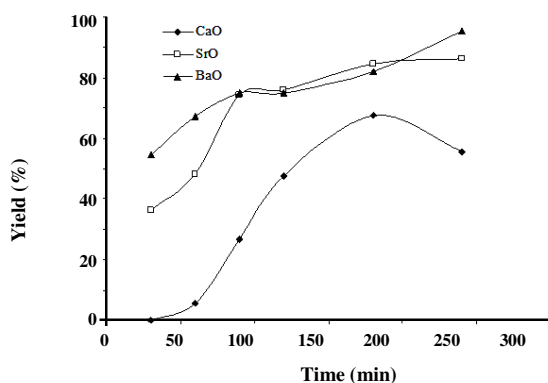


Fig. 4: Profile of biodiesel yield versus reaction time for the unsupported metal oxide catalysts.

after 180 min of the reaction while BaO still showed a gradual increase. In the case of CaO catalyst, a significant drop in the yield was observed after 180 min which could be attributed to the shifting of the reaction direction from forward to reverse reaction or the production of other undesired substances. The presence of additional minor components was detected in the GC results but due to limitations in the FAME analysis procedure used in this study, identification and quantification of those minor components were not possible. This observation was not made by Kim *et al.* [2] in their work using the same catalyst to transesterify soybean oil and the difference could be attributed to the fatty acid composition of the oils.

The biodiesel yield achieved using CaO reached its peak in 180 min with a biodiesel yield of 67.5 %. The conversion for SrO in the first 90 min showed a sharp increase followed by a moderate increase up to 240 min, reaching the highest possible yield of 86.4 %. BaO with an upward trend throughout the range of reaction time studied showed the best yield of 95.4 % in 240 min. The behaviors of SrO and BaO catalysts were found to be the almost similar with a slightly better conversion for the latter catalyst. The lower basicity of the catalyst was also responsible for this drop by slightly promoting esterification of free fatty acids with glycerol [23]. Also, the transesterification process is a reversible reaction in which the reaction can reverse in favor of the formation of diglycerides or triglycerides under certain conditions. This reversal was not clearly observed in the case of the other two catalysts. Thus, in addition to low biodiesel yield, CaO catalyst also promoted the formation of undesired by-products.

#### Effect of methanol to oil ratio

Methanol to oil molar ratio has been reported to be an effective variable in determining the course of the transesterification reaction. Theoretically, 3 molecules of methanol are needed to fully react with 3 molecules of fatty acids in a triglyceride molecule. However, excess methanol is critical in order to promote the forward reaction leading to the formation of methyl esters. In this study, a molar ratio 3:1 was used as the starting point and the ratio was varied until 15:1 while reaction time was fixed at 120min and temperature was kept constant at 60 °C.

As shown in Fig. 5, all catalysts showed an increase in the biodiesel yield as the methanol to oil ratio was increased to its peak which was generally reached at 9:1. SrO and BaO catalysts showed a yield of 73.5% and 79.1 %, respectively at the highest points. This result was consistent with that reported by Kim *et al.* [2] who used high pressure reactor for this purpose. But, it was lower than 12:1 that was reported by Vyes *et al.* [21] for Jatropha oil. Therefore, the optimum ratio was influenced by the types of reactants, reactor set up and catalysts used. Beyond this point, the yield dropped and SrO and BaO catalysts demonstrated no significant difference. No desired effect could be obtained by increasing the ratio from 12:1 to 15:1 for all catalysts. In this region, similar

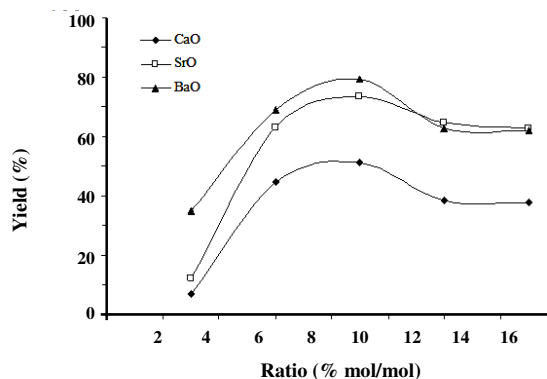


Fig. 5: Profile of biodiesel yield versus methanol to oil molar ratio for different metal oxide catalysts.

behavior is generally reported, regardless of the systems used [2,21,27].

A methanol to oil ratio higher than theoretical was generally needed in this study, as a portion of alcohol was in vapor phase and could not have much effective contact with the oil. The amount of the evaporated portion was greatly influenced by the reaction temperature, pressure and reactor set up. Initial increase in the methanol concentration shifted the reaction towards the formation of methyl esters. When the optimum value (9:1) was exceeded, the biodiesel yield dropped as excess methanol started to affect the interphase area between the alcohol and oil due to their poor immiscibility. Similar conclusion was also been made by Kawashima *et al.* [5]. The effect was relatively more significant at higher conversions as monoglycerides and diglycerides that presented in the reactor system while the conversion was low would act as emulsifiers to promote the interaction between methanol and oil [28].

#### Effect of reaction temperature

Studying the effects of temperature by keeping other parameters constant led to the results as presented in Fig. 6. In general, different types of catalysts demonstrated low yields at low temperatures and they gradually increased with increasing temperature. Sharper increases in the yield were recorded below 60 °C followed by a rather plateau for all the catalysts beyond that temperature. This result was consistent with that reported by Liu *et al.* [14] for soybean oil-SrO system and that reported by



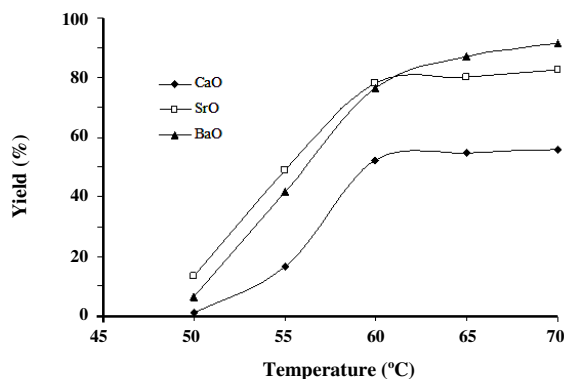


Fig. 6: Profile of biodiesel yield versus reaction temperature for different metal oxide catalysts.

Ngamcharussrivichai *et al.* [27] for palm kernel oil-CaO system. Similar behavior was demonstrated by all 3 catalysts tested in this study. Therefore, this behavior was concluded to be a general characteristic to the transesterification process rather than an oil-catalyst system dependent. However, it is interesting to note that the biodiesel yield in the case of BaO catalyst continued to increase beyond 65 °C but at a relatively lower rate. This result proved the high activity of this catalyst as compared to the other alkaline earth metal oxide catalysts.

As the reactor was operated at atmospheric pressure and the normal boiling point of methanol is 64.7 °C, methanol would be present in vapor phase beyond the boiling temperature. Therefore, it had little contact with oil to undergo transesterification. This explained the plateau, observed in the biodiesel yield at temperatures higher than 65 °C. However, the high catalytic activity of BaO only resulted in minimal increase in the yield beyond that temperature. In this case, methanol that had been condensed back to the reaction vessel at a slightly lower temperature than the boiling point still managed to react with the oil before its temperature increased to reach its boiling point. However, low concentration of methanol in the reacting vessel would certainly reverse the reaction. The highest yield of 91.4 % was observed in this temperature range using BaO catalyst, followed by 82.7 % and 55.8 % for SrO and CaO catalysts, respectively.

#### Statistical analysis

Earlier, effect of catalyst loading was studied at 2 different levels i.e. 3 % and 8 % and the results are

as shown in Fig. 3. In the RSM modeling study, focus was only given to the other 3 process variables. Catalyst loading variable was purposely excluded to avoid too complicated RSM modeling if done simultaneously with 4 variables. Furthermore, the catalyst loading used in this study was well within the normal range reported in earlier literatures [2, 4].

The experimental data obtained were then fitted to a historical design in order to statistically evaluate and analyze the results using Response Surface Methodology (RSM). The main used variables were the reaction time (A), methanol to oil ratio (B) and temperature (C). Based on the data, effects of reaction time were evaluated at six levels while those of methanol to oil ratio and reaction temperature were evaluated at five levels.

By using coded values, quadratic models were developed by the software and modifications in some terms were performed to reach the significance level for each term based on the *F* value. The model mathematical expressions obtained for the transesterification of palm oil to biodiesel using CaO, SrO and BaO catalysts are given in Eqs. (2), (3) and (4), respectively.

$$\text{Yield}_{(\text{CaO})} (\%) = -973.05761 + (0.96292A) + (13.79454B) + (25.97831C) - (0.0023776A^2) - (0.64673B^2) - (0.19224C^2) \quad (2)$$

$$\text{Yield}_{(\text{SrO})} (\%) = -1294.97447 + (0.66286A) + (21.24842B) + (36.68669C) - (0.00156608A^2) - (0.99251B^2) - (0.27777C^2) \quad (3)$$

$$\text{Yield}_{(\text{BaO})} (\%) = -1262.81975 + (0.17049A) + (14.31682B) + (37.04037C) - (0.67797B^2) - (0.27207C^2) \quad (4)$$

These equations suggest that the expressions for biodiesel yield are largely quadratic and consistent forms of expression were obtained for the catalysts. However, no term with respect to  $A^2$  appeared in the expression representing BaO catalyst. As the coefficient is of negative sign, the simulated yield continued to increase at longer reaction time. This conclusion was consistent with the experimental observation as shown in Fig. 4. All the interactions between the other terms (AB, AC and BC) were aliased by the software. These models could therefore be used to predict the behavior of the biodiesel production process.

The main focus of this study was to comparatively model the performance of different metal oxides as heterogeneous catalysts for biodiesel production.

Table 2: Properties of fresh and reused catalysts.

Catalyst	Surface area (m <sup>2</sup> /g)		Total pore volume (cm <sup>3</sup> /g)		Average pore diameter (Å)		Basic strength		Basicity (mmol/g)	
	fresh	reused	fresh	reused	fresh	reused	fresh	reused	fresh	reused
CaO	20	18	0.027	0.023	45.3	45.0	15.0 < H <sub>+</sub> < 18.4	15.0 < H <sub>+</sub> < 18.4	0.011	0.010
SrO	10	9	0.036	0.034	132.7	133.0	18.4 < H <sub>+</sub> < 26.5	18.4 < H <sub>+</sub> < 26.5	0.018	0.018
BaO	4	4	0.040	0.039	123.8	121.4	18.4 < H <sub>+</sub> < 26.5	18.4 < H <sub>+</sub> < 26.5	0.022	0.019

No emphasis was given on optimization of the reaction variables. Therefore, discussion on optimization seemed to be navigating away from the main focus. As such, the ANOVA results were deemed sufficient to generate necessary conclusions to address the objectives of the present study.

The significance of each coefficient in the equations above was determined by Student t-test and p-values [25]. The ANOVA for yield models for the 3 types of catalyst used to estimate the response as a function of reaction time, methanol to oil ratio and temperature are shown in Table 1. For the transesterification process using all the catalysts, highly significant results at 99 % of confidence level were observed. The coefficients of determination ( $R^2$ ) of 0.9322, 0.9469 and 0.9676 for CaO, SrO and BaO catalysts, respectively, were also reasonably good to suggest the applicability of the models to represent the process carried out under various conditions. The correlations were accurate up to biodiesel yields of 67.5 %, 86.4 % and 95.4 % for CaO, SrO and BaO catalysts, respectively.

The small value of “Prob.>F” (less than 0.05) indicated the significance of the model terms. The non-significant value of ‘lack of fit’ for both of the models (more than 0.05) suggested that the quadratic models were statistically valid for the present study. The results showed that the data obtained could fit the model equations very well as given in Equations (2-4). As a conclusion, sufficiently accurate mathematical expressions of quadratic types were successfully established from the available experimental data to simulate the experimental data of biodiesel yield within the range of experimental conditions studied. The applicability of similar models could be evaluated for the possible extension to other catalyst systems, other types of oil or wider ranges of process variables.

### Characterization of catalysts

#### Surface analysis

The surface area of the fresh and reused catalysts based on the nitrogen adsorption-desorption (multipoint BET) method are tabulated in Table 2. It was found that CaO catalyst had the largest surface area of 20 m<sup>2</sup>/g despite showing lower catalytic activity. Meanwhile, the fresh BaO catalyst was found to have a surface area of 4 m<sup>2</sup>/g. Thus, it can be concluded that in contrast to heterogeneous gas reactions, surface area played minor roles in the liquid phase transesterification reaction. The pore volumes for the fresh CaO, SrO and BaO catalysts were 0.027 cm<sup>3</sup>/g, 0.036 cm<sup>3</sup>/g and 0.040 cm<sup>3</sup>/g, respectively which did not show significant difference from a practical point of view. The average pore diameters were observed to occur within meso size range so that significant diffusion limitation problem was not expected to occur during the reaction. As noted in Table 2, no significant changes in terms of surface area and pore volume between the fresh and reused catalysts. Thus, it could be concluded that changes in the catalytic behaviors of the metal oxide catalysts were not mainly attributed to changes in the physical characteristics of the catalysts. The chemical states of the active components were deemed to pose more significant influence on the catalytic activity of the catalysts.

#### Hammett indicator method

The basic strength test results of the alkaline earth metal oxide catalysts are tabulated in Table 2 and they were generally similar with those reported by in the literature [4, 23]. Based on the results, CaO catalyst showed significantly lower basicity than the other two catalysts. Nevertheless, comparison between the basicity of SrO and BaO catalysts could not be made due to limitations in the Hammett indicator method. The basicity

of the catalyst was assumed to be a factor which could explain almost similar catalytic activity as demonstrated by SrO and BaO catalysts. The basic strengths of the fresh and reused catalysts were found to be almost similar. Thus, it could be concluded that no significant chemical changes occurred on the active components of the catalysts.

#### Catalyst basicity values

The basicity values of the catalysts are also represented in Table 2. The results are in good agreement to that reported by Zhu *et al.* [24]. BaO catalyst was found to be highly basic with a basicity of 0.022 mmol of benzoic acid/g of catalyst and the basicity value of CaO catalyst was noted to be the lowest among the alkaline earth metal oxide catalysts. This could explain the lower activity of this catalyst as compared to SrO and BaO catalysts. The measured basicity of SrO catalyst was lower than that of BaO catalyst although the basic strength of both catalysts were the same. The basicity value of BaO catalyst dropped significantly after one time of use in the transesterification. Meanwhile, the basicity of SrO and CaO catalysts remained almost the same before and after the process.

The catalytic activity of the catalysts generally increases with the increase in atomic number. This is in reverse order to the results obtained in surface analysis i.e. BaO ( $4 \text{ m}^2/\text{g}$ ) < SrO ( $10 \text{ m}^2/\text{g}$ ) CaO ( $20 \text{ m}^2/\text{g}$ ). Therefore, it could be concluded that active surface area was not the leading determinant that influenced the reaction. The basic properties were found to be the major parameters for the catalytic activity among the catalysts employed in this study. For the alkaline earth metal oxide catalysts, it was considered that the strength of the basic site was governed by the electronegativity of the conjugated metal cation. Since the large electronegativity intensifies the electron attractive force for the conjugated metal cation, the basic characteristics of the oxygen anion weakens [23].

#### Scanning Electron Microscopy (SEM)

Scanning Electron Micrographs (SEM) of the heterogeneous catalysts obtained before and after the transesterification process samples are presented in Fig. 7. After the reaction, the catalysts were removed from the centrifuge tube and properly washed with n-hexane

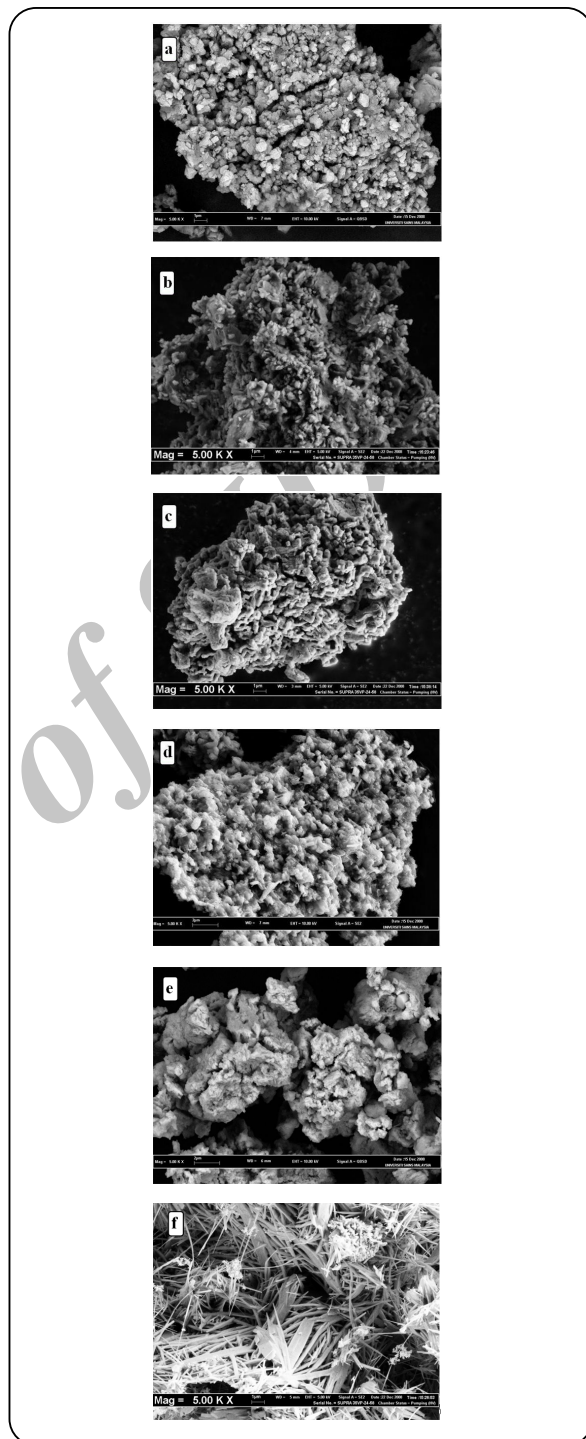


Fig. 7: Scanning Electron Micrographs (SEM) of (a) CaO catalyst before reaction, (b) CaO catalyst after reaction, (c) SrO catalyst before reaction, (d) SrO catalyst after reaction, (e) BaO catalyst before reaction, (f) BaO catalyst after reaction.

to remove any impurities attached to the surface. The catalyst was then placed in a furnace, heated to 500 °C at an increasing rate of 5 °C/s for 3 h for re-calcination. It can be observed from the micrographs that for CaO and SrO catalysts, the changes of the catalyst before and after use were not significant as compared to those of BaO catalyst. This result was consistent with the basicity results of BaO which showed a significant drop after use. The SEM images of the fresh catalysts show irregular shapes of catalyst particles. BaO catalyst appeared to be made up of more condensed mass of catalyst with visible macropores. The lower surface area of BaO catalyst can also be confirmed by Fig. 7. The appearance of BaO and SrO catalysts was consistent with the surface analysis results with respect to the average pore diameters that were relatively larger than that of CaO catalyst.

The micrographs also show that transesterification process caused some changes on the surface texture of the heterogeneous catalysts. For CaO catalyst, the particles were ground to form roundish shaped-particles. Meanwhile, the match stick-like particles in SrO catalyst appeared to undergo fragmentation to form smaller pieces. From all the characteristics of the catalysts, it was concluded that physical changes occurred after the reaction.

#### *Lixiviation of catalyst*

The stability of the alkaline earth metal oxide catalysts in terms of their lixiviation into the biodiesel layer was also studied. As methanol was used in variable amounts during the study, accurate measurement of the metal was not possible bearing in mind different degrees of conversion taking place during the process. The same goes to the palm oil as the limiting reactant. Indeed, it was more difficult as near complete conversions were achieved in this study. The analytical methods used simply converted all lixiviated metals into soluble components for AAS measurement. Table 3 shows the amounts of dissolved Ca, Sr and Ba in biodiesel after transesterification process. The amounts of Ca, Sr and Ba in biodiesel for ultrasonic cavitation systems were found to be merely 2.7 and 19.5 for Ca and Sr, respectively while it was 368.3 mg/L for Ba. It was found that BaO had the highest residual amount detected in biodiesel while CaO showed the least.

The result obtained in this study indicated that BaO had the highest solubility in biodiesel and appreciable

**Table 3: Lixiviation of metals from the catalysts into the biodiesel layer.**

Catalyst	Concentration (mg/L)
CaO	2.7
SrO	19.5
BaO	368.8

leaching occurred. The leaching of CaO in the etherification of glycerol has also been reported by *Ruppert et al.* [29]. In general the amount of metal remaining in biodiesel for CaO and SrO catalysts were in trace amounts, while BaO showed significantly larger amount dissolved catalyst in the product. It should also be noted that this result was in the reverse sequence to that shown by the surface areas of the spent catalysts. As a conclusion, SrO should be a more reliable catalyst for the transesterification process due to high activity and stability. The biodiesel produced was also expected to have better quality as less metal was found in the biodiesel product.

#### **CONCLUSIONS**

Performance of 4 different alkaline earth metal oxide catalysts in the transesterification process of palm oil was thoroughly studied. Preliminary studies revealed that MgO was not a suitable catalyst. Heavier alkaline earth metal oxides appeared to be more readily interacting with triglyceride molecules in palm oil to act as better catalysts. Significant improvement in the biodiesel yield with increasing catalyst loading was only achievable when the yield was low. In the transesterification reaction, increasing methyl ester concentration would affect the equilibrium. Thus, further experiments were carried out using BaO, CaO and SrO catalysts to study the effects of reaction time, methanol to oil ratio and temperature. In the case of CaO catalyst, a significant drop in the yield was observed after 180 min which could be attributed to the shifting of the reaction direction from forward to reverse reaction. All the catalysts showed an increase in the biodiesel yield with increasing methanol to oil ratio and it peaked at 9:1. In the case of BaO catalyst, biodiesel yield continued to increase above 65 °C but at a lower rate while for the other two catalysts, it dropped. The best yield was observed with BaO catalyst which reached a highest yield of 95.4 % followed by SrO

with a yield of 86.4 %. A mathematical model was formed using available experimental data by means of a historical design. The process behaviors under various conditions were successfully simulated and the results were proven to be statistically significant at 99 % of confidence level. The characteristics of the catalysts before and after use, were also elucidated. The results led to the conclusion that despite showing slightly lower catalytic activity than BaO, SrO should be a better catalyst for this application as it showed lixiviation into the reaction mixture during the reaction.

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