



# Evaluating the optimum operating parameters on transesterification reaction for biodiesel production over a $\text{LiAlO}_2$ catalyst



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## HIGHLIGHTS

- $\text{LiAlO}_2$  was firstly used as a novel catalyst for transesterification reaction.
- Conversion efficiency of soybean oils to biodiesel using  $\text{LiAlO}_2$  can reach 97.45%.
- The catalytic results revealed that  $\text{LiAlO}_2$  maintained its activity after six catalytic runs.

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## ABSTRACT

The  $\text{LiAlO}_2$  catalyst was prepared by solid-state reaction and then applied to the biodiesel production by transesterification reaction between methanol and soybean oil. This was the first attempt to use  $\text{LiAlO}_2$  as a catalyst for biodiesel production. It was found that the catalyst of 4 (mol( $\text{Li}_2\text{CO}_3$ )/mol( $\text{Al}_2\text{O}_3$ )) being calcined at 900 °C showed the optimum activity. XRD, BET and FE-SEM demonstrated that the Li compound was incorporated into  $\text{Al}_2\text{O}_3$  to form  $\text{LiAlO}_2$  with an enhanced basicity. The maximum conversion achieved 97.5% with 2 h reaction time at 65 °C, 24:1 M ratio of methanol to oil and 8 wt.% of catalyst.  $\text{LiAlO}_2$  could be easily recovered and reused for six cycles without significant deactivation.

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## 1. Introduction

Under the effects of energy crisis, biomass energy, with the strengths of renewability and low pollution, is considered as a substitute for petroleum to release the energy crisis in a short period of time [1–3]. Biodiesel, produced by vegetable oil and animal fat through transesterification, is a kind of renewable energy, which presents the characteristics of biodegradability and non-toxicity. Besides, it emits less exhaust than fossil diesel does so that it is an environment-friendly fuel. Such an alternative fuel has been widely developed for the increasing utilization of petroleum, expanding local air pollution, and global green house [4–6]. A complete biodiesel technology is regarded as the complex system engineering, covering several techniques of catalyst preparation, transesterification reaction, and waste oil reuse [7–9].

However, major quality related problems were encountered and it was the main hindrance for large scale industrial production of biodiesel by homogeneously catalyzed transesterification. Production costs were rather high as the process involved catalyst could not be recovered or reused, and the separation of fatty acid methyl esters (FAMES) from the catalyst generated large amounts of wastewater, resulting in the loss of useful materials [10,11]. These problems provided an impetus to search for basic solid and more stable catalysts [12]. In recent years, alkali metal (Li, Na, K) or alkali earth salts were loaded on metal oxide ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ) for improving the catalytic activity of mixed oxide catalysts [10–15].

Nevertheless, the use of basic solid catalysts generally requires more severe reaction conditions to obtain higher conversion, for example, high catalyst amount, high temperature and long reaction time, for the transesterification reaction than in the case of homogeneous catalysts. Furthermore, there are some problems in the low reaction rate, easy deactivation and the high viscosity increasing the mass transfer resistance. However, this reaction is associated with several difficulties in using basic solid catalysts,

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from an industrial perspective, involving the surface active sites being easily decayed upon exposing the catalyst to air. The chemisorption of carbon dioxide and water on the surface sites form carbonates and hydroxyl groups, respectively [13–19]. Most of the basic solid catalysts need to be resolved the removal of water and carbon dioxide from the surfaces to enhance their catalytic activities [20]. Chen et al. [21] and Wang et al. [22] found that  $\text{Li}_2\text{CO}_3$  catalytically tolerated the exposure to air. This presented important benefits when considering the industrial application of  $\text{Li}_2\text{CO}_3$  as a solid catalyst, and the possibility of storing and handling the activated catalyst without taking special actions prevented from contact with the ambient air.

Additionally, lithium-based catalysts showed a very high activity promoting transesterification reaction [21–23]. Xie et al. [24] reported that significant enhancement of catalytic activity was achieved for NaOH supported  $\text{Al}_2\text{O}_3$  leading to a highest basicity. Zabet et al. [25] reported that CaO was better dispersed on the  $\text{Al}_2\text{O}_3$  support and enhanced the conversion. Modification of the previously synthesized catalyst with  $\text{Al}_2\text{O}_3$  to improve its structure and properties was among the factors [24,25]. The compound  $\text{LiAlO}_2$  had favorable thermophysical, chemical, and mechanical stabilities at high temperatures [26]. In addition,  $\text{LiAlO}_2$  could be used as a catalyst and catalytic support because of its excellent electron transfer properties, high surface alkali, and a higher catalytic activity than the common  $\text{Al}_2\text{O}_3$  support [20]. Furthermore, it was suitable for transporting the reactants and products, resulting in a low diffusion resistance in the catalytic process. Therefore,  $\text{LiAlO}_2$  had great potential for the use as a catalyst.

In the present work,  $\text{LiAlO}_2$  was used as the heterogeneous catalyst in the soybean oil transesterification reaction with methanol for biodiesel production. To the best of our knowledge, this was the first attempt to use  $\text{LiAlO}_2$  as a catalyst for biodiesel production. Effects of several parameters, such as calcination temperatures, methanol/oil molar ratio, catalyst amount, reaction temperature and reaction time, were studied. Moreover, the catalyst reuse in various oil transesterification reactions was evaluated in order to perform a biodiesel production.

## 2. Materials and methods

### 2.1. Catalyst preparation

Soybean oil (Great Wall Enterprise Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Taiwan),  $\text{Al}_2\text{O}_3$  (Shimakyu's Pure Chemicals, Osaka, Japan), and  $\text{Li}_2\text{CO}_3$  (Shimakyu's Pure Chemicals, Osaka, Japan) were used as received.

The solid-state reaction was used for the preparation of Li–Al mixed oxide catalyst.  $\text{Al}_2\text{O}_3$  powder was added to an aqueous solution containing  $\text{Li}_2\text{CO}_3$ . After stirring and being dried at 110 °C for 12 h. The mixture was thoroughly ground, followed by calcination in air.

### 2.2. Transesterification

Transesterification reactions were carried out in a flat-bottomed flask equipped with a reflux condenser and a magnetic stirrer. Soybean oil was added to the flask and heated. In order to minimize the mass transfer limitations, each was mixed with stirring at 300 rpm. All experiments were performed at atmospheric pressure. After the reaction, deionized water was added to the reaction mixture to stop the reaction. Biodiesel and glycerol layers were easily separated because of a difference in their densities. The supernatant was filtered using common filter paper, and excess methanol and water were evaporated prior to FAME analysis. To optimize the reaction conditions, experiments were performed by varying

reaction parameters, such as reaction temperature, reaction time methanol/oil ratio, catalyst amount and conversion of various oils to biodiesel.

### 2.3. Catalyst characterization

The base strength of the as-prepared catalyst ( $\text{H}_+$ ) was determined using Hammett indicators. All samples were characterized using XRD with Cu  $K\alpha$  radiation (MAC MXP18, Tokyo, Japan,  $\lambda = 1.54056 \text{ \AA}$ ). The microstructure of the as-prepared catalyst was observed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7401F, Tokyo, Japan). The specific surface area was analyzed using Brunauer–Emmett–Teller (BET) surface area measurements (Micromeritics Company ASAP, 2010).

### 2.4. Analytical methods

The FAME concentration expressed as the biodiesel purity of the product was determined using a gas chromatograph (Thermo Trace GC Ultra, Thermo Co., Austin, Texas, USA) equipped with a flame ionization detector and a capillary column (Tr-biodiesel (F), Thermo Co., length: 30 m; internal diameter: 0.25 mm; and film thickness: 0.25  $\mu\text{m}$ ). Nitrogen was used as the carrier gas at a flow rate of 2 mL/min. The oven temperature program started at 120 °C with an increase to 220 °C at a rate of 30 °C/min and an increase to 250 °C at a rate of 10 °C/min. The temperature of the programmed temperature injector was 90 °C for 0.05 min and increased to 260 °C (programmed temperature) at a rate of 10 °C/min. The diluted solution with methyl heptadecanoate was added as an internal FAME standard. FAME amounts were calculated using the internal standard method (according to the EN 14 103 method). The most common peaks were observed at C16:0, C17:0, C18:0, C18:1, C18:2, and C18:3 as shown in Fig. 1. The conversion was determined according to the following equation

$$\text{Conversion \%} = \frac{\Sigma A - A_{\text{EI}}}{A_{\text{EI}}} \times \frac{C_{\text{EI}} \times A_{\text{EI}}}{m} \times 100\%$$

$\Sigma A$ : Sum of areas of all peaks ranging from C14:0 to C24:0,  $A_{\text{EI}}$ : Heptadecanoic acid methyl ester IS area,  $C_{\text{EI}}$ : Concentration (mg/mL) of Heptadecanoic acid methyl ester solution,  $V_{\text{EI}}$ : Volume of Heptadecanoic acid methyl ester solution added to sample,  $m$ : Mass of the sample (mg).

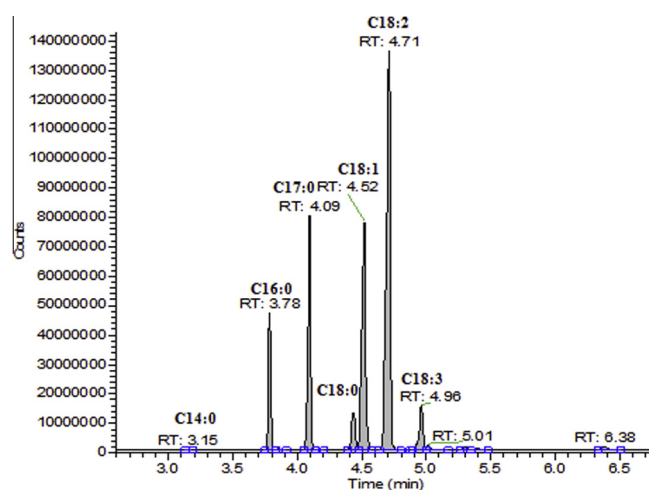
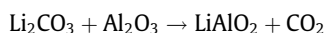


Fig. 1. Chromatogram obtained from GC-FID analysis of FAME.

### 3. Results and discussion

#### 3.1. Characterization of the LiAlO<sub>2</sub> catalyst

Fig. 2 shows the XRD pattern of LiAlO<sub>2</sub> calcined at 600–1000 °C for 4 h. The main peaks corresponding to LiAlO<sub>2</sub> (JCPDS 01-073-1338), Al<sub>2</sub>O<sub>3</sub> (JCPDS 83-2080), and Li<sub>2</sub>CO<sub>3</sub> (JCPDS 87-0728) were the main components of cement. Although LiAlO<sub>2</sub> was a complex material and the main peaks of its XRD pattern usually overlaid one another, the major phase change in LiAlO<sub>2</sub> was observed after its calcination. From above results, it could be deduced that LiAlO<sub>2</sub> appeared an amorphous phase when the calcination temperature was lower than 800 °C. On increasing the calcination temperature to 900 °C, crystallization occurred, with the phase transformation to crystalline LiAlO<sub>2</sub>. The preparation of LiAlO<sub>2</sub> by using Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> was a solid-state reaction. As the temperature was increased, the lattice surface and the internal state changed, leading to a continuous increase in the reactivity of Li<sub>2</sub>CO<sub>3</sub>. When the reaction temperature reached the melting point of Li<sub>2</sub>CO<sub>3</sub> (650 °C) [21], Li<sub>2</sub>CO<sub>3</sub> entered a molten state. Within the temperature range 800–900 °C, the following equation



strongly shifted to the right. This was possibly resulted from the complex reactions between Li and Al compounds; Li<sup>+</sup> was sucked into the gap in the Al compound crystal layers and reacted with Al<sup>3+</sup> to produce LiAlO<sub>2</sub>. Suski and Tarniowy [27] identified the crystallographic form of LiAlO<sub>2</sub> produced in the reaction. Table 1 summarizes the base strengths of Al<sub>2</sub>O<sub>3</sub> and LiAlO<sub>2</sub> in various Li: Al<sub>2</sub>O<sub>3</sub> molar ratios. The results showed that a Li: Al<sub>2</sub>O<sub>3</sub> molar ratio >2 resulted in the formation of the active solid base catalyst (LiAlO<sub>2</sub>) with H<sub>c</sub> ranging from 9.8 to 15. Thus, the incorporation of lithium compounds into Al<sub>2</sub>O<sub>3</sub> could result in a remarkable increase in the number of solid basic sites and hence the catalytic activity.

The FE-SEM images of LiAlO<sub>2</sub> calcined in air at 900 °C are shown in Fig. 2. LiAlO<sub>2</sub> had the uniform micro scale plate-type and particle-type mixed structure and 2–5 μm in lateral size as shown in Fig. 3(a). It appeared that LiAlO<sub>2</sub> powder tended to agglomerate into larger particles. Fig. 3(b) shows the elemental composition of LiAlO<sub>2</sub> determined using energy-dispersive X-ray spectroscopy. According to the figure, Li and Al were the main components. Fig. 3(c) shows the nitrogen adsorption–desorption isotherm curves of LiAlO<sub>2</sub>. The LiAlO<sub>2</sub> catalyst exhibited type III nitrogen adsorption–desorption isotherm. The LiAlO<sub>2</sub> catalyst showed a distinct hysteresis loop in the larger range of ca. 0.4–1.0 P/P<sub>0</sub>, which

**Table 1**

Base strengths of Al<sub>2</sub>O<sub>3</sub> powder and the prepared catalyst in various Li: Al<sub>2</sub>O<sub>3</sub> molar ratios.

Catalyst	Li/Al <sub>2</sub> O <sub>3</sub> molar ratio	Basic strength	Conversion (%)
Al <sub>2</sub> O <sub>3</sub>	0/1	H <sub>c</sub> <7.2	0.15
Li/Al <sub>2</sub> O <sub>3</sub>	1/1	7.2<H <sub>c</sub> <9.8	64.59
Li/Al <sub>2</sub> O <sub>3</sub>	2/1	9.8<H <sub>c</sub> <15.0	60.87
Li/Al <sub>2</sub> O <sub>3</sub>	3/1	9.8<H <sub>c</sub> <15.0	97.09
Li/Al <sub>2</sub> O <sub>3</sub>	4/1	9.8<H <sub>c</sub> <15.0	97.11
Li/Al <sub>2</sub> O <sub>3</sub>	5/1	9.8<H <sub>c</sub> <15.0	93.74

\* Reaction conditions: 12.5 g soybean oil; methanol/oil molar ratio, 24:1; catalyst amount, 6 wt.%; reaction time, 2 h; methanol reflux temperature and conventional heating method.

suggested the presence of a macropore structure. In BET surface area measurements, the specific surface area of LiAlO<sub>2</sub> was 1.02 m<sup>2</sup>/g. The inset in Fig. 3(c) shows the pore size distribution of LiAlO<sub>2</sub>. The pore size distribution calculated using the BJH method showed a broad pore size ranging from 70 to 110 nm.

The surface morphology of LiAlO<sub>2</sub> was examined using FE-SEM. Fig. 4 presents the FE-SEM images of LiAlO<sub>2</sub> samples with a spherical and impermeable porous surface. Small mineral aggregates and agglomerated particles were presented when the molar ratio increased because of the formation of metal oxides. According to the figure, spherical particles of various sizes with an average diameter of approximately 10–100 μm accumulated on the surface.

#### 3.2. Reaction studies

##### 3.2.1. Effect of calcination temperatures on the transesterification reaction

Table 2 shows various calcination temperatures for LiAlO<sub>2</sub>-catalyzed transesterification. In order to investigate the effects of calcination conditions, several calcination temperatures (600, 700, 800, 900 and 1000 °C) were considered, the conversion was increased and the optimal calcination temperature for the catalyst was at 900 °C. At this temperature, the highest conversion of 94% was achieved; the conversion rate decreased when the temperature was 1000 °C, and a further increase in the calcination temperature suppressed the catalytic activity of LiAlO<sub>2</sub>. As can be seen, a calcination temperature of 800 °C was not sufficient to produce highly active LiAlO<sub>2</sub> for transesterification and, according to the literature [28], the deactivation of the catalyst after its calcination at high temperature is probably the result of the loss of active sites, by the sublimation and agglomeration into the structure. Therefore, the optimal calcination temperature was 900 °C in this study.

##### 3.2.2. Effect of methanol/oil molar ratio g and catalyst amount on the transesterification reaction

The influence of methanol/oil molar ratio on the conversion over LiAlO<sub>2</sub> is indicated in Fig. 5. Because transesterification is an equilibrium reaction, the ester formation can be increased by employing an excess amount of methanol to drive the equilibrium toward the product formation [27]. According to Fig. 4, the conversion rate increased considerably with an increase in the amount of methanol. An increase in biodiesel yield from 72% to 90% by mass was obtained when the methanol to oil ratio was increased from 6:1 to 24:1 but decreased to 4% with the methanol/oil mole ratio 30:1. The optimum molar ratio of methanol/oil was found to be around 24:1. Yee et al. [29] indicated that the methanol/oil molar ratio should be higher than the stoichiometric ratio of these substances to drive the reaction toward completion (i.e., the formation of methyl esters). The lower biodiesel yield might be due to the high alcohol content (more than optimal ratio) which interfered with the phase separation of glycerol due to an increase in the solubility of glycerol in methanol.

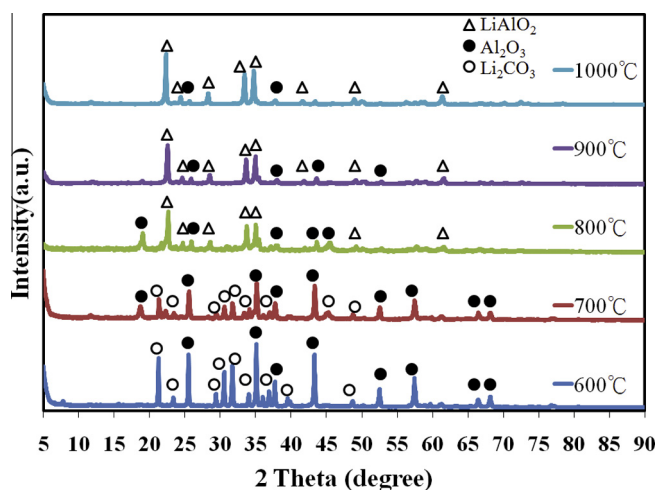
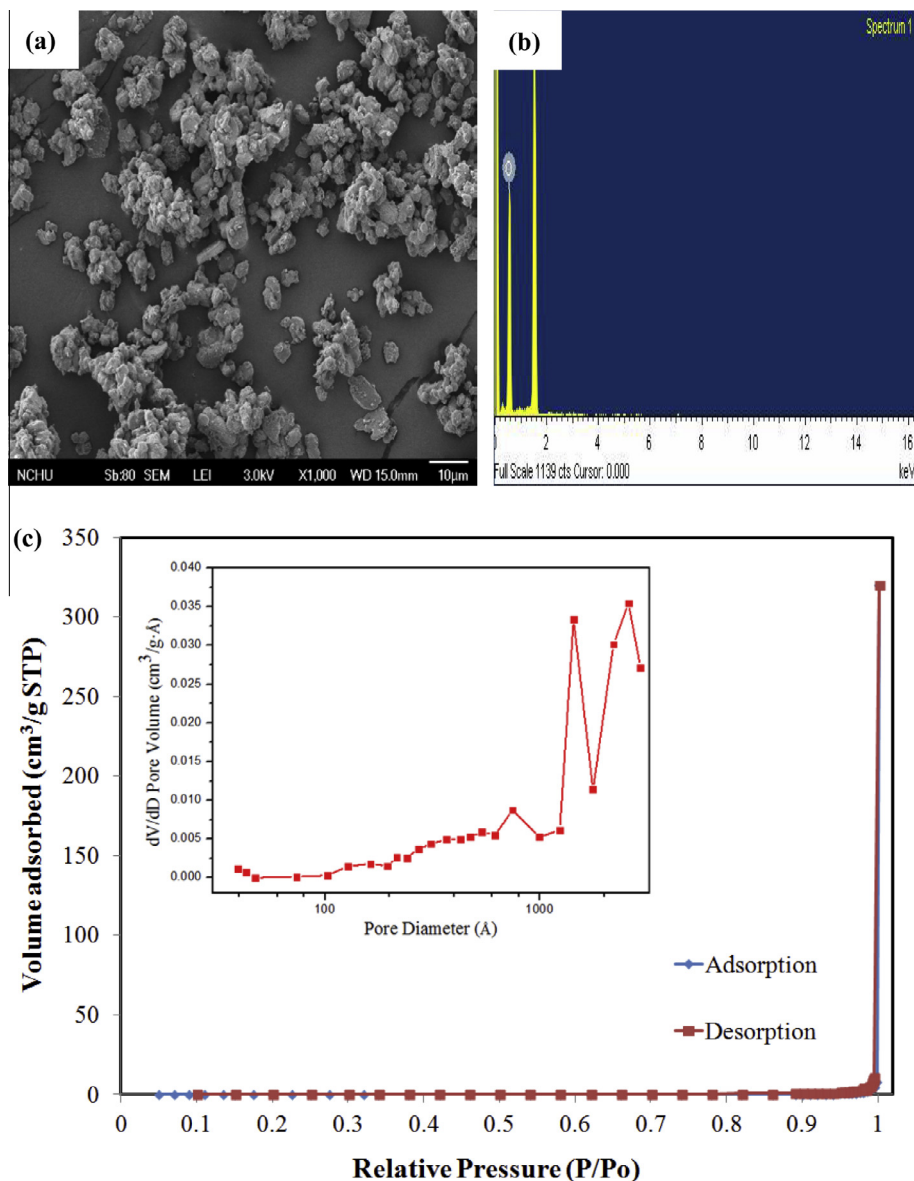


Fig. 2. XRD pattern of LiAlO<sub>2</sub> prepared at various calcination temperatures.



**Fig. 3.** (a) Morphology, (b) elemental analysis, and (c) nitrogen adsorption – desorption isotherm and pore size distribution of  $\text{LiAlO}_2$  calcined in air at  $900^\circ\text{C}$  according to FE-SEM.

Moreover, the amount of catalyst also affected the rate of reaction. The  $\text{LiAlO}_2$  catalyst was used for studying the effect of catalyst loading (2, 4, 6, 8 and 10 wt.%) with the reaction temperature  $65^\circ\text{C}$  and the methanol/oil molar ratio 24:1. The conversion result is shown in Fig. 5. The conversion was found to increase with the increase in the catalyst amount from 2 to 8 wt.% and then decrease with the increase in the catalyst amount above 8%. The conversion was found to be the maximum at 8 wt.% of catalyst amount when compared to 2, 4 and 6 wt.% of  $\text{LiAlO}_2$  catalyst amount. This might be due to the formation of mixing problem and resistance of mass transfer [30] at higher catalyst loading. Wang et al. [31] also observed similar results, when the conversion rate increased with an increase in the catalyst amount.

### 3.2.3. Effect of reaction temperature and time on the transesterification reaction

Fig. 6 shows the effects of the reaction temperature and time on the conversion rate. The reaction temperature was a crucial factor

in the entire process. Therefore, the reaction was conducted at various temperatures. According to Fig. 6, the conversion rate increased with an increase in the reaction temperature. The conversion gradually increased from  $45^\circ\text{C}$  to  $75^\circ\text{C}$  and reached the maximum 95.7 at  $65^\circ\text{C}$ . Both free fatty acid and triglycerides initially required the activation of their respective carboxylic or carbonyl functional groups to start the reaction. To favor the methanol nucleophilic substitution on free fatty acids, a comparatively high reaction temperature was required to activate this carbonyl group [32]. Thus, temperature clearly influenced the reaction rate and biodiesel conversion. According to a previous study, the reaction temperature dominated the reaction rate, and the conversion rate increased with an increase in the reaction temperature [33]. However, methanol was easily volatilized at  $75^\circ\text{C}$  to reduce the amount of methanol to participate in the reaction. Fig. 5 indicated that the conversion was found to increase with the increase in the catalyst amount from 1 to 6 h and then decrease with the increase in the catalyst amount above 2 h. The conversion then

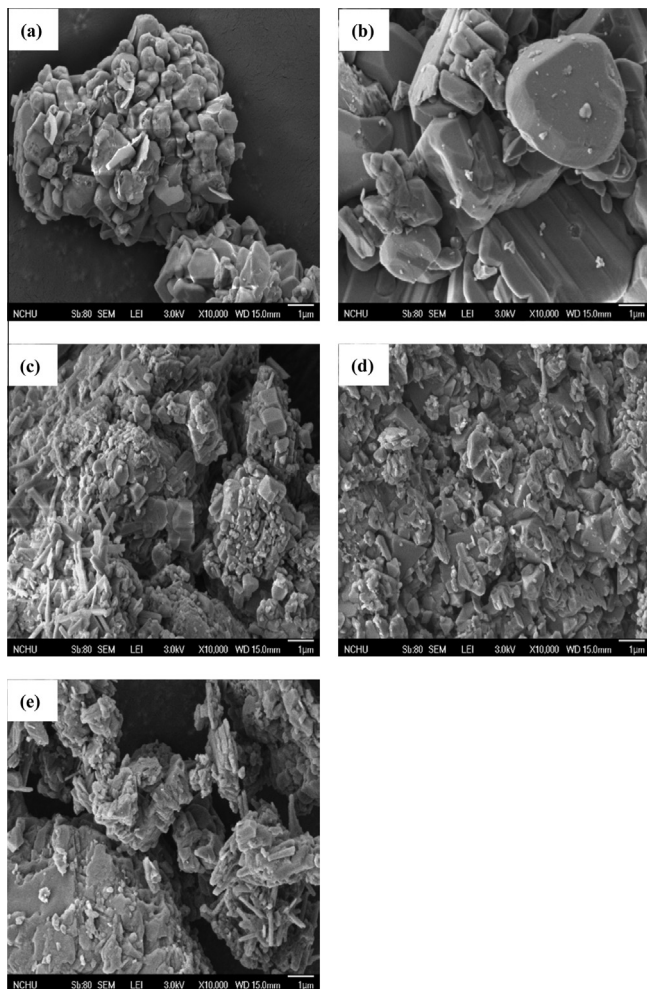


Fig. 4. FE-SEM images of  $\text{LiAlO}_2$  used in the solid-state reaction at  $900\text{ }^\circ\text{C}$  for 4 h with  $\text{Li}:\text{Al}_2\text{O}_3$  molar ratios of (a) 1:1, (b) 2:1, (c) 3:1, (d) 4:1, and (e) 5:1.

decreased probably due to the formation saponification at longer reaction time. The optimized reaction temperature for the transesterification of soybean oil to biodiesel thus was around  $2\text{ h}$ .

The earlier research of solid base catalyst for transesterification reaction is shown in Table 3. Comparing  $\text{LiAlO}_2$  with other various solid base catalysts [21–23,34], it could be clearly found that  $\text{LiAlO}_2$  showed the good catalytic performance for a transesterification reaction. For various solid base catalysts,  $\text{LiAlO}_2$  showed the higher catalytic activity (used for 5 cycles) than that of  $\text{Li}_2\text{SiO}_3$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{CaO}$  on conversion. When comparing the experimental results in this study with  $\text{CaO}$  catalyst, the activity of  $\text{LiAlO}_2$  was higher than that of  $\text{CaO}$ , while  $\text{LiAlO}_2$  showed the better conversion (exposure time for  $72\text{ h}$ ) than  $\text{CaO}$ . The conversion

Table 2  
Influence of calcination temperature on the conversion rate.

Calcination temperature ( $^\circ\text{C}$ )	Conversion (%)
600	32.65
700	31.75
800	63.46
900	94.62
1000	2.46

\* Reaction conditions:  $12.5\text{ g}$  soybean oil; methanol/oil molar ratio, 24:1; catalyst amount, 6 wt.%; reaction time, 2 h; methanol reflux temperature and conventional heating method.

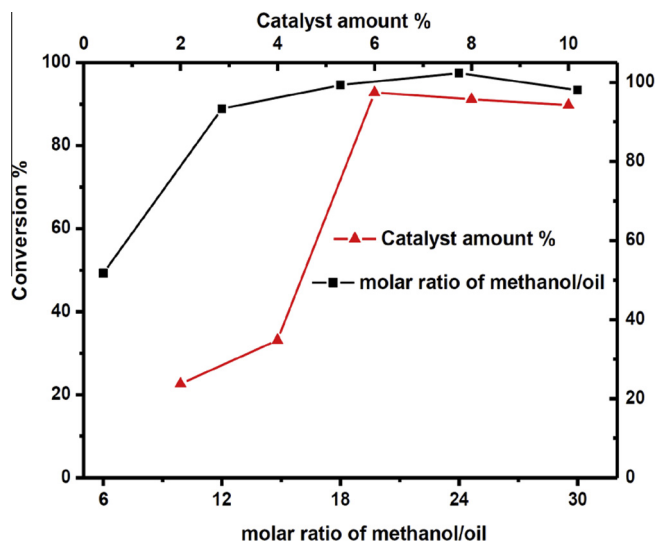


Fig. 5. Influence of the catalyst amount and methanol:oil molar ratio on the conversion rate (reaction conditions: soybean oil;  $12.5\text{ g}$ , reaction temperature;  $65\text{ }^\circ\text{C}$ , and reaction time;  $2\text{ h}$ ).

rates of castor oil and waste cooking oil to biodiesel are shown in Table 3. It was found that  $\text{Li}_4\text{SiO}_4$  was the most suitable catalyst giving 82.99% and 94.3% conversion. The good catalytic performance was dependent on the strength of basic sites as well as upon their amount. Table 3 also showed that the basic strength and the catalytic activity were affected with various materials of solid base catalyst, and the large basic strength led to the high activity at transesterification reaction.

### 3.3. Reusability of the catalyst

Fig. 7 shows the effect of air on the catalytic activity of  $\text{LiAlO}_2$ . This study investigated the effects of exposure to air on the catalytic activity of transesterification reaction. According to the figure, no difference in the conversion rate (93.7–85.9%) between the air-exposed catalyst ( $24\text{--}72\text{ h}$ ) and the freshly prepared

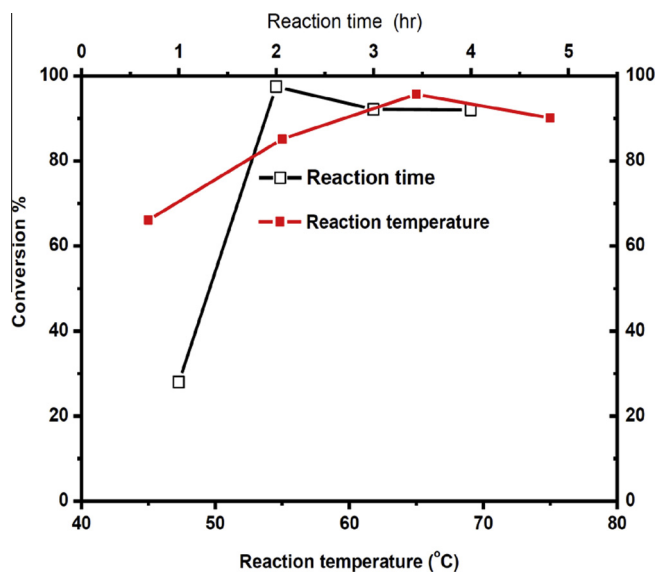
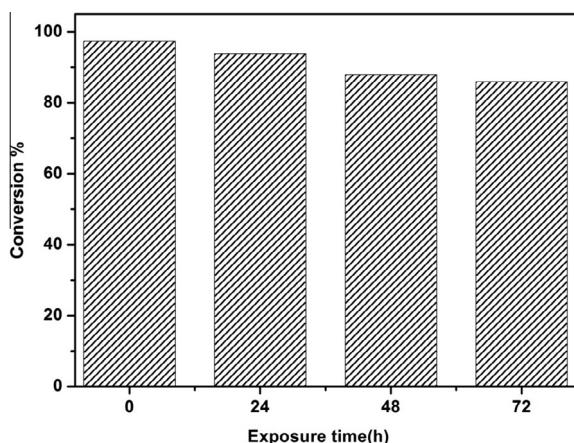


Fig. 6. Influence of reaction time and reaction temperature on the conversion rate (reaction conditions: soybean oil;  $12.5\text{ g}$ , methanol:oil molar ratio; 24:1, and catalyst amount; 6 wt.%).

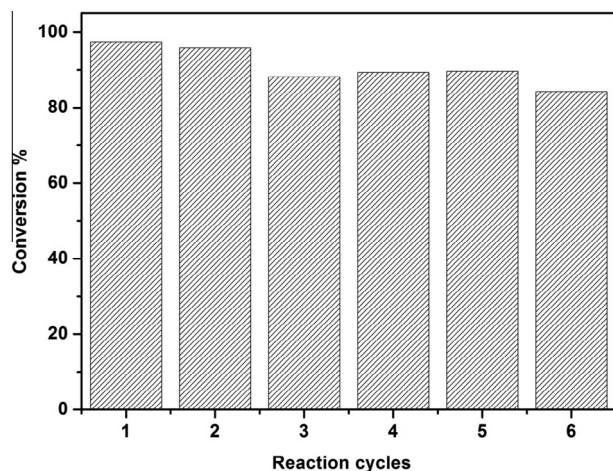
**Table 3**  
Comparison of conversion by different catalyst.

	Catalyst				
	LiAlO <sub>2</sub>	Li <sub>4</sub> SiO <sub>4</sub>	Li <sub>2</sub> SiO <sub>3</sub>	Li <sub>2</sub> CO <sub>3</sub>	CaO
Best conversion (%) <sup>a</sup>	98.06	98.17	96.12	95.50	96.16
Conversion (%) <sup>a</sup> (used for 5 cycles)	90.13	93.46	88.41	89.10	11.21
Exposure time (72 h) <sup>a</sup>	85.72	94.24	95.47	96.9	1.07
Castor oil (high oleic acid)	5.13	82.99	81.46	83.11	12.81
Waste cooking oil	2.80	94.31	86.51	84.68	25.39
Basic strength (H <sub>-</sub> )	9.8<H <sub>-</sub> <15.0	15.0<H <sub>-</sub> <18.4	15.0<H <sub>-</sub> <18.4	9.8<H <sub>-</sub> <15.0	15.0<H <sub>-</sub> <18.4
Reference	–	21, 23	35	22	21–23, 35

<sup>a</sup> For soybean oil.



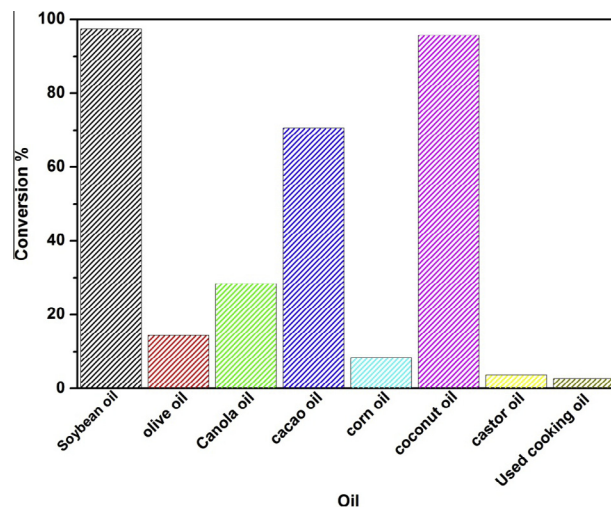
**Fig. 7.** Influence of LiAlO<sub>2</sub> exposed to air for 24–72 h on the conversion rate (reaction conditions: soybean oil; 12.5 g, methanol:oil molar ratio; 24:1, and catalyst amount; 6 wt.%).



**Fig. 8.** Reusability of LiAlO<sub>2</sub> after six reaction cycles (reaction conditions: soybean oil; 12.5 g, methanol:oil molar ratio; 24:1, catalyst amount; 6 wt.%, and reaction temperature; 65 °C).

catalyst (97.5%) was observed, verifying that the catalytic sites of LiAlO<sub>2</sub> were tolerant toward CO<sub>2</sub> and H<sub>2</sub>O contained in air. Thus, LiAlO<sub>2</sub> was air-insensitive, resulting in easy catalytic reaction.

The catalytic results revealed that LiAlO<sub>2</sub> maintained its activity after six catalytic runs (Fig. 8). The conversions of soybean oil were 97.45%, 95.77%, 88.18%, 89.33%, 89.63% and 84.24% when the catalyst was used for 6 cycles. When the filtered liquid after the transesterification was analyzed by ICP for evaluating the degree of



**Fig. 9.** Comparison of the conversion rates of various oils (reaction conditions: soybean oil; 12.5 g, methanol:oil molar ratio; 24:1, catalyst amount; 6 wt.%, and reaction temperature; 65 °C).

lixiviation of the active phase, the transesterification reaction produced FAME contained 0.3 ppm of lithium. Thus, the LiAlO<sub>2</sub> catalyst showed a high operational stability and LiAlO<sub>2</sub> was an air-insensitive catalyst, facilitating its practical application. Compared to the previous results over other heterogeneous base catalysts [35,36], a lower reaction temperature and better reusability were observed for the LiAlO<sub>2</sub> catalyst.

#### 3.4. Optimization of the reaction parameters for different oil using LiAlO<sub>2</sub> catalyst

The conversion rates of different oil to biodiesel are shown in Fig. 9. The conversion rates of soybean oil, olive oil, canola oil, cacao oil, corn oil, coconut oil, castor oil, and used cooking oil to biodiesel were 97.45%, 14.41%, 28.43%, 70.57%, 8.44%, 95.74%, 3.65%, and 2.65%, respectively. A higher concentration of free fatty acids than that of an alkali catalyst should not be used for transesterification because of the possibility of saponification [37]. The results showed that FAME conversion in the used cooking oil and castor oil with high free fatty acid concentration was considerably affected. Therefore, the performance of the same catalyst under the same reaction conditions varied for different oil.

#### 4. Conclusion

LiAlO<sub>2</sub>, synthesized by a simple solid-state reaction, was very active in the transesterification of soybean oil. Several reaction variables were studied, and the optimal catalyst amount was found to be 6% (w/w). The methanol/oil molar ratio of 24:1 yielded the

highest conversion rate. In addition, increasing the reaction time to 2 h resulted in the highest level of activity of  $\text{LiAlO}_2$ . Under such a condition, the yield of biodiesel reached over 97.5%. Additionally, the catalyst could be repeatedly used for more than 6 runs and  $\text{LiAlO}_2$  was air-insensitive. This biphasic system enabled the easy separation of products from  $\text{LiAlO}_2$ , and the  $\text{LiAlO}_2$  showed satisfactory recyclability.

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