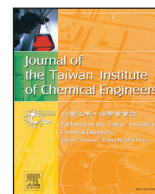




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Potential of using ceramics wastes as a solid catalyst in biodiesel production

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ABSTRACT

Reusing waste products is one of the milestones of progress toward environmental sustainability; producers can add value by reusing waste products. This study reports that ceramics wastes (CWs) are suitable raw materials for preparing a solid-base catalyst for biodiesel production. This study synthesized biodiesel from soybean oil using transesterification over a CWL-800-2. CWL-800-2 can be used directly for biodiesel production without being further dried or thermal pretreated, avoiding the usual activation of solid catalysts at high temperature. The effects of the calcination temperature and duration, methanol/oil ratio and catalyst amounts on the conversion are also reported in this paper. The solid base catalyst was highly active, air-insensitive and can be reused for at least four cycles without loss of activity. The catalysts were characterized using XRD, FE-SEM, FTIR, BET and the Hammett indicator method.

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1. Introduction

Currently, both human population and urbanization are increasing worldwide; consequently, the quantity of waste generated by agricultural, industrial, and municipal sources is steadily increasing [1]. Numerous methods exist for recycling waste materials. For example, the raw materials may be extracted and reprocessed, and the wastes can be transformed to new materials by subjecting them to chemical reactions. When considering any waste management hierarchy, one must recall the three essential principles: reduce, reuse, recycle; these principles facilitate minimization of the quantities of waste materials that must be sent to disposal sites [2–4].

Nowadays, homogeneous basic catalysts are most preferred in the commercial production of biodiesel because of their low cost and high availability [5,6]. Although homogeneous catalysts are the most common catalysts for catalyzing transesterified animal or plant oils into biodiesel, they possess severe problems; for example, some catalysts cannot be recovered or reused; some catalysts have high cost and low efficiency and generate large amounts of wastewater [7,8]. In general, the purification of biodiesel produced through homogeneous catalysis requires a vast quantity of water. Using heterogeneous catalysts could definitely improve biodiesel production processes and alleviate some problems associated with homogeneous catalysts. Heterogeneous solid-base catalysts are

advantageous because they can be easily separated and are recyclable, ecofriendly, and environmentally benign [9–11].

Ceramics wastes (CWs) are abundant, cost effective sources of Al and Si; they contain large amounts of Si and Al compounds (such as Al_2O_3 , FeO_x , SiO_2 , TiO_2), along with small quantities of impurities. Because CWs contain both Si and Al components, CWs can be employed as inexpensive raw materials for synthesizing high-value catalysts [12]. In recent years, some interesting studies have successfully modified the structures of various surface metal oxide species in order to optimize the catalytic properties of these materials for specific applications. Potential advantages include high reusability, high ease of separation from the product, modifiable catalyst properties, increased stability, and ease of storage. Modified catalyst host materials are mainly associated with two distinctive properties: (1) have large specific surface areas, which enable high loading of base sites and (2) during processing, can be easily separated from the reaction medium. In this context, some recently developed Li-based catalysts have been proven to display unexpected catalytic properties and stability [13–16]. Dai et al. [17] prepared a LiAlO_2 catalyst through solid-state reaction that could enhance the conversion of oil to biodiesel. Wang et al. [18] realized a significant improvement in catalytic activity by using SiO_2 and Li_2CO_3 ; they successfully loaded large quantities of reactants to basic sites. CWs have considerable potential for commercialization as prepared catalysts given their high yield and ease of control as well as low cost.

As an alternative to current commercial catalysts, this paper reports an effective and affordable waste materials-based method for biodiesel production. Aided by a simple solid-state reaction,

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the present study utilizes CWs to prepare solid-base catalysts, with Li_2CO_3 as the activating agent.

2. Materials and methods

2.1. Materials

The heptadecanoic acid methyl ester, ACS-grade methanol, and reagent-grade Li_2CO_3 were purchased from Uni-Onward Co. (Taiwan), ECHO Chemical Co. (Miaoli, Taiwan), and Shimakyu's Pure Chemicals (Osaka, Japan), respectively. Soybean oil, castor oil, canola oil, olive oil, Rapeseed oil and Cocoa ester were purchased from Great Wall Enterprise Co. (Taiwan). Ceramics wastes was picked in the National Taichung University of Education

2.2. Catalyst preparation

The catalyst was prepared using a solid-state reaction. A 5 g of CWs powder was added to an aqueous solution containing 9 g of Li_2CO_3 . The as-prepared solution was dried at 120 °C for 24 h. Finally, the CWs and Li_2CO_3 mixing powder was thoroughly ground and calcined at 800 °C in air for 4 h. The as-prepared sample was washed with 700 ml of anhydrous methanol and dried at 95 °C under a vacuum for 1 h to remove absorbed base sites from the catalyst surface. The as-prepared catalysts were labeled on the basis of the calcination temperature (500–800 °C) and calcination durations (1–4 h), for example, CWL-500-1, CWL-800-4).

2.3. Reaction procedures

The conversion of soybean oil to biodiesel was performed in a 250 ml flat-bottomed flask, equipped with a reflux condenser and a magnetic stirrer. The reactor was initially filled with 12.5 g of soybean oil, which was heated to 65 °C for 2 h while stirring at 300 rpm. The reactant was stirred evenly to avoid splashing in the flask at the stirring speed. The timing of the reaction was initiated as soon as the mixture of the methanol and catalyst was added into the reactor. The effects of the molar ratio of methanol to oil (12:1–36:1) and catalyst/oil weight ratio (2–8 wt%) on the conversion of triglycerides to biodiesel were investigated. All of the experiments were performed at atmospheric pressure. After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction [15]. The water contents have a significant inhibiting effect on the transesterification of glycerides with alcohols that use alkaline or acid catalysts, because water causes the reaction change to saponificate. The biodiesel and glycerol layers were easily separated because of differing densities of 0.86 and 1.126 g/cm³, respectively. A supernatant was filtered through a common paper filter, and excess methanol and water were then evaporated before to fatty acid methyl ester (FAME) analysis.

2.4. Catalyst characterization

Hammett indicators were used to assess the basic strength of the as-prepared catalyst (H_-): 2 mL of Hammett indicators were added to each catalyst sample (~100 mg) and shaken. Then, the mixture was allowed to equilibrate for 2 h; equilibrium can be confirmed through the lack of further changes in the color of the mixture. The phases of the resulting products were analyzed using a powder diffractometer (AC MXP18, Tokyo, Japan, $\lambda = 1.54056 \text{ \AA}$) at 295 K from 20° to 80° (step interval = 0.02°). In addition, the microstructure of the as-prepared catalyst was observed through field-emission scanning electron microscopy energy-dispersive spectroscopy, (FESEM-EDS; JEOL, JSM-7401, Tokyo, Japan). Moreover, the particles' specific surface areas were assessed through nitrogen adsorption by using a surface area

analyzer (BET; Micromeritics, Gemini 2370 C) and by applying the Brunauer–Emmett–Teller (BET) equation. Finally, the magnetization curves and hysteresis loop of the samples were obtained using a vibrating sample magnetometer (model 4HF ADI) at room temperature under a maximum field of 18 kOe.

2.5. Analytical methods

The biodiesel purity of the product, expressed in terms of the concentration of fatty acid methyl esters (FAMES), was evaluated through gas chromatography (Thermo Trace GC Ultra, Thermo Co., Austin, Texas, USA). The employed gas chromatography system included a 30 m (length) \times 0.25 mm (internal diameter) \times 0.25 μm (film thickness) capillary column (Tr-biodiesel (F), Thermo Co.), a flame ionization detector, a programmable column oven, and a programmable temperature injector. The temperature in the column oven was programmed as follows: the initial temperature was 120 °C; it then increased to 220 °C at 30 °C/min and further increased to 250 °C at 10 °C/min. The injector temperature was programmed as follows: the initial temperature was 90 °C for 0.05 min; it then increased to 260 °C at 10 °C/min. The carrier gas was nitrogen (flow rate = 2 mL/min). The conversion was determined per the following equation. Conversion % = $\frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$ where $\sum A$ is the total area of all peaks from C14:0 to C24:0 and A_{EI} is the heptadecanoic acid methyl ester IS area. C_{EI} and V_{EI} are the concentration (mg/mL) and volume (L) of the heptadecanoic acid methyl ester solution added to the sample, respectively; m represents the sample mass (mg).

3. Results and discussion

3.1. Characterizations of as-prepared catalyst

The XRD spectra of the samples obtained at calcination temperatures of 500–800 °C are illustrated in Fig. 1. At 500 °C, strong diffraction peaks were observed in SiO_2 (JCPDS 078–1253). However, the intensity of the SiO_2 phase substantially decreased at 600 °C. The observed diffraction peaks were characteristic of Li_4SiO_4 and LiAlO_2 . Upon calcination at 700 °C, CWs and Li_2CO_3 undergoing decarbonization processes leads to the formation of Li_4SiO_4 (JCPDS 020–0637) and LiAlO_2 (JCPDS 044–0224). The catalyst products' spectra were very similar; their main crystalline structures corresponding to CWs were transformed to mixtures of crystalline Li_4SiO_4 and LiAlO_2 phases after solid-state synthesis with Li_2CO_3 . In each sample, the primary active site for the reaction was the mixture of crystalline Li_4SiO_4 and LiAlO_2 .

Fig. 2 shows the XRD analysis of four catalyst products prepared with calcination durations of 1, 2, 3 and 4 h at 800 °C. The Li_4SiO_4 and LiAlO_2 phases appeared with calcination, and the main crystalline structures of these catalysts, which corresponded to CWs, were transformed to Li_4SiO_4 and LiAlO_2 phases after solid-state synthesis with Li_2CO_3 . Both Li_4SiO_4 and LiAlO_2 followed distinct calcination durations (*i.e.*, 1–4 h). All calcinations had Li_4SiO_4 and LiAlO_2 diffraction peaks, but the intensities of the diffraction peaks increased with increasing calcination duration. Weak Li_4SiO_4 and LiAlO_2 diffraction peaks followed 4 h of calcination. This is because with increases in calcination duration, Li_4SiO_4 and LiAlO_2 begin to agglomerate, which tends to block the Li_4SiO_4 and LiAlO_2 phases. That has been calcined for an excessively long period is likely due to the loss of Li_4SiO_4 and LiAlO_2 phases through sublimation into and agglomeration inside the structure [6]. As a result, regardless of the calcination duration, the Li_4SiO_4 and LiAlO_2 phases were observed for all trials in the present study.

When the reaction temperature reached the melting point of Li_2CO_3 (650 °C), Li_2CO_3 entered a molten state. Within the temperature range 800–900 °C, the following equation

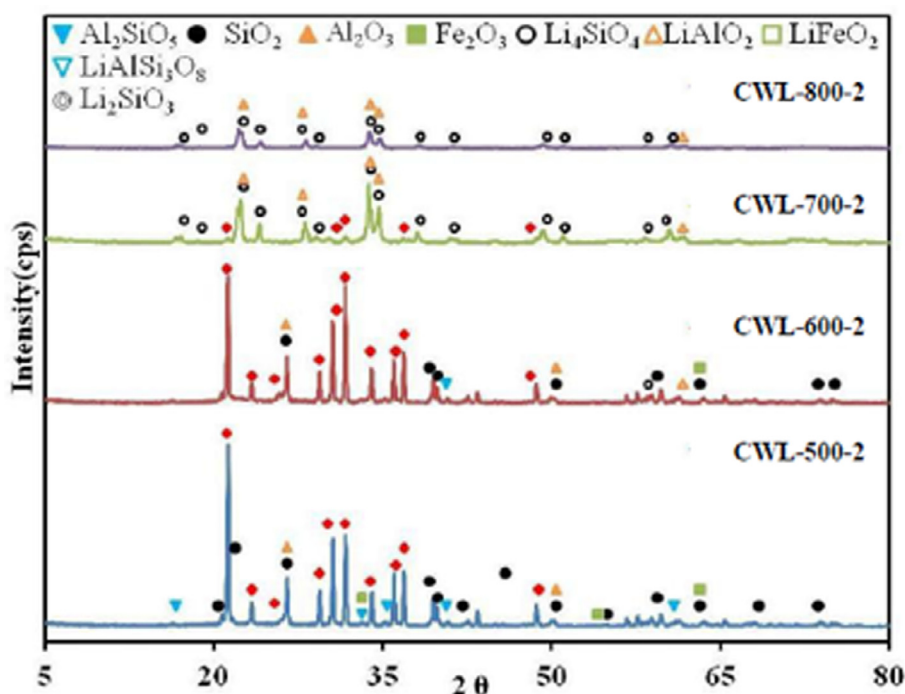


Fig. 1. XRD patterns of catalyst products prepared at various calcination temperatures.

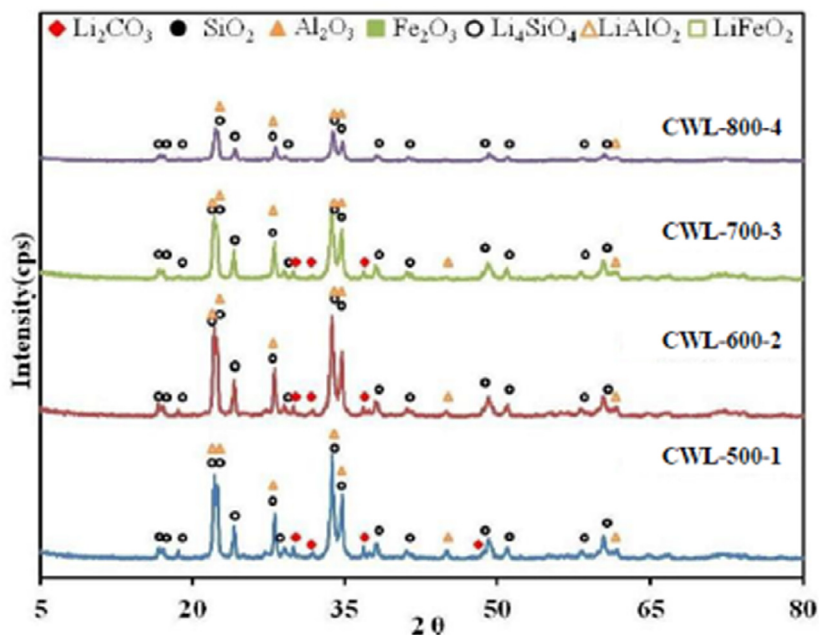
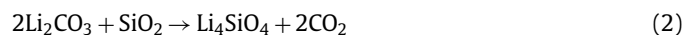


Fig. 2. XRD patterns of four catalyst products prepared with various calcination duration.



strongly shifted to the right. This was possibly resulted from the complex reactions between Li and CWs compounds; Li^+ was sucked into the gap in the CWs compound crystal layers and reacted with CWs compounds (Si, Al) to produce Li_4SiO_4 and LiAlO_2 . When the calcination temperature reaches 800 °C, there are stronger diffraction peaks of the Li_4SiO_4 and LiAlO_2 phase. The Table 1 showed that the higher the calcinations temperature the

higher the conversion achieved with the Li_4SiO_4 and LiAlO_2 . The increasing calcinations temperature led to the crystallization of the catalyst into a new structure. It is possible that the presence of Li-O-Si, Li-O-Al species, where the metals are in close interaction, results in a more active layer of surface sites, which in turn leads to higher conversions.

Table 1 summarizes the chemical and physical properties of catalyst products, including basic strength, pore size, and surface area. The specific surface areas were between 0.21 and 2.22 m^2g^{-1} . Thus, the conversion can be concluded to be not directly influenced by the surface area and pore volume; nevertheless, the

Table 1
Physical and chemical properties of the CWL catalyst.

Catalyst	Basic strength	Specific surface area (m ² /g)	Pore diameter(Å)	*Conversion (%)
Li ₂ CO ₃ ^[19]	9.8 < H ₋ < 15.0	2.20	499	94.2
Li ₄ SiO ₄ ^[20]	9.8 < H ₋ < 15.0	1.81	392	98.2
LiAlO ₂ ^[17]	9.8 < H ₋ < 15.0	1.02	787	97.1
CWL-500-2	9.8 < H ₋ < 15.0	0.28	772	51.3
CWL-600-2	9.8 < H ₋ < 15.0	0.21	767	98.6
CWL-700-2	9.8 < H ₋ < 15.0	0.56	542	98.4
CWL-800-2	9.8 < H ₋ < 15.0	1.11	453	99.6

*Reaction conditions: 12.5g soybean oil; methanol/oil molar ratio, 30:1; catalyst/oil weight ratio, 4 wt%; reaction time, 2 h; reaction temperature, 65 °C.

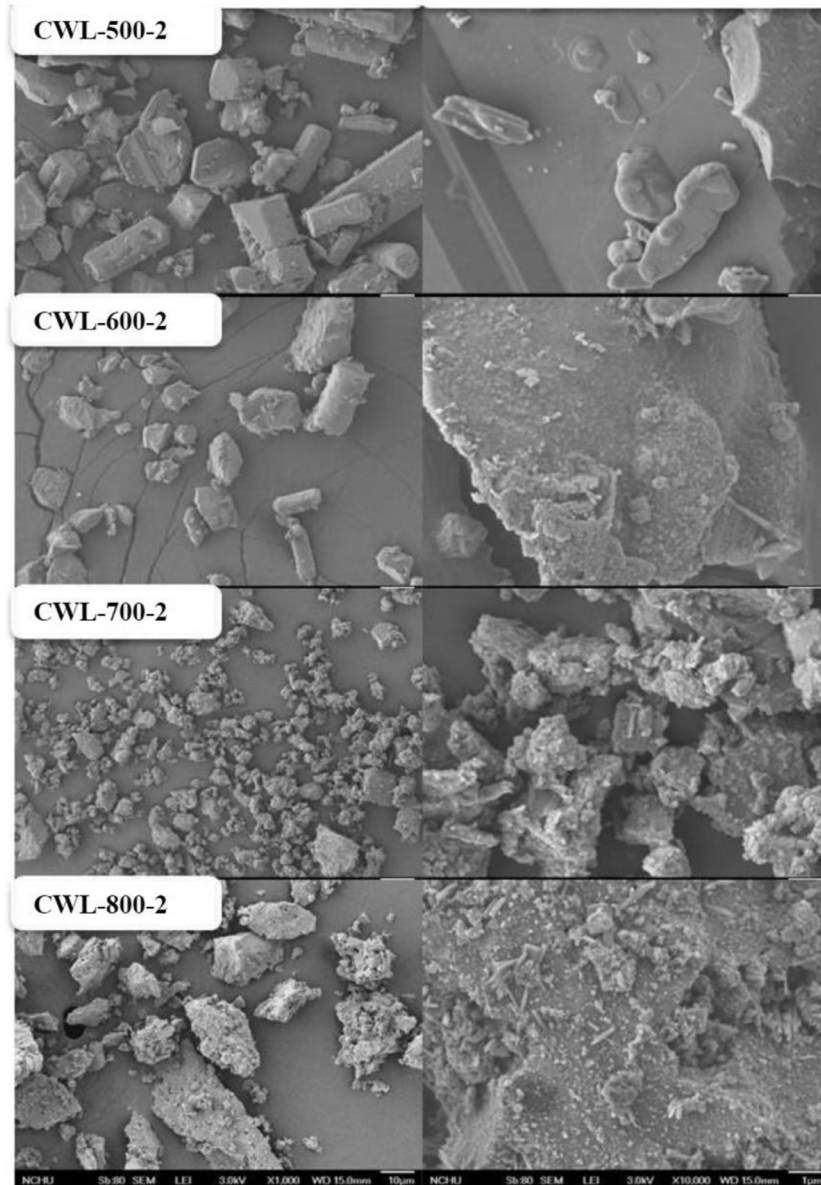


Fig. 3. FE-SEM images of catalyst products prepared at various calcinations temperatures. (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C.

conversion results agree closely with the basic strength generated from the large quantities of active Li-O sites at the tested calcination temperatures [19,20].

Fig. 3 depicts the FE-SEM images of the catalysts synthesized at various calcination temperatures in the range 500–800 °C. Fig. 3(a) depicts the morphologies of the catalyst samples acquired through solid-state synthesis; the morphologies range from irregular

thin sheets to irregular square blocks. Fig. 3(b) shows irregular square crystals of size 0.5–20 µm. The sample shows nonhomogeneous polyhedral agglomerates. Fig. 3(c) shows irregularly shaped plates of the catalyst products that were of size 10–20 µm. The sample shows nonhomogeneous polyhedral agglomerates. Fig. 3(d) illustrates homogeneous and coralloid crystals and clarifies that the catalyst product was composed of dense and nearly coralloid

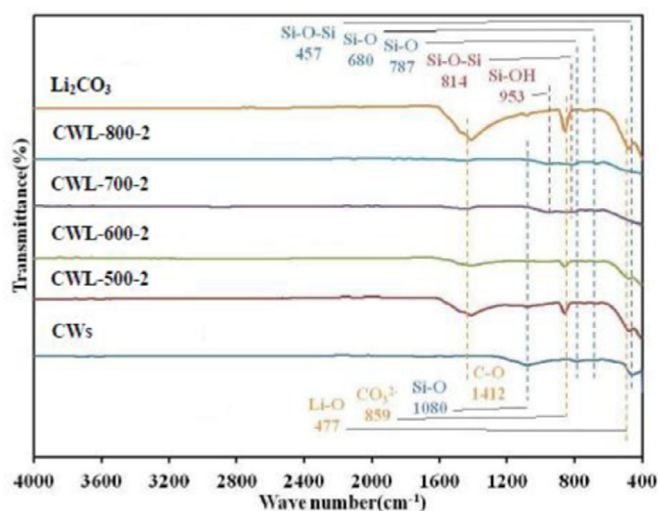


Fig. 4. FTIR patterns of catalyst products prepared at various calcination temperatures.

crystal particles of approximate size 10 μm . This result is consistent with the nitrogen adsorption-desorption results (Table 1).

Catalysts can be characterized on the basis of their FT-IR spectra. The peaks at 1412 and 859 cm^{-1} in Fig. 4 are attributable to the stretching vibration of C–O and the deformation vibration of C–O–C, respectively [19]. The main IR bands at 680, 787, and 1080 cm^{-1} are attributable to Si–O stretching modes [21], whereas those 457 cm^{-1} are attributable to Si–O–Si bonds [22]. The peak intensity of the C–O phase decreases when the calcination temperature increases. Upon calcination at 700 $^{\circ}\text{C}$, CWs and Li_2CO_3 undergo decarbonization processes that lead to the formation of catalyst. The absorption bands attributable to the Li–O groups were at 477 cm^{-1} [16]. The CWL-800-2 catalyst demonstrated high transesterification conversion.

3.2. Reaction studies

In a search for optimal conditions, we investigated various parameters including catalyst/oil weight ratio, calcination temperature and duration, and the methanol: oil molar ratio.

When in the calcination temperature increases from 500 to 600 $^{\circ}\text{C}$, the conversion of soybean oil increased smoothly to the maximum value, as shown in Fig. 5. It is possible that the close interaction of Li_4SiO_4 and LiAlO_2 produced large numbers of active sites on material surfaces, which in turn may have elevated the conversion rate [13]. The calcination temperature in this study was 800 $^{\circ}\text{C}$. In the manufacture of catalyst products, adequate calcination duration is essential for complete decomposition. Fig. 5 illustrates the effects of calcination duration on the conversion rate; calcination duration significantly influenced the transesterification reaction, with conversion increasing with increase in calcination duration. The finding evidences that the FAME formation rate is low when the calcination duration is short, but the FAME formation increases as the calcination duration approaches the maximum value of 2 h. The calcination duration significantly influences the transesterification reaction, where the conversion increased with an increase in calcination time. The increasing calcination time leads to obtain a complete decomposition into a new structure. It is possible that the presence of Li_4SiO_4 and LiAlO_2 structure, where the Li_4SiO_4 and LiAlO_2 are in close interaction, results in a more active sites of surface, which in turn leads to higher conversions rate. It was suggests that the Li_4SiO_4 and LiAlO_2 contained

a large amount basic sites of $9.8 < H_c < 15.0$, causing the catalysts for the high activity towards transesterification reaction.

The earlier research of solid base catalyst for transesterification reaction is shown in Table 1. Comparing CWL-800-2 with other various solid base catalysts [17,19–20], it could be clearly found that CWL-800-2 showed the good catalytic performance for a transesterification reaction. For various solid base catalysts, CWL-800-2 showed the higher catalytic activity than that of Li_2CO_3 , Li_4SiO_4 and LiAlO_2 on conversion.

Furthermore, this study examined the influence of the methanol: oil molar ratio on transesterification. One of the important variables affecting biodiesel production is the methanol: triglycerides molar ratio. To drive the reaction toward completion, the methanol: oil molar ratio should be higher than the stoichiometric molar ratio; the equation should be shifted to the right-hand side to maximize biodiesel production [18], and excess methanol can be recycled. Table 2 clarifies that the conversion rate increased with further increase in the molar ratio from 12, with the maximum conversion rate realized at a methanol: oil molar ratio of 30. The maximum conversion (99.4%) was obtained for CWL-800-2.

Moreover, the effect of CWL-800-2 loading on transesterification was examined. As shown in Table 2, the conversion rate improved considerably when the catalyst loading was raised from 2 to 8 (wt. %). However, when the catalyst loading was higher than 4 (wt%), any increases showed limited effects on conversion. Similar data have been reported by Wang et al. [23]. With increase in the CWL-800-2 loading, the conversion rate increased. Excess mass transfer content may influence the catalyst and catalytic conversion performance [24]. Therefore, 4 (wt. %) is the appropriate catalyst loading here.

3.3. Catalyst reusability

A further investigation included in the present study was the effects of air exposure (temperature 25 ± 2 $^{\circ}\text{C}$, relative humidity: $50 \pm 5\%$) on CWL-800-2 (7 day air exposure) catalytic activity. Table 2 shows the impact of exposure to air of CWL-800-2. According to Table 27, the conversion rate (99.5%–93.4%) for converting the air-exposed catalyst (24–168 h) into fresh CWL-800-2 (99.5%) indicated that the catalytic sites of CWL-800-2 were tolerant toward CO_2 and that H_2O caused exposure to air [25]. Thus, CWL-800-2 is air-insensitive, facilitating the reaction.

CWL-800-2 was found to maintain its activity after five catalytic runs (Table 3). CWL-800-2 was used continuously in the soybean oil transesterification. During four cycles, the conversion was 93.3% for CWL-800-2. It is reasonable to conclude that stability is always crucial for catalyst reusability. Reusability of the solid catalyst is another crucial concern in developing novel solid catalysts for biodiesel production under heterogeneous conditions. The catalytic results revealed that CWL-800-2 maintained its activity after four catalytic runs, showing that this solid catalyst can be reused-without activation. The results showed that the conversion decreased by compared with that of fresh catalysts, so it could be concluded that the slight decline of the activity was due to more Li^+ being leached into the biodiesel [26].

The rates of conversion of different oils to biodiesel are presented in Table 2. A higher concentration of free fatty acids (FFA) (vs. alkali catalyst) should be avoided in transesterification because of the likelihood of saponification [27]. In this study, high free fatty acid concentration substantially affected conversion. Thus, the same catalyst is expected to perform differently under the same reaction conditions but with different oils. The presence of water and FFA in base-catalysed transesterification is usually considered known to inhibit the reaction by promoting saponification. Triglyceride hydrolyses into FFA and glycerol in the presence of water

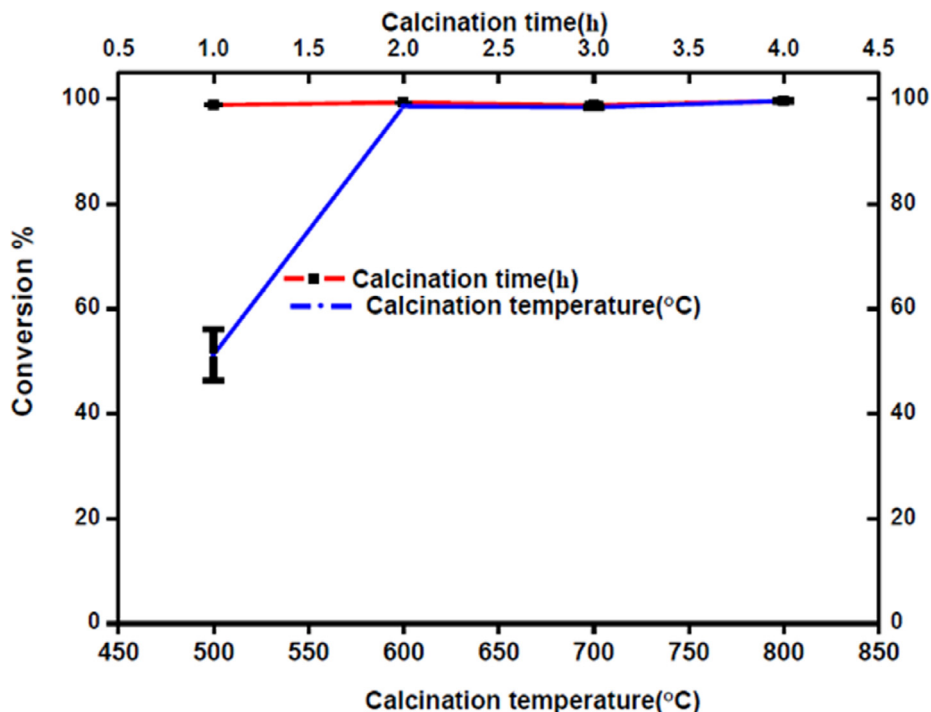


Fig. 5. Influences of calcination temperature and duration on the conversion reaction on the conversion rate (Reaction conditions: 12.5 g soybean oil; methanol/oil molar ratio, 30:1; catalyst/oil weight ratio, 4wt%; reaction time, 2 h; reaction temperature, 65 °C.).

Table 2

The catalytic performance of CWL-800-2 catalysts for transesterification of soybean oil with methanol.

Mole ratio of methanol/oil	Catalyst/oil weight ratio (%)	Exposure time (days)	oils	*Conversion (%)
12	4	–	Soybean oil	90.53 ± 0.03
18	4	–	Soybean oil	97.84 ± 0.38
24	4	–	Soybean oil	98.44 ± 0.45
30	4	–	Soybean oil	99.79 ± 0.09
36	4	–	Soybean oil	99.64 ± 0.03
30	2	–	Soybean oil	99.70 ± 0.04
30	4	–	Soybean oil	99.37 ± 0.16
30	6	–	Soybean oil	99.21 ± 0.02
30	8	–	Soybean oil	99.79 ± 0.09
30	4	1	Soybean oil	99.55 ± 0.13
30	4	3	Soybean oil	98.69 ± 0.12
30	4	5	Soybean oil	98.43 ± 0.25
30	4	7	Soybean oil	93.46 ± 1.31
30	4	–	Soybean oil	99.31 ± 0.50
30	4	–	Coconut oil	94.96 ± 0.41
30	4	–	Olive oil	93.52 ± 0.50
30	4	–	Castor oil	87.34 ± 0.91
30	4	–	Rapeseed oil	89.60 ± 0.04
30	4	–	Cocoa ester	94.54 ± 1.39

Table 3

Reusability of CWL-800-2 catalysts after five reaction cycles.

Reaction cycles	Mole ratio of methanol/oil	Catalyst/oil weight ratio	*Conversion (%)
1	30	4	99.68 ± 0.14
2	30	4	97.54 ± 0.49
3	30	4	72.33 ± 0.91
4	30	4	41.43 ± 1.22
5	30	4	27.24 ± 0.91

while FFA reacts with basic catalyst to form soap. Soap formation complicates Methyl ester separation thereby lowering the content. The effect of addition FFA on Methyl ester content using CWL-800-2 is shown in Table 2. It was found with increasing amount of FFA, the conversion is decreasing.

4. Conclusion

An effective CWL-800-2 catalyst was successfully synthesized from CWs and Li_2CO_3 and showed catalytic activities towards triglyceride transesterification. In the results, it is found that the

utilization of methanol to oil molar ratio 30, with 4% catalyst loading, gives a biodiesel yield of 99.3%. Moreover, CWL-800-2 can be reused, without activation, for at least 4 catalytic runs, maintaining biodiesel yields close to 93.3%. The preparation of low-cost solid-base catalysts from waste materials has various economic and environmental advantages. The idea is to produce new composite materials (including catalysts and some inputs such as methanol) can be reused in whole or in part. This technology offers promising applications in different fields.

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