

Transforming Low-cost Waste Experiments Gloves to Proper Catalyst for Biodiesel Production

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Abstract

Reusing waste products is one goal of environmental sustainability and has become an option to add value to producers. The SiO_2 is obtained after the calcinations of waste experiments gloves above 900 °C, then thermal activation with Li_2CO_3 to prepare base catalysts for the transesterification of soybean oil. The prepared waste experiments gloves (WEG) catalysts are characterized by X-ray diffraction (XRD), and the Hammett indicator to obtain their physical and chemical properties. Effects of thermal activation with Li_2CO_3 amount, alcohol/oil ratio (mol/mol), and catalyst amount (wt % of oil) on the activity of waste experiments gloves catalysts are also investigated. Transesterification with heating shows the FAME conversion 96.7% with 1 wt % waste experiments gloves and Li_2CO_3 being calcined at 800°C for four hours and with the oil/methanol molar ratio 1:36 for 3 hour. The catalysts were characterized using XRD, SEM-EDS, BET, and TGA test

Keywords: Waste glove, Biodiesel, Transesterification, Solid catalyst.

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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. 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 [1-4]. Although transesterification reaction is relatively fast and records high conversions in homogeneous catalyst systems, it has the formation of soap and a decrease in biodiesel yield. Compared with homogeneous basic catalysts, heterogeneous catalysts can avoid saponification of FFAs and are easily separated from product mixtures. Heterogeneous catalysis in the separation process is easier than in homogeneous catalysis [5, 6]. In addition, the heterogeneous method exhibits the advantage of eliminating the formation of soap, thus omitting the requirement of washing water and allowing the reusability of the catalyst. The use of a solid-base heterogeneous catalyst in the process provides several advantages, including the elimination of a quenching step to separate water and the ester phase as well as the elimination of soap formation [7, 8].

Waste glove (WEG) contains highest amounts of silicon compounds among nature substances. WEG contains highest amounts of silicon compounds among nature substances, SiO_2 would exist more than 70 wt% after thermal decomposition and calcinations, which is amorphous with mesoporous structure, high porosity, and high specific surface area. Therefore, this porous structure material should be excellent to be used as the catalyst. The WEG is the most promising method to commercialize to prepared catalyst due to the advantages of low cost, high yield, and easy control.

Our previous study had applied a Li_2SiO_3 on the transesterification. It had been demonstrated that Li_2SiO_3 catalyst has a high conversion for the transesterification [9]. This study uses WEG as a low-cost material to prepare the solid base catalyst using Li_2CO_3 as an activating agent through a solid state reaction for the biodiesel production. The prepared solid base catalysts are characterization by XRD FE-SEM, EDX and BET to obtain their physical and chemical properties. In the present study, the objective of this study was to investigate solid catalysts use in biodiesel production, examine the optimum conditions of themethanol/oil ratio, catalyst amounts, reaction time and reaction temperature. These catalysts appeared to be promising candidates to replace conventional homogeneous catalysts for biodiesel production because the reaction times are low enough to be practical in continuous processes and the preparations are neither difficult nor costly.

2 Experimental

2.1 Materials and Preparation of the Catalyst

Soybean cooking oil (Great Wall Enterprise Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Miaoli, Taiwan), reagent grade Li_2CO_3 (Shimakyu's Pure Chemicals, Osaka, Japan) was used as received.

A sample of waste glove (WEG) was converted into SiO_2 powder by heating WEG at 900°C for 4 h. The results showed that a highly active solid catalyst could be obtained by mixing and well grinding WEG e with Li_2CO_3 calcined in air for 4 h.

2.2 Transesterification reaction procedure

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 effects of the molar ratio of methanol to oil (3:1-30:1) and catalyst/oil weight ratio (1-7 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. A supernatant was filtered through a common filter paper, and then excess methanol and water were evaporated prior to the fatty acid methyl ester (FAME) analysis.

2.3 Instruments and analytical methods

The base strength of the as-prepared catalyst (H_+) was determined using Hammett indicators. 2 h were allowed to elapse for reaching the equilibrium after which no additional color change took place. The characterization of the as-prepared catalysts was performed using a powder X-ray diffractometer (XRD, MAC MXP18, Tokyo, Japan), with $\text{Cu K}\alpha$ radiation, over a 2θ range from 20 to 80° , with a step size of 0.04° , and at a scanning speed 3° min^{-1} . The FAME concentration, expressed as the biodiesel purity of the product, was determined using a gas chromatography system (Thermo trace GC ultra, Thermo Co., Austin, Texas, USA), equipped with a flame ionization detector, a capillary column (Tr-biodiesel (F), Thermo Co., 30 m in length with 0.25 mm i.d. and 0.25 μm film thickness), the programmed column oven, and a programmed temperature injector. The oven temperature program consisted of starting at 120°C (hold 1 min), increasing at a rate of $30^\circ\text{C min}^{-1}$ to 220°C (hold 1 min), and then increasing at a rate of $10^\circ\text{C min}^{-1}$ to 250°C (hold 1 min). The temperature of the programmed 3 injectors was 90°C for 0.05 min, and programmed to 260°C at a rate of $10^\circ\text{C min}^{-1}$. Nitrogen was used as a carrier gas with a flow-rate of 2 ml min^{-1} . The amount of FAME was calculated using the internal standard (methyl heptadecanoate) method, according to method CNS 15051.

3 Results and Discussion

3.1 Characterizations of as-prepared powders

Figure 1 shows the XRD results of WEG, Li_2CO_3 (JCPDS 87-0728), and the as-prepared catalyst. The parent material, waste peanut husks, is crystalline and consists of α -cristobalite (JCPDS 89-3434) and tridymite (JCPDS 73-0469). The crystalline phase of the waste peanut husks is transformed to Li_4SiO_4 (JCPDS 74-2145) and a few Li_2SiO_3 (JCPDS 37-1472) phase after the solid state synthesis with Li_2CO_3 . XRD analyses do not show the presence of impurities (Li_2CO_3 and SiO_2), which might form after the experiment from a decomposition reaction of Li_4SiO_4 with moisture and CO_2 in the air. It can be seen that, the samples showed the diffraction peaks characteristic of the Li_4SiO_4 . Upon calcination, the as-received WEG and Li_2CO_3 underwent decarbonization and dehydration

processes that led to the formation of Li_4SiO_4 . In order to understand the effect of the $\text{WEG}/\text{Li}_2\text{CO}_3$ mole ratio on the transesterification activity, the catalysts were calcined at $\text{WEG}/\text{Li}_2\text{CO}_3$ mole ratio. The main crystalline structure of these samples corresponds to the WG was transformed to the Li_4SiO_4 (JCPDS 37-1472) and a few Li_2SiO_3 (JCPDS 70-0330) phase after solid state synthesis with Li_2CO_3 . When $\text{WEG}/\text{Li}_2\text{CO}_3$ mole ratio increased to 4, the heights of the diffraction peaks belonging to Li_4SiO_4 increased further.

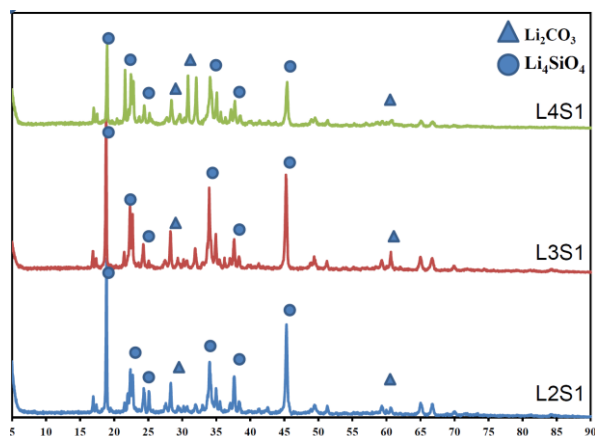


Figure 1 XRD patterns of as-prepared catalyst by the solid state reaction at 800 °C, 4 h; for Li/WEG molar ratio = 2/1, 3/1, and 1/4.

Figure 2 (a) presents FE-SEM images of the WG sample and the chemical composition of the ash determined by EDS. The FE-SEM micrograph of the WG indicates that the surface is spherical and impermeable porous in nature. Elemental composition with EDS shows that SiO_2 is the mainly detected component (Fig 2 b). The WEG exhibited the type III nitrogen adsorption–desorption isotherm (Fig 2 c). The type III isotherm of WEG generally shows prominent adsorption at high relative pressures (P/P_0), indicating macropore adsorption. The corresponding BET specific surface area was calculated to be $0.89\text{ m}^2/\text{g}$. The pore size distribution calculated from the BJH method showed a broad pore size ranging from 1000–1200 nm (Fig. 2 d).

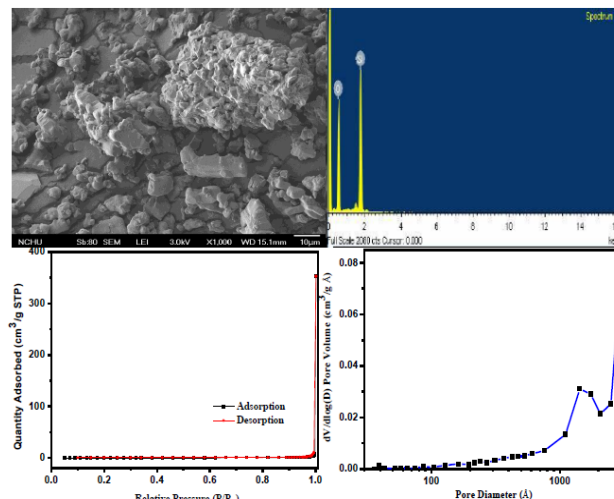
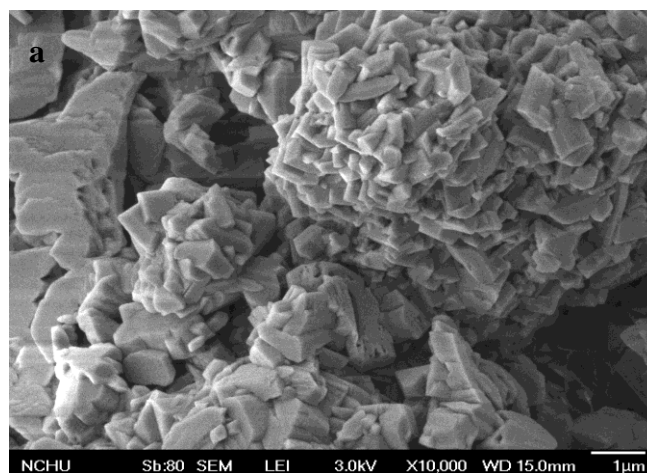


Figure 3 (a) FE-SEM morphology and EDS elemental analysis (b) Nitrogen adsorption–desorption isotherm and pore size distribution of WG powder.

FE-SEM images of as prepared catalyst by the solid state reaction at 800 °C, 4 h; for Li/WG molar ratio 4/1, 3/1, and 2/1. The surface morphology of the catalysts was examined by FE-SEM (Figure 3). For the sample with Li/WG (2/1) obtained at 800 °C (Figure 3 (a)) a lot of amorphous silica still exists and keeps their initial microstructure. Some homogeneous irregular plates crystals, having very smooth surface with a mean diameter of 50μm. Figure 3 (b) shows irregular-shaped particles of the Li/WG morphology ranged between 10 and 20 μm. The sample shows non-homogeneous polyhedral agglomerates. The particles and amorphous silica disappear. While at molar ratio (1/4), see in Figure 3(c), the particles show the obvious agglomeration. When the Li/Si molar ratio is up to (4/1), the particles show nonhomogeneous polyhedral crystals with the side length of about 20μm.



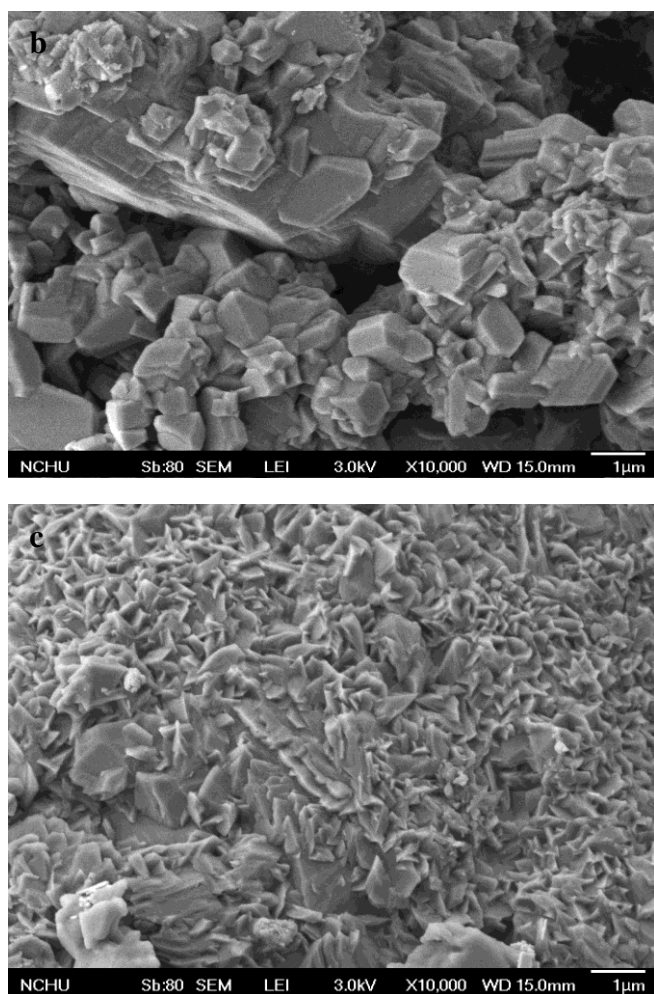


Figure 3 FE-SEM images of as prepared catalyst by the solid state reaction at 900 °C, 4 h; for WG/Li molar ratio (a) 2/1 (b) 3/1 (c) 4/1.

3.2 Transesterification reaction condition optimization

To make direct comparisons, the same reaction conditions, as shown in Table 1, were employed for each catalyst in all experiments. The reaction conditions were not optimized for the highest reaction yield; however, they provided a way to compare the activities of the catalysts. Obviously, it is observed from Table 1 that the WG exhibited no activity. However, when Li_2CO_3 was modified WEG, the catalysts showed catalytic activities. Thus, it is essential to Li_2CO_3 was modified WEG to generate the catalytic activities for the transesterification reaction.

Table 1. Base strengths of WEG and prepared catalyst for WG/Li molar ratio.

catalyst	WG/Li molar ratio	Basic strength	*Conversion (%)
WEG	0	$H_- < 7.2$	0.36
WEG/Li	2/1	$7.2 < H_- < 9.8$	96.9
WEG/L	3/1	$9.8 < H_- < 15.0$	85.5
WEG/L	4/1	$9.8 < H_- < 15.0$	84.5

*Reaction conditions: 12.5 g soybean oil; methanol/oil molar ratio, 18:1; catalyst amount, 1wt%; reaction time, 4 h; methanol reflux temperature and conventional heating method .

Figure 4 shows different calcination temperature of the WG/Li powder (2/1) through the transesterification process. With the calcination temperature at 500°C, the conversion achieves 72.6%, while the conversion achieves 80% when the temperature is higher than 600°C, and the higher conversion 96.9% appears on the calcination temperature at 800°C.

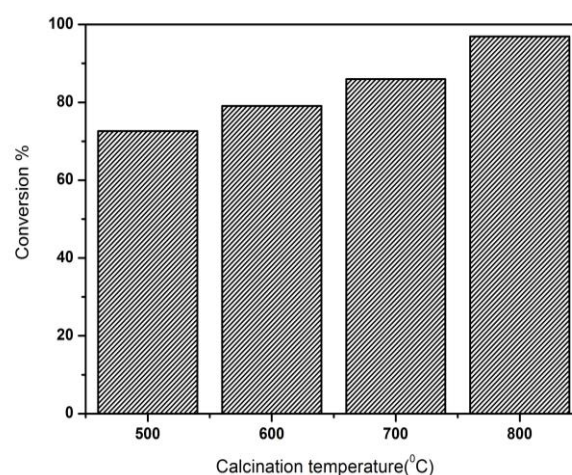


Figure 4 Influence of calcination temperature on the conversion.

As shown in **figure 5**, the conversion reaches a plateau value at the catalyst weight percentage between 2 and 8%. Additional catalysts increase the contact opportunity of the catalyst and the reactant, which directly influence the reaction speed and the conversion. The stoichiometric molar ratio of methanol to oil for the transesterification is 3:1; however, the methanol to oil molar ratio should be higher than that of the stoichiometric molar ratio in order to drive the reaction towards completion and shift it to the right hand side to produce more FAME. In **Figure 5**, the result suggests that the rate of FAME formation is lower at lower molar ratios of methanol and increases when the molar ratio reaches the maximum value of 30. The increase in conversion is due to the shift in equilibrium towards the formation of FAME. These results indicate that the

maximum conversion is 98.8%. The excess methanol can be collected and recycled.

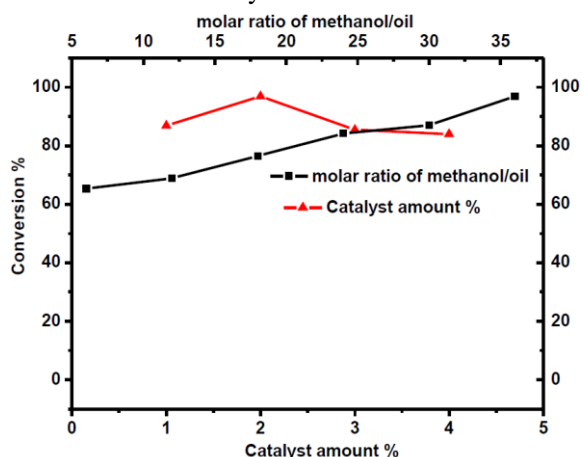


Figure 5 Influence of catalyst amount and methanol/oil molar ratio on the conversion.

Figure 6 displays the effects of reaction time and reaction temperature on conversion. The conversion was increased steadily within the reaction time range of 1 h, and thereafter remained nearly constant as a result of a nearly equilibrium conversion. For the transesterification of refined soybean oil with methanol (1:30) using 6 wt. % catalyst, four different temperatures were used. After 2 h, conversions were 98.2, 93.4, 85.0, and 53.4 % for 65, 55, 45, and 40, respectively. Temperature clearly influenced the reaction rate and the biodiesel purity.

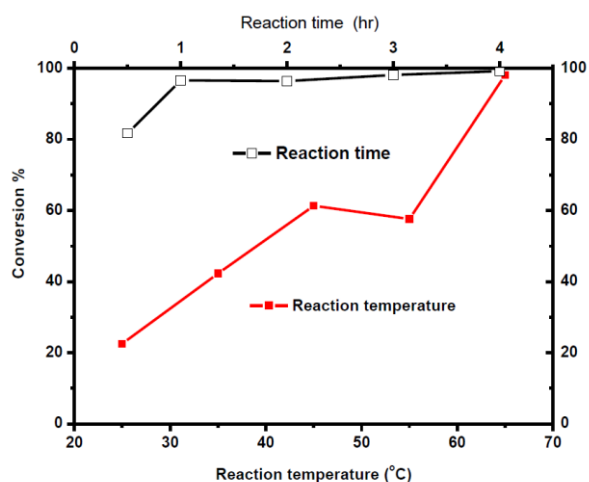


Figure 6 Influence of reaction time and reaction temperature on the conversion.

Figure 7 shows that catalyst exhibits a fairly good operational stability, i.e., 97.9% of the conversion for the first reaction and 83.1% of the conversion retained for

the fifth reaction. It clearly indicates the advantage of solid base catalyst for the reaction stability and the possible feasibility can be enhanced in industrial production.

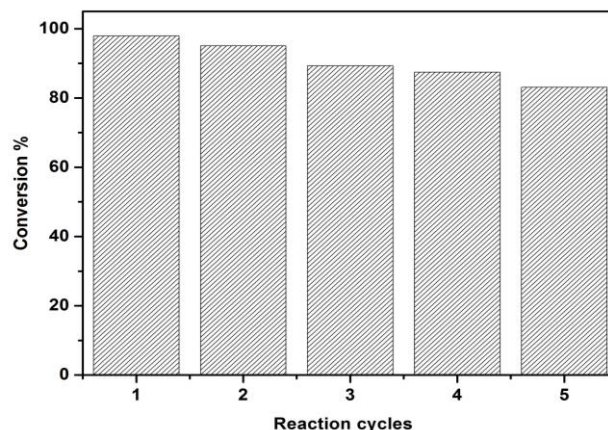


Figure 7 Reusability study after five reaction cycles for catalyst.

4 Conclusions

WEG as the solid base catalyst is easy to synthesize using a solid-state reaction and can directly be used for biodiesel production without further catalyst synthesis processes, involving either drying or thermal treatment. The waste peanut husks as the solid base catalyst demonstrate excellent catalytic activity and stability catalytic activity of transesterification reactions. Developing WEG as the solid base catalyst for biofuels production would become a new and promising way for biofuels production in the future.

Acknowledgments

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