

Transesterification of soybean oil to biodiesel catalyzed by waste glass solid base catalyst

Jing-Yu Wang, Yong-Ming Dai^a, Chiing-Chang Chen^{a*}

^aDepartment of Science Application and Dissemination, National Taichung University of Education, Taichung, Taiwan

*Email: ccchen@mail.ntcu.edu.tw

Abstract

This study uses waste glass as a low-cost material to prepare the solid base catalyst with lithium carbonate as an activating agent through a solid state reaction for the biodiesel production. The results show that a highly active solid catalyst could be obtained by mixing and well grinding waste glass with lithium carbonate calcined in air for 4 h. The prepared solid base catalyst is characterized by XRD, BET, SEM and FTIR for the physical and chemical properties. This study aims to discuss the transesterification with the proportion of waste glass and lithium carbonate and control the alcohol-oil ratio of catalysts with various proportions to achieve the highest biodiesel conversion rate, achieve the maximum economic benefit, and reduce the cost. A complete biodiesel technology chain, as the complex system engineering, covers several technical aspects, including the preparation of catalysts, transesterification, and the reuse of used oil. Under the optimal reaction conditions of methanol/oil molar ratio 18:1, 6% (wt/wt oil) catalyst amount, and the reaction temperature of 65 °C for 2 h, there is a 99.8% conversion to the biodiesel from soybean oil. The waste glass as the solid base catalyst demonstrates excellent catalytic activities and stable catalytic activities in transesterification.

Keywords: Waste glass, Lithium Carbonate, Biodiesel, Transesterification, Solid base catalyst

NSC Project no.: NSC 102-2622-M-142-001

1 Introduction

Conventional processes of biodiesel production involve in using catalysts under mild temperatures (60–80°C) and atmospheric pressure [1]. The transformation between fatty acids contained in vegetable oil (e.g., rapeseed, sunflower, or soybean oil) and low-molecular weight alcohol (methanol) could form the alkyl ester of fatty acids such as FAME [2-4]. The currently employed commercial processes of biodiesel rely on the transesterification catalyzed by homogeneous alkaline catalysts (NaOH or KOH dissolved in methanol, a corrosive liquid) [5, 6]. However, there are several difficulties in this reaction. The catalysts cannot be recovered, must be neutralized, and cannot be reused, and the separation of fatty acid methyl ester (FAME) from the catalyst during the process also generates large volumes of wastewater. This results in the loss of useful materials, and produces large quantities of water since the purification of the ester phase is subsequently necessary. The use of heterogeneous solid catalysts could be an attractive solution to overcome these disadvantages. Heterogeneous solid base catalysts have several advantages such as ease of catalyst separation, recyclability, eco-friendliness and environmental benignity. One way to reduce the cost of catalysts is to use waste as the catalytic materials. In addition to reducing the cost of procuring and synthesizing the catalytic material, this approach creates additional revenue opportunities [7].

The problem of waste accumulation exists

worldwide, specifically in densely populated areas. Most of these materials are left as stockpiles, landfill materials or illegally dumped in selected areas. Therefore, introducing another means of disposal by recycling is nationally required. Besides, using waste materials as catalysts (instead of discarding them) also reduces the cost of waste handling and disposal. The waste materials used as heterogeneous catalysts being studied so far include waste oyster shells, waste rice husks, and egg shells [8-11]. Closed loop recycling is the best sustainable method to re-use waste streams back into new production, as it will create energy savings, reduce the demand on primary mineral resources and divert materials away from landfill. Therefore, due to these manufacturing criteria, the amount of waste glass (WG) will be increased. Hence, finding alternative outlets to absorb the rejected tonnes of post consumer waste recycled glass is indeed a major worldwide concern [12].

Our previous study applied Li_4SiO_4 to the transesterification. It demonstrated that Li_4SiO_4 catalyst had a high conversion for the transesterification. This study uses WG 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 characterized by XRD, FE-SEM, EDX and BET to obtain their physical and chemical properties. In the present study, the objective of this study is to investigate the solid catalyst use in the biodiesel production and examine the optimum conditions of the methanol/oil ratio, catalyst amounts, reaction time and reaction temperature. These catalysts appear to be promising candidates to replace conventional homogeneous catalysts for the 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), and reagent grade Li_2CO_3 (Shimakyu's Pure Chemicals, Osaka, Japan) were used as received.

After being thoroughly washed with deionized water, WG was filtered and air-dried at room temperature. A sample of WG was heated at 800 °C for 4 h. The results showed that a highly active solid catalyst could be obtained by mixing and well grinding steel-making slag 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 the 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_L) 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 °C min⁻¹ to 220 °C (hold 1 min), and then increasing at a rate of 10 °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 °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 catalysts

The XRD patterns of the as-received samples are shown in **Figure 1**. It can be seen that, the samples showed the diffraction peaks characteristic of the Li_4SiO_4 . Upon calcination at 800°C , the as-received WG 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 calcination temperature on the transesterification activity, the catalysts were calcined at different temperatures and their crystalline structures analyzed using X-ray diffraction (XRD). Figure 1 shows the resulting XRD spectra after calcining the Li_4SiO_4 catalyst at 800°C . It can be observed that the spectra of the samples are very similar. The main crystalline structure of these samples corresponds to the WG was transformed to the Li_4SiO_4 (JCPDS 34-1416) and a few Li_2SiO_3 (JCPDS 70-0330) phase after solid state synthesis with Li_2CO_3 .

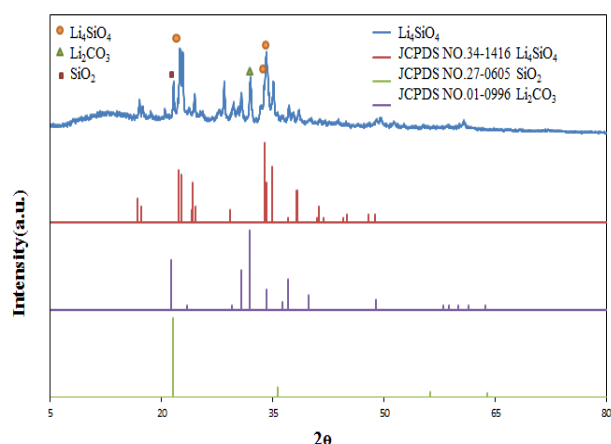


Figure 1 The XRD patterns of WG, Li_2CO_3 and as-prepared catalyst (Li_2CO_3 /WG weight ratio of 2).

Figure 2 (a) presents FE-SEM images of the waste silicone being converted into WG powder and the chemical composition of the WG powder determined by EDS. The FE-SEM micrograph of the WG powder indicates that the surface is spherical and impermeably porous in nature. Elemental composition with EDS

shows that SiO_2 is the main detected component (Figure 3 b). The SiO_2 powder exhibits the type III nitrogen adsorption–desorption isotherm (Figure 3 c). The type III isotherm of LPMSN generally shows prominent adsorption at high relative pressures (P/P_0), indicating the macropore adsorption. The corresponding BET specific surface area is calculated to be $1.81\text{m}^2/\text{g}$. The pore size distribution calculated from the BJH method shows a broad pore size ranging in $65\text{--}137\text{ nm}$ (Figure 3 c).

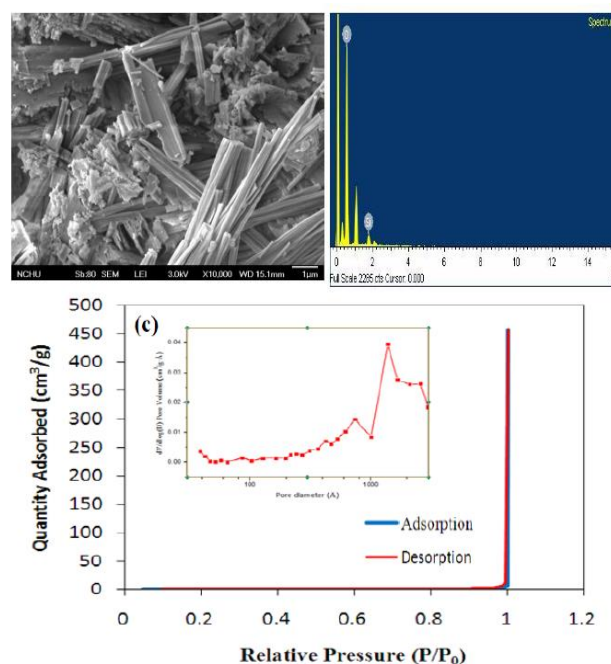


Figure 2 (a) FE-SEM morphology (b) EDS elemental analysis and (c) Nitrogen adsorption – desorption isotherm and pore size distribution of WG powder.

3.2 Transesterification reaction condition optimization

The investigated variables include the catalyst amount (g), the methanol/oil ratio (mol/mol), the reaction time (h), and the reaction temperature ($^\circ\text{C}$). The catalyst amount varies in the range of 2-8 wt. %. As shown in **Figure 3**, the conversion increases as the catalyst amount increasing 2-6 wt. %. The conversion reaches a plateau value at the catalyst weight percent between 6 wt. %. Stoichiometrically, the transesterification of soybean oil requires three moles of methanol for each mole of oil [7]. Since transesterification reaction is a reversible reaction, excess methanol would shift the equilibrium towards the direction of FAME formation. As evidenced in the **Figure**

3, when the methanol loading increases, the conversion increases considerably. The maximum conversion ratio is 98.1% at the methanol/oil molar ratio of 18/1.

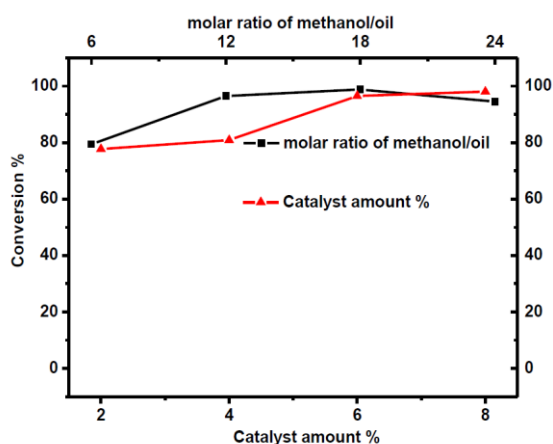


Figure 3 Influence of catalyst amount and methanol/oil molar ratio on the conversion

Figure 4 displays the effects of reaction time on the conversion. The conversion increases steadily within the reaction time range of 1 h, and thereafter remains nearly constant as a result of a nearly equilibrium conversion. Reaction time is an important factor affecting the whole process. That transfer rate increases with time and has a maximum value at 1 hour. Then transfer rate declined obviously, which might be resulted from saponification within long reaction time.

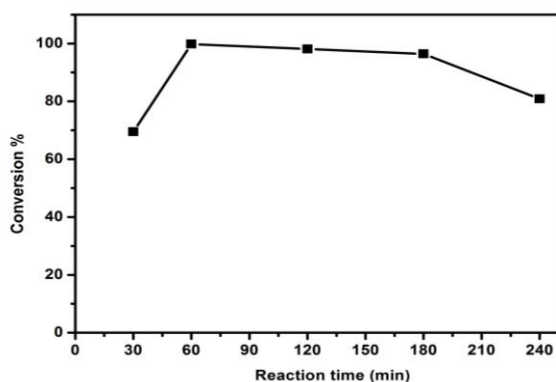


Figure 4 Influence of reaction time on the conversion.

The effect of exposure to air on the catalytic activity of transesterification reaction was examined for Li_4SiO_4 . **Figure 5** shows no obvious difference in the FAME conversion (92.4-96.7 %) between the air-exposed catalyst (1-3 day) and the fresh one (99.8 %), which verified that the catalytic sites of catalyst was tolerant to CO_2 and H_2O

contained in air. Under the reacting condition, it was inferred that CO_2 and H_2O interacting with the catalytic sites were eliminated due to the acidic property of methanol. The catalyst was the solid base catalyst having the advantage of tolerance to air-exposure, which will cause easy operation of the catalytic reaction.

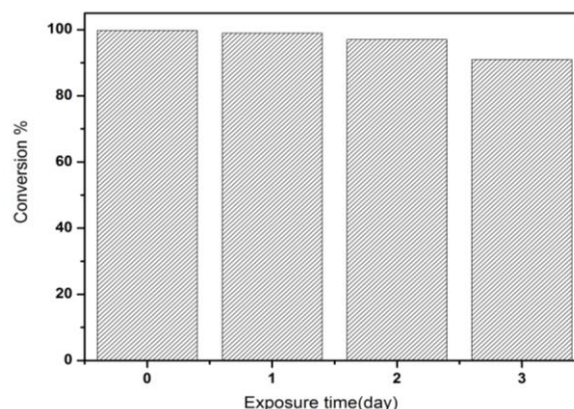


Figure 5 Influence of exposure time to air on the conversion.

After the transesterification being completed, the samples are recovered using simple decantation. The remaining catalyst in the reactor is used for catalyzing the next batch of transesterification. As can be seen from **Figure 6**, a biodiesel purity of 93% could be obtained even after recycling the catalyst 5 times. Because the amount of catalyst used in the next run is lower than the initial run, it might partly be responsible for the reduced biodiesel purity during the subsequent run. This indicates that the catalyst has greater stability in the transesterification reaction.

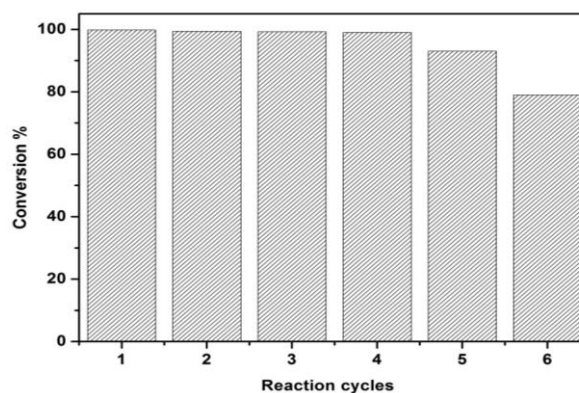


Figure 6 Reusability study after five reaction cycles for catalyst

4 Conclusions

This study revealed glass reprocessing as a silica source to synthesize a Li_4SiO_4 catalyst for possible applications in biodiesel production. Experimental results show that as-prepared catalyst demonstrated excellent catalytic activity because of its basic strength (H_+), above 15.0. In many base-catalyzed reactions, solid base catalysts are easily poisoned by carbon dioxide and water. The as-prepared catalyst is tolerant to water and carbon dioxide and the catalytic activity of transesterification reactions were not significantly lower because no obvious LiOH formed on the catalyst surface and Li_2CO_3 was yet a efficient solid base catalyst ($\text{H}_+ > 9.8$). It clearly indicates the advantage of solid base catalyst for reaction stability and the possible feasibility can be enhanced in industrial production.

Acknowledgments

The authors thank NSC Taiwan under the grant of NSC 101-2622-M-142-001 for financially supporting this study.

References

- [1]. F. Ma, M.A. Hann. "Biodiesel production: a review", *Bioresonance Technology*, 70, pp.1-15, 1999.
- [2]. A.P. Vyas, N. Subrahmanyam, P.A. Patel. "Production of biodiesel through transesterification of jatropha oil using $\text{KNO}_3/\text{Al}_2\text{O}_3$ solid catalyst." *Fuel* 88, pp. 625-668, 2009.
- [3]. Demirbas. "Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey." *Energy Conversion and Management*, 44, pp. 2093-2109, 2003
- [4]. Talebian-Kiakalaieh, N.A.S. Amin, H. Mazaheri. "A review on novel process of biodiesel production from waste cooking oil." *Apply Energy*, 104, pp. 683-710, 2013.
- [5]. S. H. Wang, Y.B. Wang, Y.M. Dai, J.M. Jehng. "Preparation and characterization of hydrotalcite-like compounds containing transition metal as a solid base catalyst for transesterification." *Applied Catalysis A: General*, 439-440, pp. 135-141, 2012.
- [6]. M. K. Lam, K. T. Lee. "Catalytic transesterification of high viscosity crude microalgae lipid to biodiesel: Effect of co-solvent." *Fuel Processing Technology* 110, pp. 242-248, 2013.
- [7]. F.H. Kasim, A.P. Harvey, "Influence of various parameters on reactive extraction of *Jatropha curcas* L. for biodiesel production." *Chemical Engineering Journal*, 171, pp. 1373-1378, 2011.
- [8]. X.L. Miao, Q.Y. Wu. "Biodiesel production from heterotrophic microalgal oil." *Bioresonance Technology*, 97, pp. 841-846, 2006.
- [9]. W. Ziku, X. Chunli, L. Baoxin. "Application of waste eggshell as low-cost solid catalyst for biodiesel production." *Bioresonance Technology*, 100, pp. 2883-2885, 2009.
- [10]. K. Masato, Y. Shin-ya, H. Jyu-suke, T. Michito. "Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol." *Applied Catalysis A: General*, 355, pp. 94-99, 2009.
- [11]. G.M. Lo'pez, A.D. Marti'n, A.C. Alba-Rubio, R. Mariscal, M. Ojeda, P.T. Brettes, "Transesterification of triglycerides by CaO : increase of the reaction rate by biodiesel addition." *Energy & Fuels*, 23, pp. 2259, 2009.
- [12]. B. Taha, G. Nounu. "Properties of concrete contains mixed colour waste recycled glass as sand and cement replacement" *Construction and Building Materials*, 22, pp.713-720, 2008.