

Application of Peanut Husk Ash as a Low-Cost Solid Catalyst for Biodiesel Production

Yong-Ming Dai, Kung-Tung Chen, Yu-Jie Wang, and Chiing-Chang Chen

Abstract—This work investigates the use of Li_2CO_3 -modified waste peanut husk ash as the solid base catalyst for the biodiesel production. The prepared waste peanut husks as the solid base catalyst are characterized by XRD, BET, SEM and TGA for the physical and chemical properties. In the present study, the biodiesel is synthesized from soybean oil through a transesterification reaction catalyzed by the solid base catalyst. Under the optimal reaction conditions of methanol/oil molar ratio 12:1, 5% (wt/wt oil) catalyst amount, and a reaction temperature of 65 °C for 4 h, there is a 98.4 % conversion to the biodiesel from soybean oil.

Index Terms—Biodiesel, transesterification, peanut husks, Li_4SiO_4 , solid base catalyst, Li_2CO_3 .

I. 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], [2]. 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 [3], [4]. Although the transesterification reaction is relatively fast and records high conversions in homogeneous catalyst systems, there are several difficulties in this reaction. The catalyst cannot be recovered and must be neutralized, and they cannot be reused and the separation of fatty acid methyl esters (FAME) from the catalyst during the process also generates large volumes of wastewater. This results in loss of useful material, 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 separation of catalysts, recyclability, eco-friendly and environmentally benign [5]. The use of heterogeneous catalysts that rely on the treatment of various catalyst supports, i.e., heterogeneous solid catalysts of CaO [6], K_2CO_3 [7], [8], SiO_2 [9], MgO [10], offers various advantages including the recovery and recycling of the catalyst. Compared with homogeneous base catalysts, heterogeneous catalysts can avoid the

saponification of FFAs and are easily separated from product mixtures [11]-[13].

Peanut husks, an agricultural waste available in large quantity, are often burned or discarded directly into farm lands. As a potential adsorbent material, peanut husks can be utilized for such purposes, as they can also bring unlimited number of economic and environmental benefits to industrial wastewater treatment. Thus, they are regarded as an abundant and inexpensive agricultural by-product [14]. Because of the high silica content, waste peanut husks can be an economically viable raw material for producing silicates and silica in recent years [15], [16]. The catalysts remain as a heterogeneous medium. Hence, the purification and washing steps can be eliminated from the process steps. 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.

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 [17]. This study uses waste peanut husks 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 was to investigate solid catalysts use in biodiesel production, examine the optimum conditions of the methanol/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.

II. EXPERIMENTAL

A. 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) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (Chameleon Reagent, Osaka, Japan) were used as received.

After being thoroughly washed with deionized water, the waste peanut husks were filtered and air-dried at room temperature. A sample of waste peanut husks was converted into peanut husks ash by heating rice husks at 900 °C for 2 h. The results showed that a highly active solid catalyst could be obtained by mixing and well grinding waste peanut husks

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Yong-Ming Dai, Yu-Jie Wang, and Chiing-Chang Chen are with the Department of Science Application and Dissemination, National Taichung University of Education, Taichung 40306, Taiwan (e-mail: ccchen@mail.ntcu.edu.tw).

Kung-Tung Chen is with the Department of Chemical and Materials Engineering, Minghsin University of Science and Technology, Hsinchu 30401, Taiwan.

with Li_2CO_3 calcined in air for 4 h.

B. 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 reactor was initially filled with 12.5 g soybean oil, which was heated to 65 °C for 3 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 methanol and the catalyst was added into the reactor. The effects of the molar ratio of methanol to oil (3:1-24:1) 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. The biodiesel and glycerol layers were easily separated due to the different densities of 0.86 and 1.126 g/cm³, respectively. 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.

C. Instruments and Analytical Methods

The base strength of the as-prepared catalyst (H_-) was determined using Hammett indicators. Approximately 50 mg of the sample was shaken with 1 ml methanol solution of the Hammett indicator. 2 h were allowed to elapse for reaching the equilibrium after which no additional color change took place. The basic strength was defined being stronger than the weakest indicator which exhibited a color change, and weaker than the strongest indicator which produced no color change. Bromthymol blue (H_- =7.2), phenolphthalein (H_- =9.8), 2,4-dinitroaniline (H_- =15.0), and 4-nitroaniline (H_- =18.4), at a concentration of 0.02 mol/L were obtained from Sigma-Aldrich (St. Louis, Missouri, USA) and used as Hammett indicators. The characterization of the as-prepared catalysts was performed using a powder X-ray diffractometer (XRD, MAC MXP18, Tokyo, Japan), with Cu K α 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 EN 14103.

III. RESULT AND DISCUSSION

A. Characterizations of As-Prepared Powders

Fig. 1 shows the XRD results of waste peanut husks(PHA),

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 PHA 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 PHA/ Li_2CO_3 mole ratio on the transesterification activity, the catalysts were calcined at PHA/ Li_2CO_3 mole ratio. The main crystalline structure of these samples corresponds to the PHA 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 . The different peaks of Li_4SiO_4 phase appear at 2θ =16.7, 17.2, 22.1, 22.5, 28.1, 29.2, 33.7, 34.8, 38.1, and the different peaks of Li_2SiO_3 phase appear at 2θ =18.9, 32, 33.2, 59.1 when the PHA/ Li_2CO_3 mole ratio is 0.5-4. When the PHA/ Li_2CO_3 mole ratio is 0.5, the diffraction peaks of Li_2SiO_3 , were observed. With an increase of the PHA/ Li_2CO_3 mole ratio, the diffraction peaks of Li_4SiO_4 become clear. When PHA/ Li_2CO_3 mole ratio increased to 4, the heights of the diffraction peaks belonging to Li_4SiO_4 increased further.

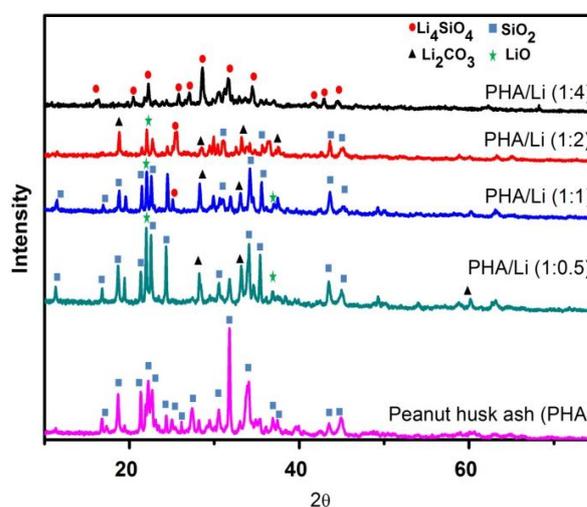


Fig. 1. PHA and as-prepared catalyst by the solid state reaction at 900 °C, 4 h; for Li/PHA molar ratio = 1/0.5, 1/1, 1/2 and 1/4.

Fig. 2a presents FE-SEM images of the PHA sample and the chemical composition of the ash determined by EDS. The FE-SEM micrograph of the PHA indicates that the surface is spherical and impermeable porous in nature. Elemental composition with EDS shows that SiO_2 is the mainly detected component, with a relatively low K and Ca content (Fig. 2b). The PHA exhibited the type III nitrogen adsorption-desorption isotherm (Fig. 2c). The type III isotherm of PHA generally shows prominent adsorption at high relative pressures (P/P_0), indicating macropore adsorption. The corresponding BET specific surface area was calculated to be 1.21m²/g. The pore size distribution calculated from the BJH

method showed a broad pore size ranging from 900–1000 nm (Fig. 2d).

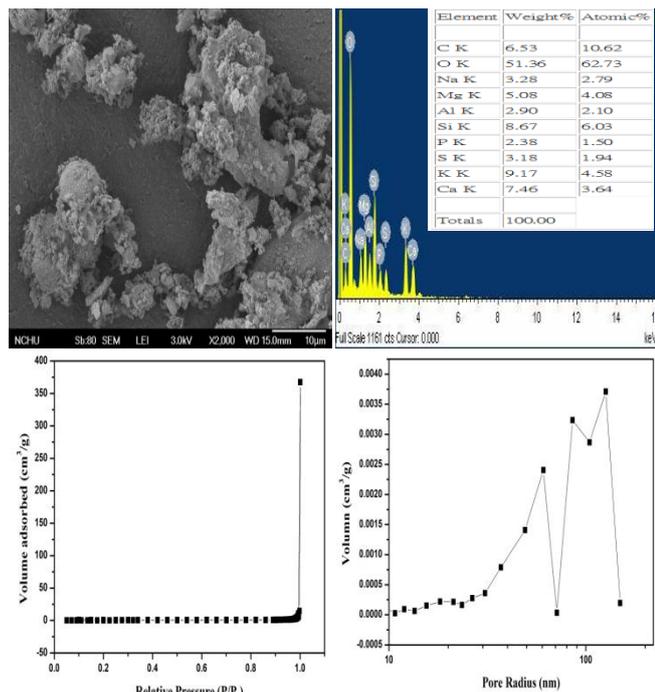


Fig. 2. Characterization of the synthesized LPMSN. (a) FESEM and (b) EDX (c) Nitrogen adsorption-desorption isotherm and (d) pore size distribution.

FE-SEM images shows the as prepared catalyst by the solid state reaction at 900 °C, 4 h, for PHA/Li molar ratio 1/0.5, 1/1, 1/2 and 1/4. The surface morphology of the catalyst is examined by FE-SEM (Fig. 3). For the sample with Li/PHA (1/0.5) obtained at 900 °C (Fig. 3a), a lot of amorphous silica still exist and keep their initial microstructure. Some homogeneous spherical crystals have very smooth surface with a mean diameter of 50µm. Fig. 3b shows the irregular-shaped particles of the Li/PHA morphology ranged between 10 and 20 µm. The sample shows non-homogeneous polyhedral agglomerates; and, the particles and amorphous silica disappear. When the molar ratio is up to (1/2), (see Fig. 3c), the homogeneous and coralloid crystal is observed. It shows that the catalyst synthesized is composed of nano-sized particles, which are about 10 µm in size, and that each particle is nearly coralloid crystal in shape and dense in density. While at molar ratio (1/4), see in Fig. 3d, the particles show the obvious agglomeration. When the Li/Si molar ratio is up to (1/4), the particles show nonhomogeneous polyhedral crystals with the side length of about 20µm.

B. Transesterification Reaction Condition Optimization

To make direct comparisons, the same reaction conditions, as shown in Table I, are employed to each catalyst in all experiments. The reaction conditions are not optimized for the highest reaction yield; however, they provide a way to compare the activities of the catalysts. Obviously, it is observed from Table I that the PHA exhibits no activity. However, when Li₂CO₃ is modified PHA, the catalysts show catalytic activities. Thus, it is essential to modify PHA from Li₂CO₃ to generate the catalytic activities for the transesterification reaction. It can be concluded that the observed activities of the Li₂CO₃-modified PHA catalysts seem to be related to their base strengths and basicity values,

i.e. the higher base strengths and basicity values of the catalysts result in the higher conversions.

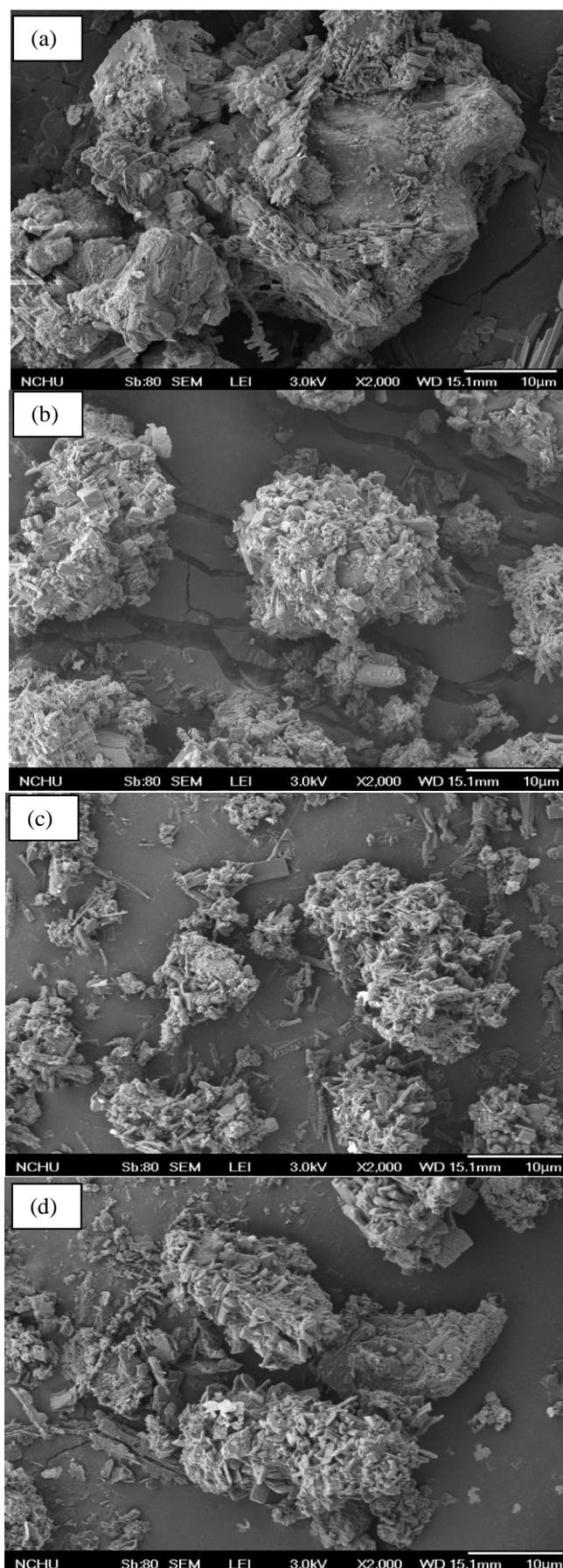


Fig. 3. FE-SEM images of as prepared catalyst by the solid state reaction at 900 °C, 4 h, for Li/PHA molar ratio (a) 1/0.5 (b) 1/1 (c) 1/2 (d) 1/4.

TABLE I: THE ARRANGEMENT OF CHANNELS

| Catalyst | Li/PHA molar ratio | Basic strength | *Conversion (%) |
|----------|--------------------|--------------------|-----------------|
| PHA | 0 | $H_- < 7.2$ | 0.36 |
| Li/PHA | 1/0.5 | $7.2 < H_- < 9.8$ | 65.8 |
| Li/PHA | 1/1 | $9.8 < H_- < 15.0$ | 88.5 |
| Li/PHA | 1/2 | $9.8 < H_- < 15.0$ | 89.5 |
| Li/PHA | 1/4 | $9.8 < H_- < 15.0$ | 77.9 |

*Reaction conditions: 12.5 g soybean oil; methanol/oil molar ratio, 12:1; catalyst amount, 1wt%; reaction time, 3 h; methanol reflux temperature and conventional heating method.

Fig. 4 shows different calcination temperature of the Li/PHA (1/4) through the transesterification process. With the calcination temperature at 900°C, the conversion achieves 46.3%, while the conversion achieves 93% when the temperature is higher than 600°C, and the higher conversion 88.9% appears on the calcination temperature at 900°C. However, the transfer rate decreases at the calcination temperature 1000°C. It might be resulted from the poison process by some unknown reaction with catalysts, indicating that high calcination temperature should be avoided.

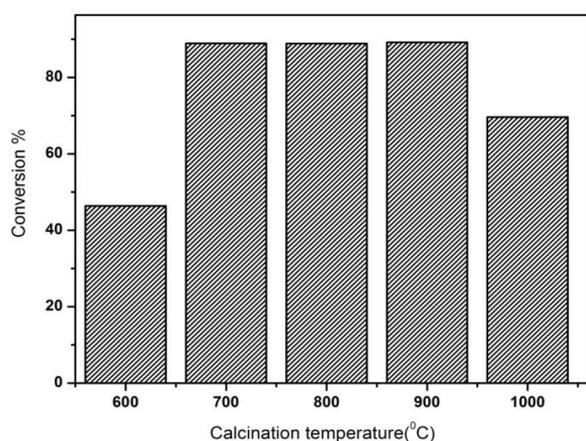


Fig. 4. Influence of calcination temperature on the conversion. (12.5 g soybean oil; methanol/oil molar ratio, 12:1; catalyst amount, 1wt%; reaction time, 3 h; methanol reflux temperature and conventional heating method).

The stoichiometric molar ratio of alcohol to oil for transesterification is 3:1; however, the alcohol 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 [18]. In Fig. 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 12. The increase in conversion is due to the shift in equilibrium towards the formation of FAME. These results indicate that the maximum conversion is 97.15% for the Li/PHA (1/4) catalysts. Further increasing the alcohol to oil ratio leads to decrease the oil concentration and accordingly decrease the reaction rate. Therefore, 12:1 is the appropriate methanol/oil molar ratio for this reaction. The excess methanol can be collected and recycled. Catalyst amount is an important parameter which affects the conversion of triglycerides to methyl esters. As shown in Fig. 5, the conversion reaches a plateau value at the catalyst weight percentage between 2 and 6 wt%. Additional catalysts increase the contact opportunity of the catalyst and the reactant, which directly influence the reaction speed and the conversion. In general, increasing catalyst amount will increase the number of active sites

available for the adsorption of the reactants, resulting in a more rapid increase in the number of sites of interaction between the reactants. However, with a further increase in the loading amount, the conversion has no significant difference. The rational reason is due to the rise of mixing problem (oil/MeOH/catalyst) and the resistance of mass transfer [19]. Under present reaction conditions, the optimal catalyst amount is 5wt%.

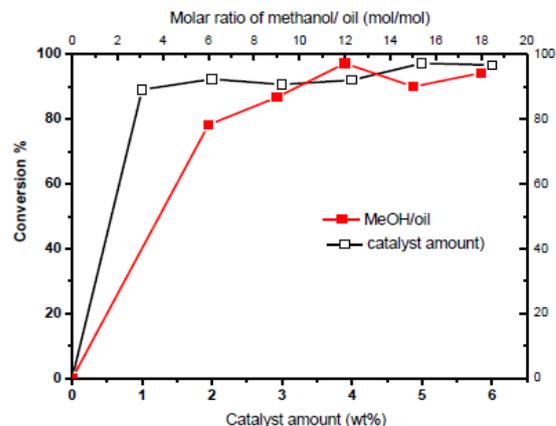


Fig. 5. Influence of catalyst amount and methanol/oil molar ratio on the conversion. (12.5 g soybean oil; reaction time, 3 h; methanol reflux temperature and conventional heating method).

Reaction time is an important factor in the whole process. Fig. 6 shows that the transfer rate increases with time and has a maximum value at 4 hour. Four different temperatures are used for the transesterification of refined soybean oil with methanol (12:1) using 5 wt% catalyst. After 3 h, conversions are 97.15, 35.65, 24.33, 43.5 and 21.59% for 65, 55, 45, 35 and 25 °C, respectively. The temperature clearly influences the reaction rate and the biodiesel purity. Glycerol on the surface of catalysts may cause catalysts loss activity. CaO has higher transesterification activity among all Alkali and alkaline earth oxides, it would react with glycerol produced from transesterification process to form Ca-glyceroxides [20]. It might be resulted from the poison process by Ca-glyceroxides is decrease reutilization. Another key aspect in the development of new solid catalysts for biodiesel production, under heterogeneous conditions, is the possibility of reutilization of the solid catalyst.

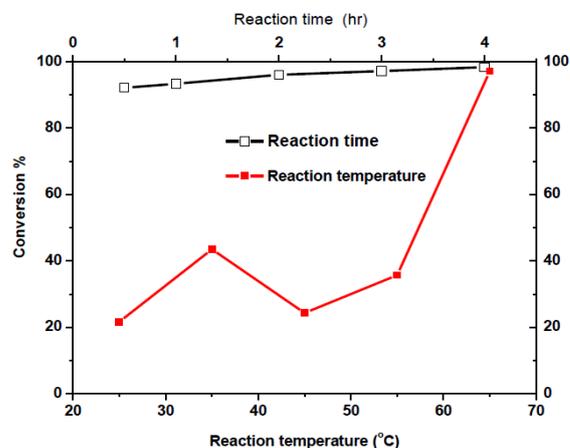


Fig. 5. T Influence of reaction time and reaction temperature on the conversion. (12.5 g soybean oil; methanol/oil molar ratio, 12:1; catalyst amount, 5wt%; methanol reflux temperature and conventional heating method).

Fig. 7 shows that Li₂CO₃-modified PHA (1/4) catalyst exhibits a fairly good operational stability, i.e., 96.84% of the conversion for the first reaction and 84.5% 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.

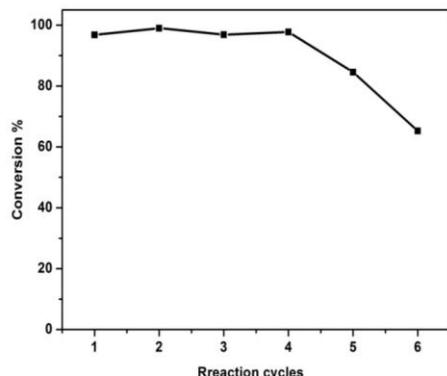


Fig. 7. Reusability study after five reaction cycles for catalyst (12.5 g soybean oil; methanol/oil molar ratio, 12:1; catalyst amount, 5wt%; reaction time, 3 h; methanol reflux temperature and conventional heating method).

IV. CONCLUSION

Li₂CO₃-modified waste peanut husks as the solid base catalyst are easy to synthesize using a solid-state reaction and can directly be used for the 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 activities and stable catalytic activities of transesterification reactions. Developing waste peanut husks as the solid base catalyst for biofuel production would become a new and promising way in the future.

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Yong-Ming Dai completed his PhD at the National Chung Hsing University (Taiwan) in 2010. He joined the group of Chiing-Chang Chen at National Taichung University of Education in 2011 as a postdoctoral fellow. His scientific interests are in the technological applications of material science, heterogeneous catalysis and energy fuel.



Kung-Tung Chen is a professor of Minghsin University of Science and Technology, Hsinchu, in Taiwan. He received his Ph.D. (1993) from the National Tsing Hua University (Taiwan). His research interests include sustainable and green chemistry, environmental remediation, and Environmental impact assessment.



Yu-Jie Wang is a graduate student of National Taichung University of Education, Taichung, in Taiwan. He joined the group of Chiing-Chang Chen in 2010 as a graduate student. His scientific interests are in the technological applications of heterogeneous.



Chiing-Chang Chen is a professor of National Taichung University of Education, Taichung, in Taiwan. He received his Ph.D. (1994) from the National Tsing Hua University (Taiwan). His main research interests: applied heterogeneous catalysis and photocatalysis to the solution of environmental problems, sustainable and green chemistry and environmental remediation.