

# Rice husk silica for the synthesis of $\text{Li}_4\text{SiO}_4$ for biodiesel production

Po-Hsiang Wang<sup>a</sup>, Jian Xun Wang<sup>a</sup>, Wen-Lian William Lee<sup>b</sup>, Tsai-Chuang Lee<sup>a</sup>, Chiing-Chang Chen<sup>a\*</sup>

<sup>a</sup>Department of Science Application and Dissemination, National Taichung University of Education, Taiwan, ROC

<sup>b</sup>Department of Occupational Safety and Health/Department of Applied Chemistry, School of Medicine, Chung-Shan Medical University, Taiwan, ROC

\*Email: ccchen@ms3.ntcu.edu.tw

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## Abstract

Reusing agricultural waste products is one goal of environmental sustainability and has become an option to add value to producers. Rice husks, a waste product in the processing of grain, are used for power generation through combustion and its burning generates another residue, rice husk ash (RHA). Rice husk ash is an adsorbent for the adsorption of organic and inorganic impurities. This work investigates the use of waste rice husks as a precursor for biodiesel production.  $\text{SiO}_2$  is obtained after the calcination of waste rice husks above 900 °C, then thermal activation with  $\text{Li}_2\text{CO}_3$  to prepare base catalysts for the methanolysis of soybean oil. Waste rice husks have never been studied in the transesterification of triglyceride system as a solid catalyst precursor. The prepared waste rice-husk catalysts are characterized by X-ray diffraction (XRD), and the Hammett indicator to obtain their physical and chemical properties. Effects of thermal activation with  $\text{Li}_2\text{CO}_3$  amount, alcohol/oil ratio (mol/mol), and catalyst amount (wt % of oil) on the activity of waste rice-husk catalysts are also investigated. The results show that highly active, air-insensitive, and reusable solid catalyst could be obtained by mixing and well grinding 1 g waste rice husks with 2.46 g  $\text{Li}_2\text{CO}_3$  and being calcined at 900 °C in air for 4 h. A 15:1 molar ratio of methanol to oil, 1 % prepared catalyst, and 65 °C reaction temperature give the best results, and the biodiesel conversion exceeds 97.7 % at 3 h of reaction.

Keywords: biodiesel, rice husk ash,  $\text{Li}_4\text{SiO}_4$ , air-insensitive, transesterification

## 1 Introduction

Rice covers 1% of the earth's surface and is a primary source of food for billions of people. Rice husks are the outer cover of rice and on average accounts for 20% of the paddy produced, on weight basis. The main characteristics of rice husks appear 16.3 MJ/kg heating value, a content of 74.0% volatile matter and 12.8% ash. These characteristics indicate that rice husks could be a good solid fuel for the boilers of various industries to produce steam, thus, conserve both energy and resources. The burning of rice husks in air always leads to the formation of rice husk ash (RHA), which is usually regarded as agricultural waste. On average each tonne of rice produces 200 kg of rice husks, which on complete combustion lead to 40 kg of RHA. No other crop residue generates a greater quantity of ash when it is burnt. The RHA is largely composed of silica (87-99%) with small amounts of inorganic salts. A hard estimation indicates that near 320,000 t/year of RHA could be generated at the region, and adequate alternative dispositions must be planned to avoid environmental effects. RHA has been widely used as a construction material for producing concrete, or as an adsorbent to adsorb organic dye, such as malachite green, and inorganic metal such as  $\text{Pd}^{2+}$  and  $\text{Cu}^{2+}$  metal ions. Due to its high silica content, RHA can be an economically viable raw material for the production of silicates and silica in recent years. Some researchers have synthesized ZSM-5 zeolite or NaY from RHA.

The utilization of waste shells as a source of CaO gives an opportunity to use it as catalyst, but also adds value to the waste generated. Calcium oxide (CaO) [1-5] is a promising basic heterogeneous catalyst for synthesizing biodiesel at mild temperatures (below the boiling point of methanol) and at atmospheric pressure, but is rapidly hydrated and carbonated by contact with room temperature air. A few minutes are adequate for CaO to chemisorb a substantial amount of H<sub>2</sub>O and CO<sub>2</sub>. In this study, RHA is used as a low-cost material to prepare solid base catalyst using Li<sub>2</sub>CO<sub>3</sub> as an activating agent by solid state reaction. To the best of our knowledge, this is the first attempt to use silica from RHA as a raw material for biodiesel production. Moreover, the catalyst is air-insensitive and can be directly used for biodiesel production without being further dried or thermal pretreated, avoiding the usual activation of solid catalysts at high temperature.

## 2 General Instructions

Soybean cooking oil (Great Wall Enterprise Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Miaoli, Taiwan), reagent grade Li<sub>2</sub>CO<sub>3</sub> (Shimakyu's Pure Chemicals, Osaka, Japan) and LiOH·H<sub>2</sub>O (Chameleon Reagent, Osaka, Japan) were used as received. Rice husks were obtained from a rice farm in Yunlin, central Taiwan.

Dry raw rice husks (RHs) were sieved to eliminate residual rice and clay particles. After thorough washing with deionised water, the RHs were filtered and then air-dried at room temperature. A sample of rice husks is converted into rice husk ash by heat-treating rice husks at 900 °C for 4 h. After washing with deionised water and filtration, the RHA were dried at 120 °C for 16 h. The results show that highly active solid catalyst could be obtained by mixing and well grinding 1.00 g RHS with 4.26 g Li<sub>2</sub>CO<sub>3</sub> calcined at 900° C in air for 4 h.

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 3 h while stirring at 300 rpm. The reactant was stirred evenly to avoid splashing in the flask at the stirring speed.

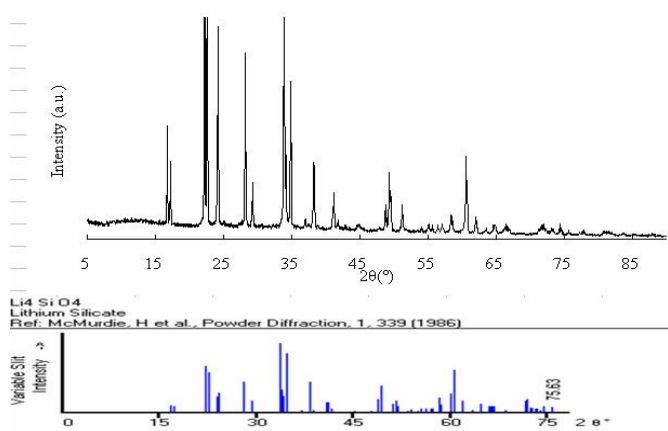
The timing of the reaction was initiated as soon as the mixture of methanol and the catalyst was added into the reactor. The effects of molar ratio of methanol to oil (3:1-24:1), and catalyst/oil weight ratio (1-2 wt. %), on the conversion of triglycerides to biodiesel were investigated. All of the experiments 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/cm<sup>3</sup>, respectively. A supernatant was filtered through a common filter paper, and then excess methanol and water were evaporated prior to fatty acid methyl ester (FAME) analysis.

The base strength of as-prepared catalysts (H<sub>-</sub>) 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<sub>-</sub>=7.2), phenolphthalein (H<sub>-</sub>=9.8), 2,4-dinitroaniline (H<sub>-</sub>=15.0), and 4-nitroaniline (H<sub>-</sub>=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 as-prepared catalysts was performed using a powder X-ray diffractometer (XRD, MAC MXP18, Tokyo, Japan), with Cu K $\alpha$  radiation, over a 2 $\theta$  range from 20 to 80° with a step size of 0.04°, and at a scanning speed of 3° min<sup>-1</sup>. FAME concentrations, expressed as the biodiesel purity of the product, were 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  $\mu$ m 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<sup>-1</sup> to 220 °C (hold 1 min), then increasing at a rate of 10 °C min<sup>-1</sup> to 250 °C (hold 1 min). The temperature of the programmed temperature

injector was 90 °C for 0.05 min, programmed to 260 °C, at a rate of 10 °C min<sup>-1</sup>. Nitrogen was used as a carrier gas with a flow-rate of 2 ml min<sup>-1</sup>. The amounts of FAME were calculated using the internal standard (methyl heptadecanoate) method, according to method EN 14103.

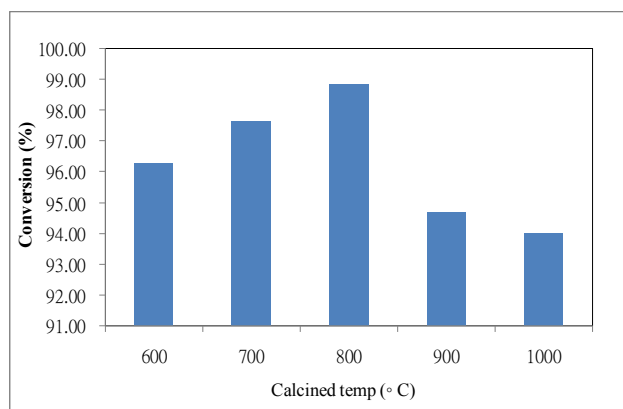
### 3 Results and Discussion

Fig. 1 shows the XRD patterns of the as prepared samples exposed to air for 24-72 h and after used. The XRD peaks were mainly consistent with Li<sub>4</sub>SiO<sub>4</sub> (JCPDS 37-1472).



**Fig. 1.** XRD pattern of as-prepared catalyst

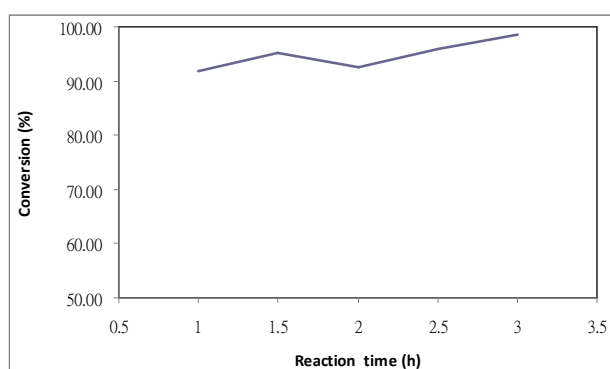
Fig. 2 shows the influence of calcination temperature (°C) on the conversion. The reaction condition was methanol/oil ratio 12:1, catalyst amount 4%, reaction time 3hr and methanol reflux temperature.



**Fig. 2.** Influence of calcination temperature(°C) on the conversion. Reaction condition: methanol/oil ratio 12:1, catalyst amount 4%, reaction time 3hr and methanol reflux

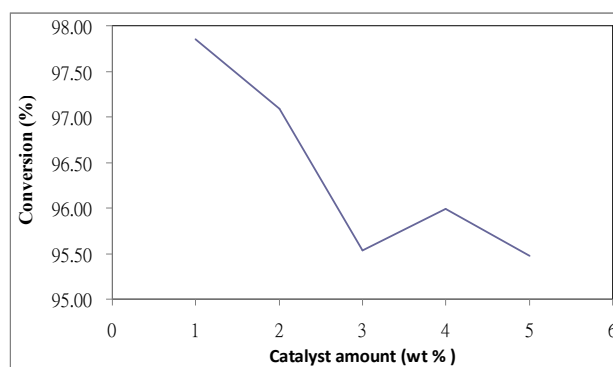
temperature.

Fig. 3 shows the influence of Influence of Reaction time (h) on the conversion. The reaction condition appeared calcination temperature 800 (°C) , catalyst amount 4% methanol/oil ratio 12:1 and methanol reflux temperature. More than 93.0 % conversion could be got within 1 h reaction time range, and thereafter remained nearly constant as a result of a nearly equilibrium conversion. For the transesterification of refined soybean oil with methanol (12:1) using 4 % catalyst, four different temperatures were used.



**Fig. 3.** Influence of Reaction time (h) on the conversion. Reaction condition: calcination temperature 800 (°C), catalyst amount 4% methanol/oil ratio 12:1 and methanol reflux temperature.

The catalyst amount was varied in the range of 1–5 % (catalyst/oil weight ratio). As shown in Fig. 4, the conversion was increased as the catalyst amount decreased from 1 to 5%. Additional catalysts increased the contact opportunity of the catalyst and the reactant, which directly influenced the reaction speed and the conversion.



**Fig. 4.** Influence of Catalyst amount (wt %) on the

conversion. Reaction condition: calcination temperature 800 (°C) %, reaction time 3hr, methanol/oil ratio 12:1 and methanol reflux temperature.

Table 1 shows the basic strength of as-prepared catalyst, CaO and Li<sub>2</sub>CO<sub>3</sub> after different exposure times to ambient air (temperature 25 ± 2 °C, relative humidity: 50 ± 5%). The effect of exposure to air on the catalytic activity of the transesterification reaction was examined. As-prepared catalyst and CaO appeared the same initial basic strength. However, the basic strength of CaO deactivated obviously following the exposure of the catalysts to air (7.2<H<sub>+</sub><9.8), thus influencing the conversion to FAME. This deactivation was probably due to the hydration, followed by carbonation on the surface, even after a 3-min exposure to air, when CaO was appreciably deactivated. This severely limited its practical application due to the need for inert atmosphere during handling, storage, reactor loading, and use.

The basic strength (H<sub>+</sub>) of catalyst was decreased to the range of 9.8–15.0 after exposure to air for 24–72 h; therefore, slight differences manifested in the soybean oil conversion between the air-exposed catalyst (94.6%–87.2%) and the fresh catalyst (97.0%), which verified the catalytic sites of as-prepared catalyst being more air-insensitive than CaO. As-prepared catalyst was the solid base catalyst with the advantage of tolerance to air-exposure, which facilitated the operation of the catalytic reaction.

**Table 1:** Base strengths (H<sub>+</sub>) of as-prepared catalyst, CaO and Li<sub>2</sub>CO<sub>3</sub> after exposure to air

Exposure time (h)	catalyst	conversion *	CaO	conversion **	Li <sub>2</sub> CO <sub>3</sub>	conversion ***
0	15.0–18.4	97.0	15.0–18.4	95.2	9.8–15.0	95.5
24	9.8–15.0	94.6	7.2–9.8	2.9	9.8–15.0	98.6
48	9.8–15.0	93.0	7.2–9.8	2.5	9.8–15.0	95.5
72	9.8–15.0	87.1	7.2–9.8	1.3	9.8–15.0	95.1
used	9.8–15.0	82.1			9.8–15.0	93.9

\*Reaction conditions: methanol to oil molar ratio= 12:1; catalyst amount= 4 wt. %; reaction temperature= 65 °C; reaction time= 3 h.

\*\*Reaction conditions: methanol to oil molar ratio= 12:1; catalyst amount= 3 wt. %; reaction temperature= 65 °C; reaction time= 2 h.

\*\*\*Reaction conditions: methanol to oil molar ratio= 30:1; catalyst amount= 10 wt. %; reaction temperature= 65 °C; reaction time= 3 h.

## 4 Conclusion

The ash produced by rice husks has been characterized and the feasibility for its use as a starting material to synthesize Li<sub>4</sub>SiO<sub>4</sub> catalyst for possible applications in the biodiesel production has been investigated. The experimental results show that the as-prepared catalyst demonstrated excellent catalytic activity because of its basic strength above 15.0. For many base-catalyzed reactions, solid base catalysts are easily poisoned by carbon dioxide and water. The high sensitivity to these molecules has prevented the solid base catalysts from being used in a practical process. The utilization of waste bioshells as a source of CaO has attracted great attention and given an opportunity to use it as a catalyst, but CaO is rapidly hydrated and carbonated by contact with room temperature air. However, the as-prepared catalyst is tolerant to water and carbon dioxide and the catalytic activity of transesterification reactions are not seriously reduced due to no obvious LiOH formed on the catalyst surface and Li<sub>2</sub>CO<sub>3</sub> yet an efficient solid base catalyst (H<sub>+</sub>>9.8). The as-prepared catalyst is not only easy to synthesize using a solid-state reaction, but also can be directly used for biodiesel production without further catalyst synthesis processes, involving either drying or thermal treatment.

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