

Transesterification of Soybean Oil to Biodiesel Catalyzed by Waste Silicone Solid Base Catalyst

Yong-Ming Dai, Jung-Hang Hsieh and Chiing-Chang Chen*

Department of Science Application and Dissemination, National Taichung University of Education, Taichung 304, Taiwan

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This study uses waste silicone 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. A sample of waste silicone is converted into SiO_2 powder by being heated at $800\text{ }^\circ\text{C}$ for 4 h. The results show that a highly active solid catalyst could be obtained by mixing and well grinding SiO_2 powder with Li_2CO_3 calcined in air for 4 h. The prepared solid base catalysts are characterized by XRD, BET, SEM and FTIR 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, 6% (wt/wt oil) catalyst amount, and a reaction temperature of $62\text{ }^\circ\text{C}$ for 3 h, there is a $99.04 \pm 0.9\%$ conversion to the biodiesel from soybean oil. The waste silicone as the solid base catalyst demonstrates excellent catalytic activities and stable catalytic activities in transesterification reactions.

Keywords: Waste silicone; Li_2CO_3 ; Solid state reaction; SiO_2 powder; Transesterification.

INTRODUCTION

Under the effect of energy crisis, biomass energy with the strengths of recyclability and low pollution is regarded as the potential substitute for petroleum to release energy crisis.¹⁻³ Using biodiesel for replacing petrodiesel has become the most popular issue in recent years. The purpose of bioresource development is to ease petroleum exhaustion problems. Biodiesel refers that recyclable animal or plant oil as feed reacts with alcohol of low molecular weight by transesterification reaction could produce fatty acid ester with long chain.⁴ Biodiesel is regarded that sources from animal or plant oil are used as a kind of non-poisonous, environmental, and recyclable motor prostituted fuel, which not only is used alone, but also can be blended with mineral diesel.⁵⁻⁶

One way to reduce the cost of the catalysts is to use wastes as catalytic materials. In addition to reducing the cost of procuring and synthesizing the catalytic material, this approach creates additional revenue opportunities. 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 shell,⁷ waste rice husk,⁸ and egg shell.⁹

Waste Silicone is one kind of industrial waste with

general size and high SiO_2 content. Waste silicone ash contains highest amounts of silicon compounds among natural substances, with which SiO_2 would exist more than 90 wt% after thermal decomposition and calcinations, which is amorphous with mesoporous structure, high porosity, and high specific surface area.¹⁰ It suits to transporting the reactors and products in a chemical reaction, resulting in the lowest diffusion resistance on catalytic process. Therefore, this porous structure material should be excellent as the catalyst. Waste sources can be used as a catalyst and source of Li_2CO_3 , which adds value to the generated waste.

Li_2CO_3 catalytically tolerated exposure to air. This has important benefits when considering the industrial application of Li_2CO_3 as a solid catalyst, and the possibility of storing and handling the activated catalyst without taking special action to prevent contact with the ambient air.¹¹ This study uses waste silicone as a low-cost material for preparing the solid base catalyst using Li_2CO_3 as an activating agent through a solid state reaction for the biodiesel production. In the present study, the objective of this study is to investigate solid catalysts used in 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 biodiesel

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* Corresponding author. Tel: +886-4-22183839; Fax: +886-4-22183530; Email: ccchen@mail.ntcu.edu.tw; ccchen@ms3.ntcu.edu.tw

production because the reaction time is low enough to be practical in continuous processes and the preparation is neither difficult nor costly.

EXPERIMENTAL

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.

A sample of waste silicone was converted into SiO_2 powder by heating waste silicone at $900\text{ }^\circ\text{C}$ for 2 h. The results showed that a highly active solid catalyst could be obtained by mixing and well grinding waste silicone with Li_2CO_3 calcined in air for 4 h.

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 (3:1-24:1) 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. 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.

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 $0.25\text{ }\mu\text{m}$ film thickness), the programmed column oven, and a programmed temperature injector. The oven temperature was programmed to start at $120\text{ }^\circ\text{C}$ (hold 1 min) with an increasing rate of $30\text{ }^\circ\text{C min}^{-1}$ to $220\text{ }^\circ\text{C}$ (hold 1 min), and then an increasing rate of $10\text{ }^\circ\text{C min}^{-1}$ to $250\text{ }^\circ\text{C}$ (hold 1 min). The temperature of the programmed 3 injectors was $90\text{ }^\circ\text{C}$ for 0.05 min and programmed to $260\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C min}^{-1}$. 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 EN 14103.

RESULTS AND DISCUSSION

Characterizations of as-prepared catalyst

To make direct comparisons, the same reaction conditions, as shown in Table 1, 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 1 that the silicone being converted into SiO_2 powder exhibits no activity. However, when Li_2CO_3 is modified into SiO_2 powder, the catalysts show catalytic activities. Thus, it is essential to modify SiO_2 powder from Li_2CO_3 to generate the catalytic activities for the transesterification reaction. It can be concluded that the observed activities of the Li_2CO_3 -modified SiO_2 powder 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.

Figure 1 shows the XRD results of SiO_2 powder, Li_2CO_3 (JCPDS 87-0728), and the as-prepared catalyst. The parent material SiO_2 powder is crystalline and consists of SiO_2 (JCPDS 029-0085). In order to understand the effect of the calcination temperature on the transesterification activity, the catalysts are calcined at different temperature and their crystalline structures are analyzed using X-ray diffraction (XRD). Figure 2 shows the resulting XRD spectra of synthesis catalyst at $600\text{ }^\circ\text{C}$, $700\text{ }^\circ\text{C}$, $800\text{ }^\circ\text{C}$ and $900\text{ }^\circ\text{C}$. It can be observed that the spectra of the samples are very similar. The main crystalline structure of these samples corresponds to the SiO_2 powder being transformed to the Li_4SiO_4 (JCPDS 37-1472) and a few Li_2SiO_3

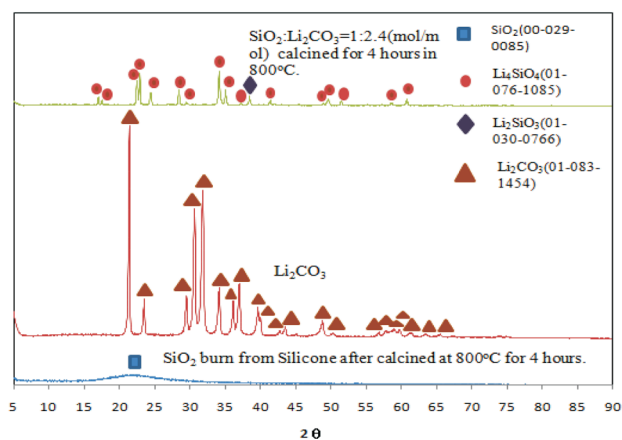


Fig. 1. Shows the XRD results of WBS, CWBS, Li_2CO_3 , and as-prepared catalyst.

Table 1. Base strengths of SiO₂ powder and the prepared catalyst for Li/SiO₂ powder molar ratio

Catalyst	Li/SiO ₂ molar ratio	Basic strength	*Conversion (%)
SiO ₂ powder	0	H ₊ < 7.2	0.36 ± 3.6
Li/SiO ₂ powder	2.2/1	7.2 < H ₊ < 9.8	83.3 ± 2.4
Li/SiO ₂ powder	2.4/1	9.8 < H ₊ < 15.0	92.7 ± 1.3
Li/SiO ₂ powder	2.6/1	9.8 < H ₊ < 15.0	89.4 ± 0.8

*Reaction conditions: 12.5 g soybean oil; methanol/oil molar ratio, 18:1; catalyst amount, 3 wt%; reaction time, 4 h; methanol re?ux temperature and conventional heating method.

(JCPDS 70-0330) phase after solid state synthesis with Li₂CO₃. It can be seen that, the samples show the diffraction peaks characteristic of Li₄SiO₄. Upon the calcination at 600 °C, the as-received SiO₂ powder and Li₂CO₃ undergoing decarbonization and dehydration processes lead to the formation of Li₄SiO₄ and Li₂SiO₃.

Figure 3 (a) presents FE-SEM images of the waste silicone being converted into SiO₂ powder and the chemical composition of the SiO₂ powder determined by EDS. The FE-SEM micrograph of the SiO₂ powder indicates that the surface is spherical and impermeably porous in nature. Elemental composition with EDS shows that SiO₂ is the main detected component (Figure 3 b). The SiO₂ 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/P₀), indicating the macropore adsorption. The corresponding BET specific surface area is calculated to be 1.81 m²/g. The pore size distribution calculated from the BJH method shows a broad pore size ranging in 65–137 nm (Figure 3 c).

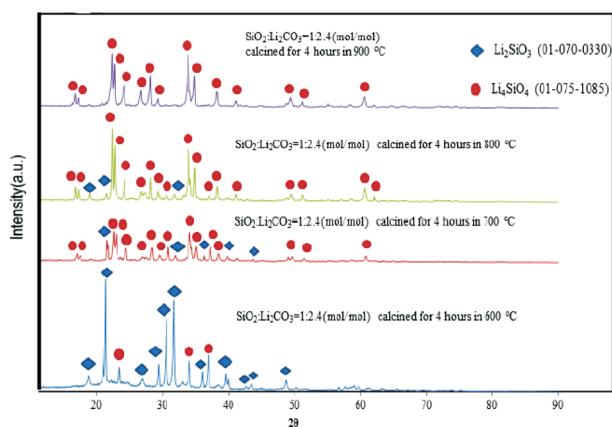
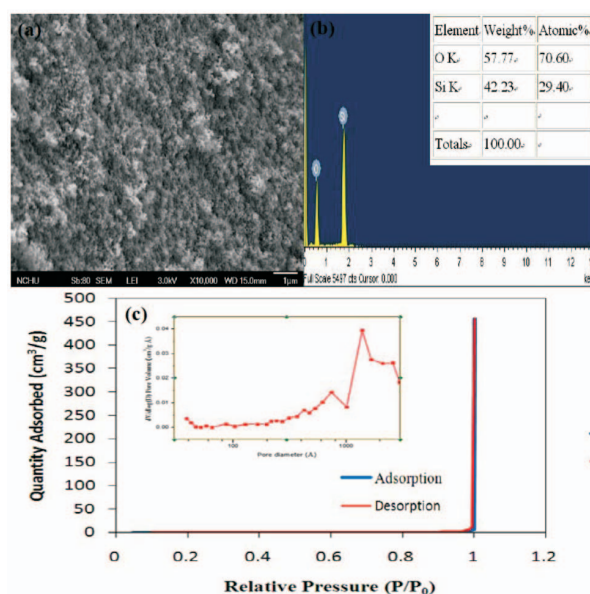
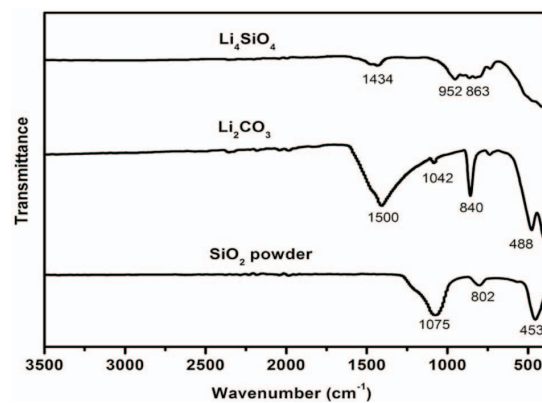


Fig. 2. XRD pattern of the catalysts prepared from different calcined temperature.

Figure 4 shows the FTIR spectra of the as-prepared catalyst synthesized using a solid-state reaction. The bands located at 1075, 802 and 453 cm⁻¹ correspond to Si–O–Si bonds.¹² Bands at 840, 1050 and 1500 cm⁻¹ are attributed to Li₂CO₃ vibrations.¹³ The CO₃²⁻ anions are probably formed on the surface of the samples by absorbing CO₂ molecules from the air after calcination. The absorption bands originating from the Si–O– and Li–O– groups locate at 453 and 488 cm⁻¹.¹⁴ The CO₃²⁻ anions are formed on the surface of the samples probably by absorbing CO₂ molecules from the air after calcining. The bands at 863, 952 and 1434 cm⁻¹ are due to the asymmetric vibrations of Si–O–Si. The similar-

Fig. 3. (a) FE-SEM morphology and (b) EDS elemental analysis (c) Nitrogen adsorption–desorption isotherm and pore size distribution of SiO₂ powder.Fig. 4. FTIR spectra of the Li₄SiO₄ catalysts, pure Li₂CO₃ and SiO₂ powder.

ity of the spectrograms indicates that the phase of Li_4SiO_4 .

Transesterification reaction condition optimization

Figure 5 shows different calcination temperature of the Li/SiO_2 powder (1/2.4) through the transesterification process. With the calcination temperature at 600 °C, the conversion achieves 87.8%, while the conversion achieves 95% when the temperature is higher than 600 °C, and the higher conversion $98.72 \pm 1.5\%$ appears on the calcination temperature at 900 °C.

The stoichiometric molar ratio of methanol to oil for the 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.¹⁵ In Figure 6, 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 $98.1 \pm 1.6\%$ for the catalysts. Further increasing the alcohol to oil ratio leads to the decrease of the oil concentration and accordingly the decrease of the reaction rate. Therefore, 18:1 is the appropriate methanol/oil molar ratio for this reaction. The excess methanol can be collected and recycled. Catalyst amount is an important parameter affecting the conversion of triglycerides to methyl esters. As shown in Figure 6, the conversion reaches a plateau value at the catalyst weight percentage between 0.375 and 9 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

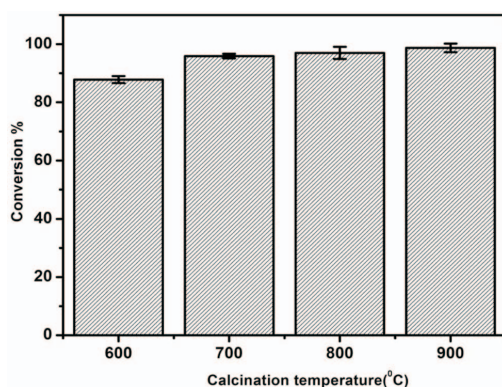


Fig. 5. Influence of calcination temperature on the conversion. (Reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, catalyst amount 3 wt.%, reaction time 2 h).

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.¹⁶ Under present reaction conditions, the optimal catalyst amount is 3 wt%.

Reaction time and temperature are important factors in the whole process. The reaction time varies in the range 1-5 h. As can be seen from Figure 7, the conversion increases steadily in the reaction time, and thereafter remains nearly constant as a result of a nearly equilibrium conversion; the maximum conversion oil is achieved at 2 h. Figure 7 shows five different temperatures being used for the transesterification of refined soybean oil with methanol (18:1) using 3 wt% catalyst. Temperature clearly influenced the reaction rate and the biodiesel purity.

After the transesterification is 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 8, a biodiesel purity of 96.6% could be obtained even after recycling the catalyst 10 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 than other catalysts do in the transesterification reaction, but its lifetime in an industrial set-

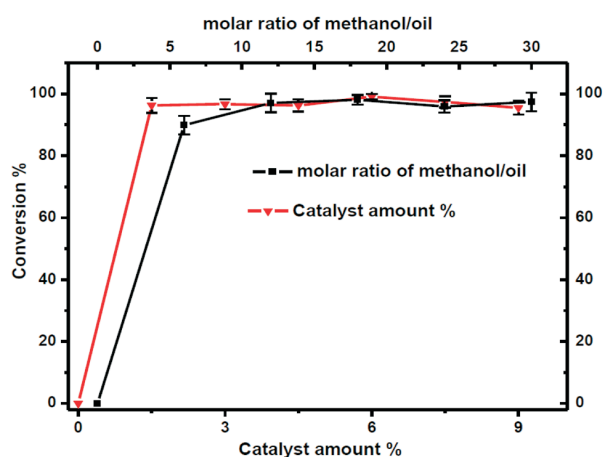


Fig. 6. Influence of catalyst amount and methanol/oil molar ratio on the conversion. (Reaction conditions: 12.5 g soybean oil, reaction temperature 62 °C, reaction time 2 h).

ting must be significantly prolonged to be practical.

To examine the catalyst stability under the reaction conditions, the concentration of Li^+ in the FAME phase is quantified by ICP-AES after the reaction. The first transesterification reaction produces FAME containing 90 ppm of lithium. Figure 9 shows that the concentration of Li^+ under different using time is below the 100 ppm. These results demonstrate extremely small quantity (free Li^+ concentration of less than 100 ppm) in the biodiesel. These results indicate that the as-prepared catalyst is suitable for the use in biodiesel production from soybean oil. The main advantage of the solid base catalyst is that it can be used repeatedly. It clearly indicates the advantage of solid base catalyst for the reaction stability and the possible feasibility can be enhanced in industrial production.

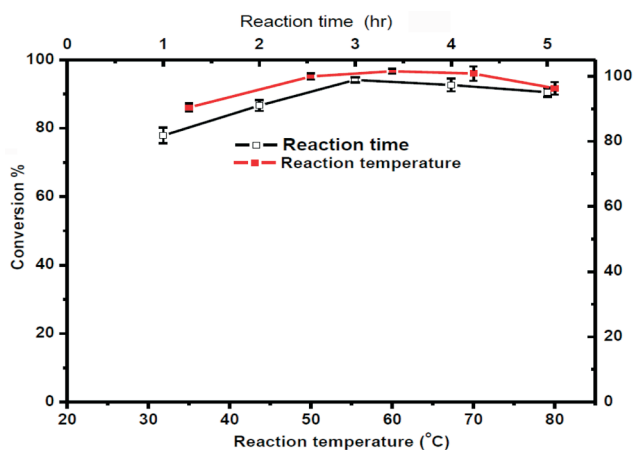


Fig. 7. Influence of reaction time and reaction temperature on the conversion. (Reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, catalyst amount 3 wt.%).

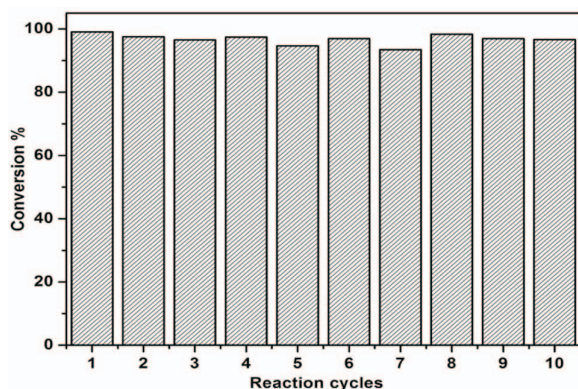


Fig. 8. Reusability study after five reaction cycles for catalyst (Reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, catalyst amount 3 wt.%, reaction temperature 62 °C).

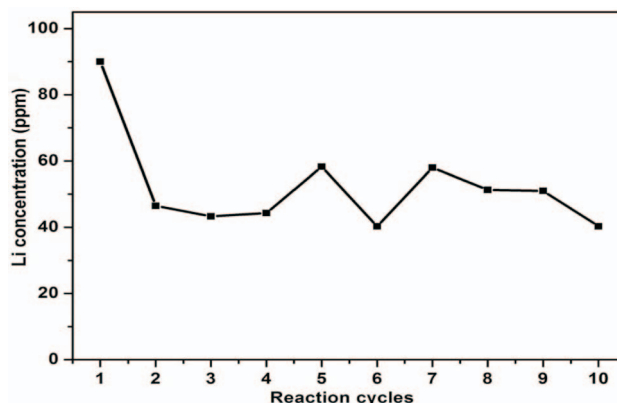


Fig. 9. The Li leaching of reaction cycles.

CONCLUSIONS

This study reveals waste silicone 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 demonstrates excellent catalytic activities because of its basic strength (H_+) above 15.0. The catalysts prove to be highly stable during successive runs of spent catalysts. Moreover, the catalysts can be reused, without activation, for at least 10 catalytic runs, maintaining the biodiesel yields close to 96%. Several reaction variables are studied and the optimal catalyst loading into the reaction media is 3% (w/w). The ratio of 18:1 produces the highest conversion. In addition, increasing the reaction time to 3 h produces the highest level of activity. It clearly indicates the advantage of solid base catalyst for the reaction stability and the possible feasibility can be enhanced in industrial production.

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