Synthesis of glycerol carbonate from dimethyl carbonate and glycerol using CaO derived from eggshells

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Abstract. Waste eggshell is proposed as a highly active catalyst for glycerol carbonate production from dimethyl carbonate (DMC) and glycerol. The effect of reaction temperature, reaction time and catalyst loading on the reaction performance were investigated in order to find a suitable operating condition. CaO derived from waste eggshell exhibits catalytic activity comparable to commercial CaO. By using CaO eggshell, glycerol conversion of 96% can be achieved within 90 min of reaction time under 2.5:1 feed molar ratio of DMC to glycerol, 0.08 mole ratio of CaO to glycerol and reaction temperature of 60°C. The catalyst was examined by XRD, TGA/DSC, SEM, N_2 adsorption-desorption and Hammett indicators method. Utilization of eggshell as a catalyst for glycerol carbonate production not only provides a cost-effective and value-added of waste eggshell as a green catalyst, but also decrease amount of waste and its treatment cost which is ecologically friendly.

1. Introduction

Biodiesel is a world-recognized renewable fuel for fossil diesel substitution. It is generally produced from transesterification of vegetable oils with alcohols in the presence of an alkaline-based catalyst which gives glycerol as a by-product. However, for every 9 kg of biodiesel production, about 1 kg of crude glycerol is formed. Consequently, the price of glycerol has fallen significantly since 2006 [1]. This has prompted to convert low cost glycerol to value-added products [2]. Moreover, converting of glycerol to value added product is crucial to secure the sustainability of biodiesel production in term of cost competitive [3]. In addition, glycerol now becomes one of the top twelve major building blocks suggested by researchers of National Renewable Energy Laboratory (NREL).

Glycerol carbonate is one of the glycerol derivatives that capture more scientific and industrial attention at present. By preliminary economic screening of NREL researchers, glycerol carbonate was proposed as one of promising glycerol utilizations for value added chemicals. Glycerol carbonate has a potential benefit as bio-lubricant, due to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis and pressure. In addition to surfactants and pharmaceuticals, glycerol carbonate can be used as a building block to synthesize polymers, such as polycarbonates, polyglycerol esters, hyperbranched polyols, and non-isocyanate polyurethanes [4]. Thus far, several routes have been explored to synthesize glycerol carbonate from glycerol [5,6] However, with industrial feasibility consideration, transesterification (or transcarbonation) of glycerol with organic carbonate sources such as dimethyl carbonate, ethylene carbonate or propylene carbonate using basic catalysts becomes the most of interest [7, 8]. CaO, one of

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the reported catalysts, is very interesting due to high activity, very cheap and easily available. Complete glycerol conversion and 95.3% yield could be achieved at 1.5 h reaction time, reaction temperature = 95°C, and dimethyl carbonate/glycerol molar ratio = 3.5. However, lower activity is found when CaO is exposed to the air and moisture environment, thus converted into $Ca(OH)_2$ and $CaCO_3$ during the reaction[9]. CaO can be derived from natural calcium carbonate ($CaCO_3$) source for example dolomite, mollusk shell, crab shell and egg shell by calcination. Egg shells are excellent source due to which composed a high content of calcium carbonate (96% of shell weight) [10]. The waste eggshell as catalyst was used in biodiesel production [11-15], synthesis of DMC [16], synthesis of H_2/syngas [17-19], etc.

In this work, we investigated the possibility of application of eggshell as a catalyst for glycerol carbonate production from glycerol and dimethyl carbonate. Suitable operating condition is investigated.

2. Materials and methods

2.1 Chemicals and preparation of catalysts

Glycerol (99.5 v/v%, Ajax Finechem Ltd) and dimethyl carbonate (≥ 99 wt%, Merck) were employed as a reactant. Butanol (99.8 v/v%, Sigma Aldrich) and and glycerol carbonate (99 wt% Sigma Aldrich) were used as the internal standard was used and calibration standard, respectively, for gas chromatography analysis. Commercial CaO was purchased from Lab reagent & Fine Chemicals Ltd. Waste eggshell contain mainly $CaCO_3$ which converted to CaO phase by calcinations at temperature 900°C for 2.5 h. The CaO was kept in desiccators to avoid contacting with CO_2 and humidity in the air.

2.2 Characterization of catalysts

The catalyst was characterized by thermo gravimetric analysis under air flow condition with a heating rate 10°C/min from 25°C to 1000°C to examine decomposition of catalyst. The morphology of catalysts were determined using scanning electron microscope (SEM). The structure and crystalline phases of calcined eggshell were analyzed by X-ray diffraction and basic strength was determined by using Hammett Indicator (H_). For basic strength determination, 25 mg of catalyst was shaken with 5 ml of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h. The following Hammett indicators were used: phenolphthalein (H_= 9.8), 2,4-dinitroaniline (H_= 15.0) and 4-nitroaniline (H_= 18.4). N_2 physisorption was performed to measure the surface area and pore volume of catalysts.

2.3. Reaction procedure

Transesterification of glycerol with DMC was performed in 250 ml three-necked flask equipped with condenser and water bath. The reaction conditions are as follows: 2.5:1 molar ratio of DMC to glycerol, 4% mole ratio of initial amount of CaO to glycerol, reaction temperature from 40°C to 60°C for 3 h.

2.4. Product analysis

The samples were analyzed by gas chromatography(Shimadzu GC-14B) with flame ionization detection (FID) using an ZB-WAX (30 m long, 0.32 mm, 0.5 μm) capillary column. Injector and detector temperatures were kept 300°C. Oven temperature started at 40°C and was increased at 15 °C/min to 240 °C which was held for 30 min.

3. Result and discussion

3.1 Characterization of CaO egg shell

According to the thermogravimetric analysis (TGA) results reported in Fig 1, the first weight loss of eggshells at approximately 300-600°C is assigned to decomposition of moisture and organic compounds, whereas the final weight loss between 600°C and 750°C is due to loss of CO_2 from carbonate converting to CaO phase. In addition, the DSC curve, attributed to an endothermic peak at around 600-700°C, confirming the decomposition of $CaCO_3$ to CaO also implies that the calcination temperature of eggshells should be above 800°C to completely CaO forming. The surface area of CaO derived from eggshell was 4.9 m^2/g. which is slightly lower than the surface area of commercial CaO (5.5 m^2/g). The strength of the basic sites was 15.0 <H_<18.4 for the fresh CaO eggshell which was similar to commercial CaO catalyst (Table 1). Both catalysts were mesopores (from BET technique) with generally irregular crystal structure as aggregate shown in SEM images (Fig.2).

Table1. BET surface area and basic strength of catalysts

Catalysts	BET surface area(m^2/g)	Basic strength (H_)
Commercial CaO	5.5	15.0< H_<18.4
CaO derived from eggshell	4.9	15.0< H_<18.4

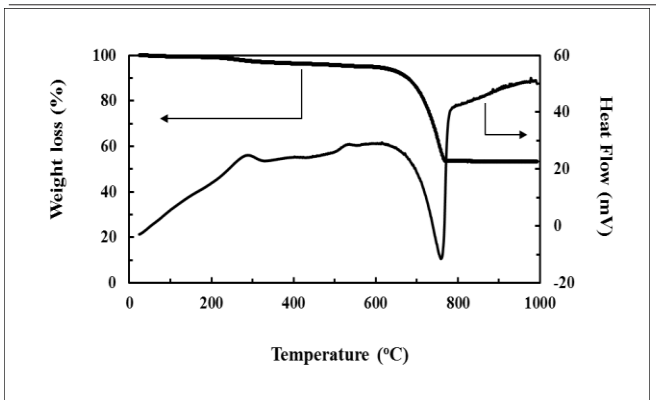

Fig. 1. TGA-DSC curves of eggshells**.**

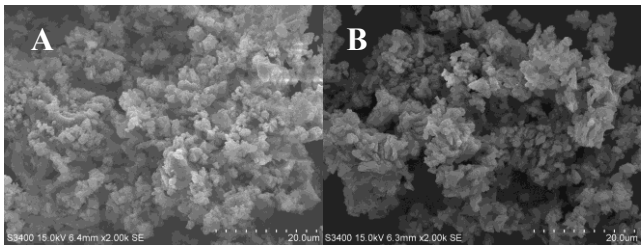

Fig.2. Morphology of (A) commercial CaO and (B) CaO eggshell.

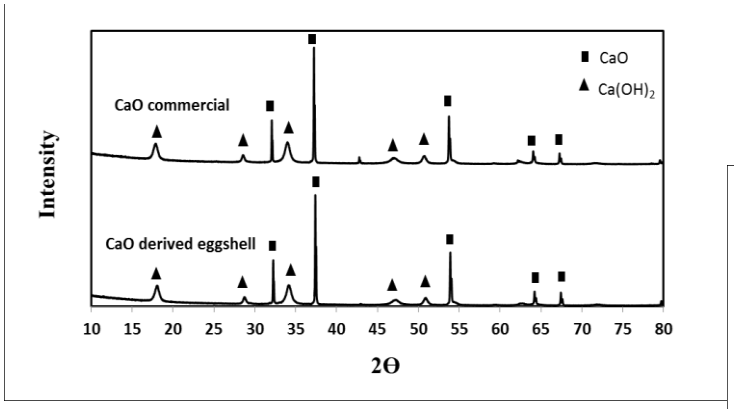

Fig. 3. XRD pattern of commercial CaO vs CaO eggshell.

The crystal structure of catalysts were obtained using an X-ray diffraction (XRD). The main composition of the calcined eggshell was CaO species while $Ca(OH)_2$ was found as a minor (Fig 3). The observation of $Ca(OH)_2$ phase might be because the sample was exposed to humidity in the air.

3.2 Catalytic activity of transesterification

Comparison between CaO derived from eggshell and commercial CaO for transesterification of glycerol with DMC are shown in Fig.4. The result shows that commercial CaO obtained complete conversion and CaO eggshell was nearly as same as one to approach glycerol conversion 96%.

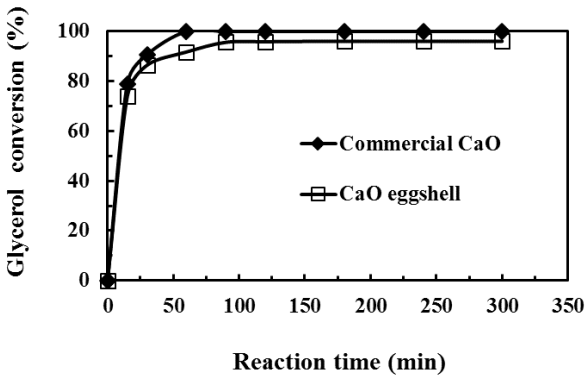

Fig. 4. Catalytic activity of commercial CaO vs. CaO eggshell.

3.3 Effect of reaction temperature

Transesterification of glycerol and DMC was investigated at varying temperature range between 40°C and 60°C under atmosphere pressure. As shown in Fig.5, initial conversion of glycerol increase with increasing reaction temperature due to the dependence of the kinetic rate with the temperature. Moreover, the equilibrium conversion increased from 83% to 91% and 96% with increasing reaction temperature from 40°C to 50°C and 60°C, respectively. Higher operating temperatures is favor due to a nature of endothermic reaction. In addition, increasing operating temperature enhance the miscibility of reactant mixture.The highest glycerol conversion of 96% can be achieved at 60°C within 90 min of reaction time.

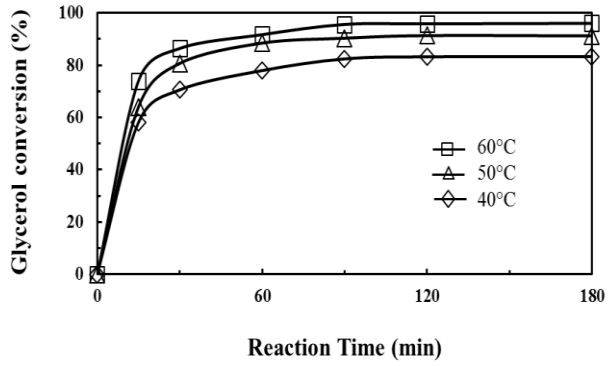

Fig. 5. Effect of reaction temperature on glycerol conversion. Reaction condition: molar ratio of DMC: glycerol = 2.5, mole ratio of catalyst to glycerol = 0.08, speed stirrer = 350 rpm.

3.4 Effect of catalyst loading

Fig.6. indicate that the amount of catalyst influence on conversion of glycerol when increasing mole ratio of CaO to glycerol from 0.02 to 0.08 the conversion was raised from 76% to 96%. This catalytic activity is enhanced due to the increase in the concentration of the active basic sites that are crucial to catalyze the transesterification reaction. Therefore mole ratio of CaO to glycerol of 0.08 was obtained the highest conversion of glycerol.

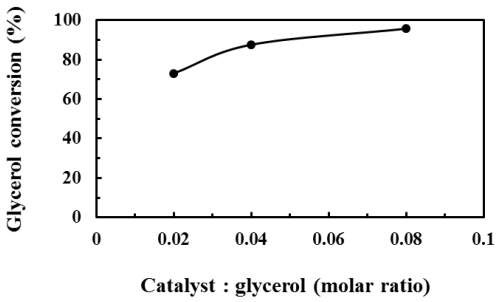

Fig. 6. Effect of catalyst loading on glycerol conversion. Reaction condition: molar ratio of DMC: glycerol = 2.5, reaction temperature = 60°C, reaction time = 90 min, speed stirrer = 350 rpm.

4. Conclusion

CaO derived from waste eggshell has strong basic sites and exhibits high catalytic activity of transesterification between DMC and glycerol. It was found CaO eggshell showed similar performance to the commercial CaO. Three reaction temperature levels of 40, 50, and 60 were investigated with different reaction time and catalyst loading. Glycerol conversion of 96% can be achieved within 90 min under suitable condition (reaction temperature of 60°C and catalyst loading of 0.08 mol/mol glycerol).

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