Microwave Assisted Solvent-Free Catalytic Transesterification of Glycerol to Glycerol Carbonate

Wai Keng Teng, Gek Cheng Ngoh, Rozita Yusoff, Mohamed Kheireddine Aroua, Joe Shen Heng

Abstract—As a by-product of the biodiesel industries, glycerol has been vastly generated which surpasses the market demand. It is imperative to develop an efficient glycerol valorization processes in minimizing the net energy requirement and intensifying the biodiesel production. In this study, base-catalyzed transesterification of glycerol with dimethyl carbonate using microwave irradiation as heating method to produce glycerol carbonate was conducted by varying grades of glycerol, i.e. 70%, 86% and 99% purity, that is obtained from biodiesel plant. Metal oxide catalysts were used with varying operating parameters including reaction time, DMC/glycerol molar ratio, catalyst weight %, temperature and stirring speed. From the study on the effect of different operating parameters it was found that the type of catalyst used has the most significant effect on the transesterification reaction. Amidst the metal oxide catalysts examined, CaO gave the best performance. This study indicates the feasibility of producing glycerol carbonate using different grade of glycerol in both conventional thermal activation and microwave irradiation with CaO as catalyst. Microwave assisted transesterification (MAT) of glycerol into glycerol carbonate has demonstrated itself as an energy efficient route by achieving 94.2% yield of GC at 65°C, 5 minutes reaction time, 1 wt% CaO and DMC/glycerol molar ratio of 2. The advantages of MAT transesterification route has made the direct utilization of bioglycerol from biodiesel production without the need of purification. This has marked a more economical and less-energy intensive glycerol carbonate synthesis route.

Keywords—Biodiesel, glycerol, glycerol carbonate, microwave irradiation.

I. INTRODUCTION

BIODIESEL is a mixture of mono alkyl esters of long chain fatty acids. It is biodegradable, non-toxic, low emission profile and produced from renewable biological sources [1]. Currently, biodiesel is being produced in increasingly large amount throughout the world [2]. The main by-product of biodiesel process is crude glycerol (GLY). In practice, every kg of biodiesel produced gives 0.1 kg of GLY as by-product. This has led to a large surplus of GLY. The projected increase in traditional application of GLY cannot absorb the booming GLY production. As a matter of fact, many products from selective transesterification of GLY have been attempted. Glycerol carbonate (GC) is the most preferable product because it is valued at 8 times higher, 2.40

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US/kg, as compared to crude GLY at 0.30 US/kg [3]. Besides, it has diverse applications in the industry as a solvent, electrolytes liquid carrier, curing agent, gel remover, liquid membrane, plant vitalizer, blowing agent and even detergent [4].

Generally, there are 3 types of GLY. They are refined GLY (used in cosmetics, pharmaceuticals and food), technical grade GLY (suitable for industrial applications) and crude GLY (raw by-product from biodiesel) [2]. The purity of crude GLY is around 40-86% while that of refined GLY is 99%. Crude GLY contains a lot of methanol, residual organic matter, soap and water.

Microwave irradiation has been increasingly popular as a heating method for transesterification reaction. It had been proven to be more efficient than the conventional water bath heating [5]. Various benefits of microwave irradiation as compared to conventional water-bath heating included internal rapid heating that reduces reaction time tremendously from 2 hours to around 15 minutes. This compensates its higher power consumption. Also, efficient and uniform heating that enables good temperature control can be achieved via microwave processing. As a result, there is no significant temperature gradient even if the reactor vessel is very large. Thus, this study reports an efficient route to produce GC from crude GLY with different metal oxide catalysts with the aid of microwave processing. In this study, immiscibility of DMC and glycerol was first investigated. Then, a screening study of different operating parameters was carried out using conventional water-bath heating method. This is followed by comparison study between the performance of crude and pure glycerol under microwave irradiation. Finally, optimization study was carried out by using the selected glycerol purity to improve the performance of transesterification under microwave irradiation.

II. EXPERIMENTAL PROCEDURE

A. Materials

Two different grades of GLY were obtained from a local biodiesel plant in Malaysia. Pure GLY, GC and metal oxide catalysts were supplied by Sigma Aldrich (USA). Dimethyl carbonate was purchased from Merck (Germany).

B. Methods

Microwave-assisted transesterification was performed in a microwave reactor (Milestones, 1200 W, 2450 MHz) equipped with an infrared temperature sensor, temperature probe, a

three-neck round-bottomed flask, electromagnetic stirrer and a condenser while conventional transesterification was carried out by mean of heating bath as shown in Fig. 1. GLY was placed into a three-neck reaction flask and mixed with metal oxide catalyst and DMC in predetermined ratio. The prepared samples were heated to the desired temperature that was measured by in situ temperature probes. Upon completion of reaction, the collected sample was cooled and centrifuged at 3500 rpm for 5 minutes to filter off the catalyst. The sample was then analysed for GC and the unreacted GLY using Waters High pressure liquid chromatograph (HPLC) apparatus equipped with a PL Aquagel-OH column (Agilent) and a RI detector (Waters 410). The mobile phase used was water and the flow rate was set at 1 mL/min. The yields of GC and conversions of GLY were determined using (1) and (2), respectively.

$$Yield, Y = \frac{GC}{GLY_{initial}} \times 100\% \qquad (1)$$

$$Conversion, C = \frac{GLY_{initial} - GLY_{residual}}{GLY_{initial}} \times 100\% \qquad (2)$$
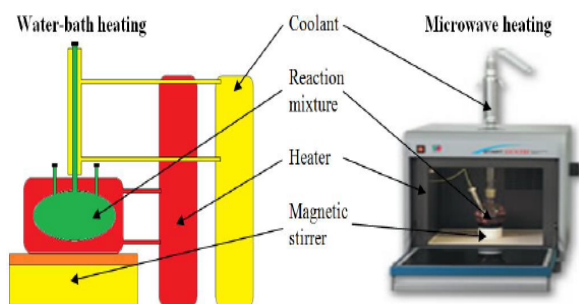

Fig. 1 Experimental set-up for transesterification

III. RESULTS AND DISCUSSION

A. HPLC Analysis

HPLC analysis was carried out to quantify the products and reactants. Using methanol as solvent, retention time of glycerol and glycerol carbonate was found to be 11.5 and 14.8 minutes respectively as shown in Fig. 2. Standard curves of glycerol and glycerol carbonate were plotted as shown in Figs. 3 (a), (b). They gave good accuracy which could be seen from the R^2 value of close to unity.
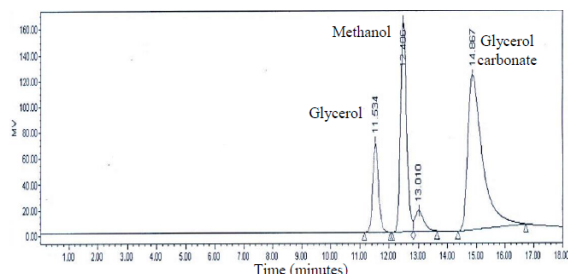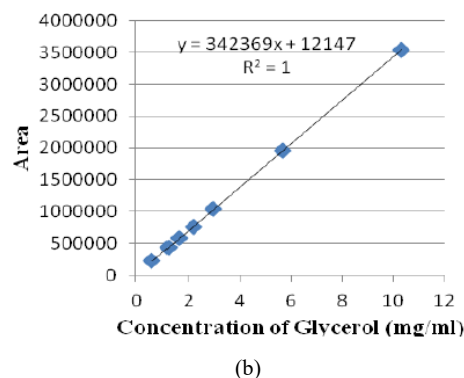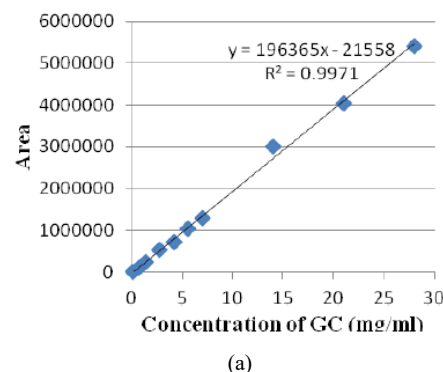

Fig. 2 HPLC analysis of the products

(a)

(b)

Fig. 3 (a) Standard curve of glycerol carbonate, (b) Standard curve of glycerol

B. Immiscibility of Reactant

The immiscibility of the reactants needs to be overcome to ensure consistent results. According to Godfrey's rule, two solvents would only be miscible in all proportion at room temperature when their difference in miscibility numbers (Δ) is less than 12, as shown in Table I. For $\Delta > 17$, heating would be required for both solvents to be miscible in all proportions. It is interesting to note that glycerol and dimethyl carbonate (DMC) were immiscible at $\Delta = 18$. Although both reactants were miscible during the reaction, problem arose during analysis. This is because HPLC analysis could only be performed at room temperature.

Several commercially available solvents such as DMSO and DMF are found to be capable of dissolving both reactants. However, they incurred additional cost and did not satisfy industrial feasibility criteria. Thus, the immiscibility problem was resolved in two ways:

i. Methanol was added into the mixture after the reaction as internal standard. This is because methanol had miscibility number of 12, which is between glycerol and DMC. Two-phase sample was found to be completely dissolved into one phase when half of the final mixture was comprised of methanol.

ii. Crude glycerol of 70% purity was used instead of pure glycerol. While pure glycerol at room temperature would have 612 centipoise, 70% crude glycerol has 14.1 centipoise [6]. This made the mixing of glycerol and DMC easier inside the reactor.

TABLE I
MISCIBILITY NUMBER OF VARIOUS COMPOUNDS [7]

Elements	Miscibility number
Glycerol	1
Glycerol carbonate	3
DMSO	9
DMF	12
Methanol	12
Ethanol	14
1-Propanol	15
t-butanol	16
Ethylene carbonate	17
Propylene carbonate	17
Dimethyl carbonate	19
Diethyl carbonate	21

C. Screening of Significant Operating Parameters

The operating conditions were screened by Plackett-Burman experimental design to select important parameters for GC synthesis. It was found that type of catalyst had the most significant influence on the yield of GC in conventional water bath heating as shown in Fig. 4. Therefore, a lot of research has been focused in finding the best catalyst that gave the best performance at minimum price. Pure metal oxide was used due to its abundant availability at cheap cost. Promising conversion and yield were obtained especially when the pure metal oxides were calcined at high temperature. This was then followed by time, DMC/GLY ratio, catalyst wt% and temperature. Stirring speed was found to be least important and can be neglected in the reaction as long as the reactants were well mixed.
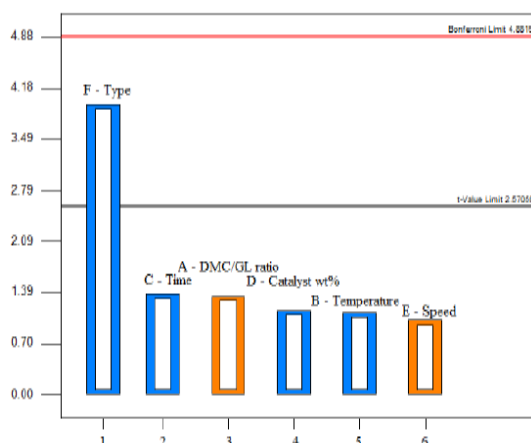

Fig. 4 Plackett-Burman design (Reaction conditions: water-bath heating, 99% purity glycerol, A: DMC/GLY: 1-3; B: Temperature: 50–75°C; C: Time: 30–90 min; D: Catalyst loading: 3-6 wt%; E: Stirring Speed: 650-1200 rpm; F: Type of Catalyst: MgO and CaO)

D. Screening of Different Purity of Glycerol

It is found that 70% purity GLY performed better than 86% and 99% purity GLY in terms of yield and conversion as shown in Fig. 5. This could be attributed to its alkaline condition and the presence of methanol in the 70% purity crude GLY. Moreover, the OH-group in both MeOH and GLY

rendered them as strong microwave absorption media to facilitate localised rotations [8]. Also, Pan et al. reported that methanol is a suitable solvent for production of GC from GLY [9]. Lowest performance of 86% purity GLY might be due to its acidity condition which is not favourable in this transesterification reaction as reported [10]. This suggests that crude GLY of 70% purity is a suitable reactant because of its better performance as well as lower viscosity. Moreover, the main by-product of biodiesel production was crude GLY. This will open up an avenue to convert crude GLY to value added products.

Unlike most of the studies that focus on utilizing technical grade GLY of 99% purity (route 1), alternative route is suggested (route 2) as shown in Fig. 6. The high cost and high viscosity of 99% purity GLY faced a challenge for large-scale manufacturing process. In fact, 99% purity GLY (technical grade) was produced from crude GLY via distillation. The alternative route utilizes current manufacturing process for direct production of GC.
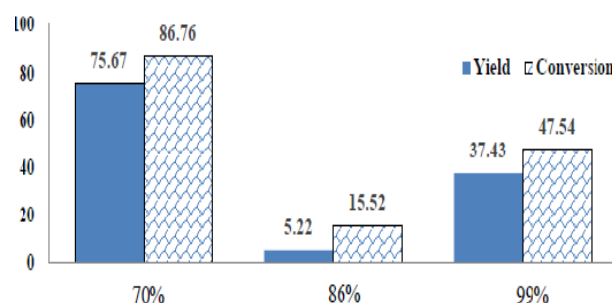

Fig. 5 Effect of glycerol purity on the transesterification of glycerol with DMC (Reaction conditions: water-bath heating, 650 rpm, 45 minutes reaction time, reaction temperature 65°C, 6wt% CaO and DMC/GLY ratio of 2)
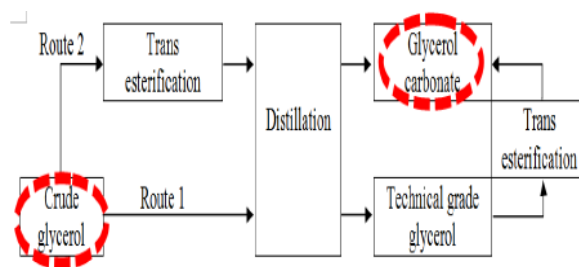

Fig. 6 Alternative route to produce GC

E. Optimization of Production of GC with the Aid of Microwave

The transesterification process was further optimized under microwave irradiation. The optimization study was carried out by utilizing full factorial design of experiments. Three selected parameters to be optimized were reaction time, reaction temperature and catalyst loading. The DMC/GLY ratio was fixed at 2 as it had been shown that this was the optimum performance [11]. All the conversion and yield was higher than 50% with the most promising ones at 94.2% yield within 5 min as shown in Fig. 7. The high efficiency was due to

microwave energy that had accelerated the reaction rate via the enhancement of catalyst's interaction with the reactant [12]. Energy was transferred from microwaves to the reactants through either resonance or relaxation and this created more molecular friction and collisions in the reaction medium and gave rise to intense localized heating. Consequently, the internal rapid heating provided by microwave heating had successfully reduced the reaction time to a modest 5 min compared with 45 min required by conventional heating. This result was comparable with other optimization studies as shown in Fig. 8. Microwave irradiation was found to be a promising route because it required short time to achieve high yield. Another report suggested that high GC yield of 95.3% was achieved [10]. However, the reaction had to be conducted in an autoclave reactor at high pressure (6 bar) to accommodate the low boiling point of DMC (90°C). Comparatively, microwave irradiation was done at atmosphere pressure and successfully reduced the reaction time to 5 minutes. Some complicated process synthesizing new catalyst from calcium oxide such as $Mg_{1.2}Ca_{0.8}O_2$ and CaO complex were proven to have better performance when applying conventional water bath heating [13]. However, microwave irradiation compensated the lower performance by using commercially available calcium oxide. This study shown that direct utilization of crude GLY from biodiesel plant to produce GC is feasible and economical process. In short, microwave assisted transesterification of crude GLY is fast and much energy-efficient GC synthesis route.
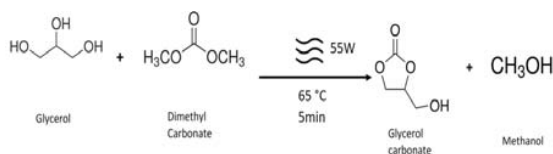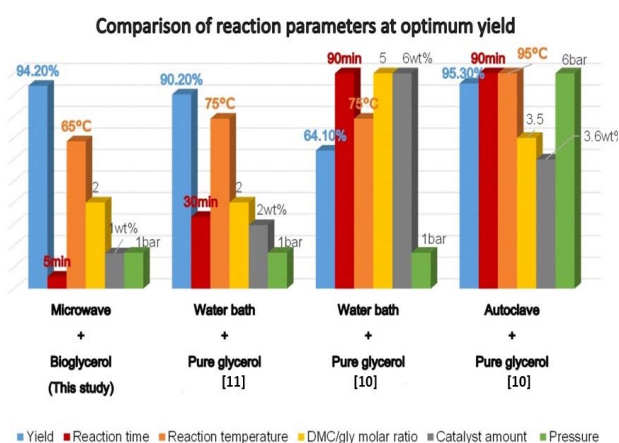

Fig. 7 Microwave assisted transesterification

Fig. 8 Comparison of microwave assisted transesterification with reported conventional transesterification

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