Investigation on the effect of ultrasonic-assisted transesterification for green synthesis of glycerol carbonate from crude glycerol

P K Lo1, S Y Leong1 and C Y Tan1
1 Department of Petrochemical Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, 31900 Kampar, Perak, Malaysia

Corresponding author: lopk@utar.edu.my

Abstract. The present work demonstrates the utilization of ultrasonic-irradiation for synthesis of glycerol carbonate (GC) with direct use of crude glycerol (C.Gly) and dimethyl carbonate (DMC). This transesterification reaction was catalysed by calcium oxide (CaO) and the effect of ultrasonic-assisted transesterification reaction was studied. In order to verify the contents of C.Gly, the C.Gly obtained from biodiesel production plant was characterized and the results showed that C.Gly consists of 71.21%w/w glycerol, 16.01%w/w of moisture, 7.10%w/w of methanol, 2.76%w/w of ash, 3.60 %w/w of soap and 10.02%w/w of matter organic non-glycerol (MONG). Subsequently, effects of reaction temperature, reaction time, molar ratios of reactants and catalyst loading on C.Gly conversion and GC yield have been investigated. The highest yield of GC (95.41%) was attained with 9 mol% of CaO catalyst loading, 3:1 molar ratio of (DMC:C.Gly) at 70 °C for 90 min. The yield of GC was observed to rise with all the reaction parameters till the optimum conditions obtained. Moreover, the yield of GC obtained from ultrasonic-assisted was compared with the conventional-heating method done in the previous study. It was noticeable that the yield of GC obtained via ultrasonic-assisted was found to be 51.44% better than conventional-heating transesterification. In conclusion, the production of GC via ultrasonic-assisted transesterification shows better feasibility than that of the conventional-heating method.

1. Introduction
Glycerol also known as 1,2,3-propanetriol and it is widely applied in pharmaceutical, cosmetics, food and chemical industries. Glycerol can be produced as a by-product from transesterification reaction in biodiesel industry as well as hydrolysis and saponification in oleochemical industry. The tremendous development and oversupply in biodiesel and oleochemical production has led to the rising of crude glycerol (C.Gly), a by-product from biodiesel and oleochemical industries.[1]. Therefore, to address these circumstances, transforming C.Gly into marketable and value-added chemical products is necessary. Glycerol can be converted into valuable glycerol derivatives by steam forming, dehydration, oxidation, carboxylation, hydrogenolysis and chlorination. Glyceric acid, acrolein, epichlorohydrine, propanediols and glycerol carbonate (GC) are some important chemicals that derived from glycerol [2]. Glycerol carbonate is one of the most notable derivatives of glycerol due to its physicochemical properties such as high boiling point, notable chemical reactivity, low toxicity, biodegradable, slight viscosity and low flammability [3,4]. Moreover, GC has been extensively used as protic solvent and
additives in polymers and resins [4], a membrane component for gas-separation [5], surfactants [6], curing agent for concrete, electrolytes component in lithium-ion batteries [7], bio-lubricants and as solvent in cosmetics [8]. GC is a promising precursor for synthesis of valuable chemicals and a potential substitute for petroleum derivatives, such as ethylene carbonate or propylene carbonate.

The production of GC using glycerol can be obtained from several reactions pathway such as (i) carboxylation with CO$_2$ [9], (ii) glycerolysis with urea [10], (iii) phosgenation with phosgene [11] and (iv) transesterification with carbonation source (i.e. alkylene and dialkyl carbonate) [3]. Production of GC via catalytic transesterification of glycerol with dimethyl carbonate (DMC) is mostly preferred over other reactions. Since, the by-product (methanol) from transesterification between glycerol and DMC is recovered, recycled and reused as a reactant for other processes like biodiesel production. Meanwhile, the by-product (glycerol) obtained from biodiesel production could be reused as the feedstock for GC synthesis. In another words, this reaction not only offers a close ended process but providing more feasibility and sustainable platforms with economic merits for industrial production apart from its mild operating conditions, non-corrosive, having excellent solvent properties and produced higher GC yield [11–13]. The yield of GC is also governed by the synthesis techniques, choice of catalyst use and reaction parameters.

Heterogeneous, homogeneous and enzymatic catalysts have reportedly been used for catalytic transesterification of GC [14,15]. The typical transesterification for GC production were mainly catalyzed by homogeneous base catalysts such as zeolites, alkaline earth metal oxide, mixed metal oxide derived from hydrotalcite [16]. Heterogeneous catalysts are more favorable than that of homogeneous catalysts due to its recovery, reusability, economical and high catalytic activity. Calcium oxide (CaO) has gained much attention owing to it has relatively high basic strength [17] and it is an environment-friendly catalyst. It is derived from low cost raw materials such as limestone, calcium hydroxide and calcium carbonate [18]. Numerous studies have been reported that CaO is one of the suitable catalysts to synthesize GC via catalytic transesterification [17–21].

Conventionally, transesterification of glycerol with DMC to synthesize GC using typical catalysts namely acid or base happens to be in immiscible phases of the reactants. It is important to maximize the interfacial surface area across the two or more immiscible phases in order to enhance the overall reaction rate. The conventional mechanical agitation technology is one of the processes that has the potential improve the mass transfer and interfacial surface area of the reactants in the reaction. Besides, advances in ultrasonication have been reported that it has the potential to enhance both chemical reactions and mass transfer in a shorter reaction time [22]. The fluid flows in a parallel direction similar with the propagation of ultrasound waves when energy of the ultrasound is applied in the liquid medium. Acoustic streaming referred to as a uniform flow induced by the absorption of acoustic energy during the passage of acoustic waves [23]. This acoustic streaming flow creates pressure-gradient difference resulting from the attenuated from the sound and this pressure gradient difference generates a circumstance including the sequential formation, growth and instantaneously imposive collapse of the cavitation of the bubbles in a liquid medium. This phenomenon results in generate local hot spot fields with enormous temperatures and pressures [24] with a lifespan of few microseconds [25]. These extreme conditions can lead to physical and chemical effects emerge at local positions of the solution in a reactor. In addition, the formation and/or collapse of the cavitation bubbles lead to the formation of physical effects, namely shockwaves, microstreaming and microjets [26]. These effects contribute in enhancing the effectiveness of mixing of solution [27], disrupting the immiscible liquid media and boosting mass transfer by disrupting the solid-liquid interface and liquid-liquid interface boundary layers.

Thus, ultrasound is a versatile, sustainable and promising environmentally friendly and sustainable technology [28] that has been extensively applied in engineering, material science, chemical, food and medicine industries [26]. Ultrasound has been applied in various divisions of a chemical process: (i) as separation of compounds [29], (ii) decompose chemical species, (iii) enhance chemical reaction rate [30], (iv) modify physical or/and chemical properties of a material [31], or (v) to identify and analyse the compounds [32]. Moreover, ultrasound is used in degassing, emulsification and filtration where these processes are required in the food industry.
To the best of our knowledge, C.Gly has not been studied in GC synthesis via ultrasound-assisted CaO catalytic transesterification. Therefore, this work is to study the effect of ultrasound on the synthesis of GC by transesterification of C.Gly and DMC using CaO catalyst. The aims of this study is to explore the effects of ultrasonic irradiation on synthesis of GC with various reaction parameters such as reaction time and temperature, molar ratio of reactants and CaO catalyst loading, analysis was mainly carried out by using gas chromatography.

2. Materials and methods

2.1. Materials
Crude glycerol (C.Gly) was obtained from a local biodiesel production plant located in Carey Island, Selangor, Malaysia and was used directly without further purification. The chemicals used in this study were glycerol carbonate standard (GC, Fisher Scientific), dimethyl carbonate (DMC, 99%, Merck), ethyl alcohol (Merck), calcium oxide (CaO, 95%, System®.), glycerol (99%, R&M Chemicals), sodium hydroxide (NaOH, R&M Chemicals), ortho-phosphoric acid (H₃PO₄, 85%, Fisher Scientific). All purchased chemicals were analytical grade.

2.2. Synthesis of glycerol carbonate
A schematic diagram of the experimental setup was illustrated in figure 1. The transesterification experiments were performed using a 250 mL screw cap flask with a diameter and height of 60 mm and 135 mm, respectively. CaO was used as the catalyst and was calcined at 900 °C for 12 hours in a furnace. The screw cap flask was initially loaded with the corresponding amount of C.Gly, DMC and calcined CaO, depending on the case. The reactants were pre-mixed at a stirring speed of 1000 rpm with a magnetic stirrer for 15 minutes at room temperature. The screw cap flask was placed above a pre-heated (desired reaction temperature) ultrasonic water bath (Elmasonic S 180 (H), power rating at 1000 W and ultrasonic frequency of 37 kHz). The reaction temperature, reaction time, molar ratio of (DMC:C.Gly) and catalyst loading ranges employed is depicted in table 1. Upon completion of the reaction, the mixture was immediately cooled to room temperature in order to halt the reaction. Subsequently, the mixture was filtered using a syringe filter (0.45 µm) to remove the used catalyst. Later, the product mixture was subjected to evaporation at 90 °C to eliminate the unreacted DMC and methanol as by-product. Finally, the product was analysed using gas chromatography (Model: GC-2010 Plus; Brand: Shimadzu Japan) equipped with flame ionization detector, a capillary column (Forte GC BPX-5: 30 m × 0.25 mm × 0.25 µm) and helium gas was used as the carrier gas. Effects of the reaction parameters conversion C.Gly and yield of GC were analysed using external standard method. Ethyl alcohol was added into the product sample. Subsequently, the result obtained was used to determine the C.Gly conversion and GC yield by the following equation (1) and equation (2) [33,34]. A plausible CaO-catalysed transesterification mechanism is depicted in scheme 1.

\[
Conversion (%) = \frac{C.Gly_{initial~mole} - C.Gly_{final~mole}}{C.Gly_{initial~mole}} \times 100\% \tag{1}
\]

\[
Yield (%) = \frac{GC_{mole}}{C.Gly_{initial~mole}} \times 100\% \tag{2}
\]
Figure 1. Experimental set-up for the ultrasonic assisted transesterification reaction.

Table 1. The experimental parameters and ranges in this work.

| Operating Parameter | Operating Parameter Range |
|---------------------|---------------------------|
| 1. Reaction temperature, (°C) | 50-85 |
| 2. Reaction time, (mins) | 15-120 |
| 3. Molar ratio of (DMC: C.Gly) | 1-5 |
| 4. Catalyst loading, (mol%) | 3-15 |

Scheme 1. A plausible CaO-catalysed transesterification mechanism.
2.3. Crude glycerol characterization methods

2.3.1. **UV-Vis spectroscopy.** The colour of C.Gly sample was determined by using a UV-Vis Spectrophotometer (HACH-DR6000™). Approximately 1 g of C.Gly sample was dissolved with 20 mL of deionized water. The absorbance value of C.Gly sample solution was recorded between the wavelength of 200 nm to 800 nm.

2.3.2. **Density.** Density of C.Gly sample was determined by using a density determining kit (Precisa). A beaker containing 450 mL of water and placed on the platform of the density determining kit. A cup together with a stopper for sample with density < 1 g/cm$^3$ was suspended on a holder. The C.Gly sample was placed on the cup and the mass of C.Gly sample was weighed in air and recorded. The weight of C.Gly sample was submerged in the filled beaker was recorded.

2.3.3. **pH.** Prior to pH measurement, a pH meter (Eutech Instruments PC 2700) was calibrated using buffer solutions with of pH 4, 7 and 10. Subsequently, the pH value was recorded by dissolving 1 g of C.Gly sample in 50 mL of deionized water.

2.3.4. **Viscosity.** Viscosity of C.Gly was measured using a Rheometer (TA Instruments-Discovery Hybrid Rheometer). The accessory (plate SST ST 40mm SMART-SWAP) was placed on bearing of the Rheometer and the accessory was perpendicularly aligned with the bearing. The temperature of the Rheometer was set at 40 °C. Appropriate amount of sample was placed on bottom platform and the accessory was adjusted until it compresses the sample. Finally, the viscosity value of sample was obtained.

2.3.5. **Alkalinity.** Alkalinity number of C.Gly sample was calculated according to ASTM D 4662-08 as shown in equation (3).

\[
\text{Alkalinity number, (mgNaOH/g)} = \frac{[(B-A) \times 39.997N]}{W}
\]

where:
- B: NaOH solution required for titration of the blank (mL)
- A: NaOH solution required for titration of the sample (mL)
- N: normality of the NaOH solution (N)
- W: weight of sample consumed (g)

2.3.6. **Glycerol Content.** Glycerol content from C.Gly was analysed using gas chromatography (Model: GC-2010 Plus; Brand: Shimadzu, Japan) equipped with a flame ionization detector (FID) and a capillary column (Model: Forte-BPX-5; 30 m x 0.25 mm x 0.25 μm). The operating conditions for sample analysis were reported in previous work [35].

2.3.7. **Ash content.** The ash content of C.Gly was determined according to ISO 2098-1972. Approximately 1 g of C.Gly sample was placed in a crucible. The ashing was done in a chamber furnace at 750 °C for 3 hours.

2.3.8. **Methanol content.** Methanol content from C.Gly was determined using a rotary evaporator (BUCHI). Approximately 1 g (W$_1$) of C.Gly was placed into a round bottle neck flask and clipped onto the rotary evaporator. The presence of methanol (W$_2$) in the C.Gly was evaporated under vacuum in a water bath at 60 °C. Methanol content in C.Gly was calculated based on equation (4):
\[
\text{Methanol content (} \% \text{ w/w)} = \left( \frac{W_2}{W_1} \right) \times 100\% \quad (4)
\]

2.3.9. Water content. Approximately 1 g \((W_3)\) of C.Gly was heated at 105 °C until a consistent weight of C.Gly \((W_4)\) is obtained. The weight loss of the sample during the heating process was referred to the evaporation of methanol and water. The total of water and methanol content \((W_5)\) was calculated using equation (5) and the water content was calculated based on equation (6):

\[
W_5 (\% \text{ w/w}) = \left( \frac{W_3 - W_4}{W_5} \right) \times 100\% \quad (5)
\]

\[
\text{Water content (} \% \text{ w/w)} = W_5 - \text{Methanol content} \quad (6)
\]

2.3.10. Soap Content. Approximately 15 g of C.Gly was weighed; the initial pH value of the C.Gly was adjusted to pH 1 using 85% of ortho-phosphoric acid \((H_3PO_4)\) at constant stirring speed for at least an hour. Upon reaching the desired pH, the solution was left at room temperature for 12 hours until two layers of solution was observed. The top layer which was free fatty acid (FFA) was collected and weighed. Soap content was determined according to the following equation (7) [36]:

\[
\text{Soap content} = \frac{304 \times \text{mass of FFA}_g}{282} \times 100\% \quad (7)
\]

Where average soap molar mass = 304; average FFA molar mass = 282

3. Results and discussion

3.1. Characterization of C.Gly

The C.Gly obtained from biodiesel production plant was characterized and the presence of impurities were presented in table 2. The physical appearance of C.Gly is in dark brown soft solid, which depicted in table 2. The C.Gly has a pH value of pH 12, it with density of 1.20 g/mL and viscosity of 48.45 Pa.s. It was observed that, C.Gly consists 71.21% of glycerol content, with high moisture content at 16.01%, ash content at 2.76%, soap content at 3.60% and matter organic non-glycerol (MONG) at 10.02%. As shown in figure 2, the UV-Vis spectroscopy result shows that C.Gly has greater absorbance of radiation and minimum transparency that led to a lower transmittance taking into the account the presence of impurities in C.Gly. Moreover, the dark brownish appearance of C.Gly can be observed through naked eye.

| Table 2. Characteristics of crude glycerol. |
|---------------------------------------------|
| **Properties** | **Crude glycerol** |
| Appearance | Dark brown soft solid |
| Density (at 21°C, g/mL) | 1.20 |
3.2. Effect of reaction temperature

Ultrasound reaction temperature is one of the critical parameters for transesterification of glycerol with DMC as this reaction is reversible. This phenomenon explains that transesterification of glycerol is an endothermic reaction [37]. The equilibrium of the reaction follows the Le Chatelier’s principle, a raise of reaction temperature in a system would gradually increase the substrate consumption, which promote the reaction equilibrium to shift towards forward direction and eventually increase the product formation. Hence, transesterification of C.Gly is thermodynamically favorable for GC synthesis [38]. In the transesterification of hydrophilic C.Gly and hydrophobic DMC, both of the reactants are immiscible. Solid base catalyst such as CaO added into the mixture of C.Gly and DMC leads to formation of three-phases. At low reaction temperature, the existence of three-phases leads to a slow diffusion and limited mass transfer rate of reaction. Therefore, a high reaction temperature of a system is required to increase the average kinetic energy of its constituent particles among reactant molecules. As kinetic energy increases, the effective collisions among particles increases and this encourage effective mixing in the bulk solution, eventually increase the reaction rate. The effect of reaction temperature for transesterification reaction was investigated with CaO as catalyst in the range of 50-85 °C. Figure 3
illustrates the effect of various temperature on C.Gly conversion and GC yield using molar ratio of (DMC:C.Gly) at 3:1, catalyst loading of 9 mol% at 90 min. At 50 °C, the conversion of C.Gly and yield of GC attained were 38.96 and 7.45%, respectively and this shows that low reaction rate at low reaction temperature. The conversion of C.Gly and yield of GC increases drastically from 50 °C to 70 °C and the yield of GC decreased slightly with further increased of the reaction temperature beyond 80 °C. The highest yield of 95.41% of GC was achieved at 70 °C. These results indicated that, as temperature increases, the number of oscillating bubbles increases. Thus, leads to more energy collision among the molecules and reduce the viscosity of mixture [12] in which overcome the immiscibility problem between C.Gly and DMC. As a result, high temperature promotes the interaction between the reactants molecules and catalyst consequently speed up the reaction rate.

![Figure 3](image)

**Figure 3.** Effect of reaction temperature on GC synthesis via ultrasonic assisted transesterification reaction of C.Gly with DMC with the presence of CaO. Operating conditions: amount of C.Gly = 0.1 mol, time = 90 mins, molar ratio of (DMC:C.Gly) = 3:1 and catalyst loading = 9 mol%.

### 3.3. Effect of reaction time

The ultrasonic irradiation time in the reaction was evaluated for the production of GC from C.Gly and DMC with the presence of CaO. Both reactants are immiscible therefore a longer reaction time was required to overcome mass transfer resistance. By employing ultrasound technique, lesser reaction time is required to achieve higher yield of product since ultrasonic irradiation has the capability to overcome mass transfer barrier [39]. Figure 4 revealed that the effect of reaction time between from 15 min to 120 min for transesterification of C.Gly with DMC while maintaining all other operating parameters constant. Reaction time at 15 min, the conversion of C.Gly was 96.74%. However, low yield of GC was obtained at 20.87%. This could possibly due to insufficient of reaction time between C.Gly and DMC to shift forward and to achieve equilibrium in the reaction. The yield of GC was significantly increased from 15 min to 90 min and the highest yield of GC was obtained at 95.41% with reaction time of 90 min. However, prolonged reaction time beyond 90 min did not affect the conversion of C.Gly but had resulted in decreased of GC yield. This may possibly due to the effect of solubility of the by-product, methanol in the reaction mixture and the possibility of methanol-DMC azeotrope formation [40] in the reaction.
Figure 4. Effect of reaction time on GC synthesis via ultrasonic assisted transesterification reaction of C.Gly with DMC with the presence of CaO. Operating conditions: amount of C.Gly = 0.1 mol, temperature = 70 °C, molar ratio of (DMC:C.Gly) = 3:1 and catalyst loading = 9 mol%.

3.4. Effect of DMC to C.GLY molar ratio
The reaction rate of transesterification can be influenced by varying the molar ratio of reactants. Theoretically, an equal molar of glycerol and carbonate source is required to synthesize 1 mol of GC and 2 mol of by-product, methanol. The effect of molar ratio for DMC to C.Gly was investigated under ultrasonic irradiation with catalyst loading of 9 mol% at 70 °C for 90 min. As illustrated in figure 5, low C.Gly conversion of 33.88% and GC yield of 23.37% were obtained when equimolar of C.Gly and DMC was employed in the reaction. This observation is similar with the findings reported by Li and Wang [20], showing a low yield of GC was obtained when equimolar of reactants was employed in the reaction. This result implied that, using equimolar reactants is insufficient for transesterification reaction to shift the equilibrium to proceed forward by converting C.Gly to GC. Moreover, strong preferential adsorption of C.Gly towards active sites of CaO catalyst due to the polar protic structure in C.Gly material, which resulting in lesser conversion at equimolar of DMC:C.Gly ratio. The maximum yield of GC attained was 95.41% with (DMC:C.Gly) molar ratio of 3:1. As mentioned earlier, C.Gly and DMC reactants are immiscible in the reaction. Excessive molar ratio of alkyl carbonate is required to overcome the immiscibility problem during the reaction. Moreover, the transesterification of C.Gly with DMC is a reversible nature reaction, it is necessary to utilize excess DMC in the reaction to shift positively the chemical equilibrium towards the greater GC production [41,42]. Based on the Le Chatelier’s principle, adding extra amount of reactant, in this case is DMC, to the transesterification reaction will shift the position of equilibrium toward formation of GC as showed in scheme 2, this phenomenon enhanced the C.Gly conversion to produce GC and methanol. However, further increase with molar ratio of (DMC:C.Gly) beyond 3:1 has an adverse effect towards the GC yield where the yield of GC decreased to 39.09% and 30.43% at molar ratio of 4:1 and 5:1, respectively. The rapid drop of GC yield probably due to C.Gly as the limiting reactant. The concentration of C.Gly decreases with the increasing molar ratio of (DMC:C.Gly) and subsequently led to low reaction rate [17]. There was no improvement in conversion of C.Gly with further addition of (DMC:C.Gly) molar ratio beyond 4:1. This result is
attributed to the dilution of C.Gly with DMC. Dilution of C.Gly in the reaction gave rise to the lowering of collision frequency between the C.Gly molecules, DMC molecules and molecules of CaO and eventually led to decrease in reaction rate. Moreover, as molar ratio of (DMC:C.Gly) increases, the ultrasonic energy per unit volume of the mixture decreases and lead to lesser formation of local hot spot fields with high temperature. Based on figure 5, this study proved that the optimum molar ratio of (DMC:C.Gly) for GC synthesize was attained at 3:1.

![Graph showing conversion and yield vs molar ratio of (DMC:C.Gly)](image)

**Figure 5.** Effect of molar ratio of (DMC:C.Gly) on GC synthesis via ultrasonic assisted transesterification reaction of C.Gly with DMC with the presence of CaO. Operating conditions: amount of C.Gly = 0.1 mol, temperature = 70 °C, time = 90 mins and catalyst loading = 9 mol%.

**Scheme 2.** Synthesis of GC via transesterification of crude glycerol and dimethyl carbonate [35].

3.5. **Effect of catalyst loading**

Catalyst of CaO is a controversial basic catalyst that has capability of abstracting a proton from the primary hydroxyl group from C.Gly. Thus, CaO was nominated as catalyst in this study. The catalyst of CaO used in this study was prior calcined to minimize the presence hydroxyl group’s in CaO and to enhance the catalyst activity. The effect of catalyst loading ranged between 3 mol% to 15 mol% under ultrasonic irradiation was investigated with (DMC:C.Gly) molar ratio of 3:1 at 70 °C for 90 min (figure 6). The increased in catalyst loading, significantly increases the conversion of C.Gly and in GC yield. However, the conversion of C.Gly and yield of GC were remained almost constant when catalyst loading beyond 9 mol%. This is due to more vacant and available active site of CaO per glycerol molecule and...
the high amount active site of CaO would promote the effective collision between the reactants and catalyst to increase the reaction rate. The enhancement in conversion of C.Gly and yield of GC is closely related to the existence of catalyst particles at an optimum loading in the sonochemical reaction, where the optimum catalyst loading boosted the cavitation activity by ultrasonic irradiation. Conversely, further increased in catalyst loading beyond 9 mol%, a slight decline in the yield was noticed. This is attributed to the high loading of CaO particles which causes the limitation of mass transfer from the bulk to the active sites of catalyst and eventually induce particles agglomeration [43] and sedimentation [44] during the reaction. Furthermore, high loading of catalyst would cause deactivation of catalyst by collision with ground state molecules of catalyst [45]. The optimum CaO loading of 9 mol% gave the highest yield of GC which was attained at 95.41%.

**Figure 6.** Effect of catalyst loading on GC synthesis via ultrasonic assisted transesterification reaction of C.Gly with DMC with the presence of CaO. Operating conditions: amount of C.Gly = 0.1 mol, temperature = 70 °C, time = 90 mins and molar ratio of (DMC:C.Gly) = 3:1.

3.6. **Comparison of conventional-heating transesterification and ultrasonic-assisted transesterification**

In previous study, conventional-heating assisted transesterification of C.Gly was conducted under conditions at 70 °C, molar ratio of (DMC:C.Gly) at 3:1 and 9 mol% of CaO for 90 min [35]. A comparison between conventional-heating and ultrasonic-assisted transesterification on conversion and yield were presented in table 3. Ultrasonic and conventional-heating methods were performed under the same reaction conditions and the results in table 3 shows that ultrasonic-assisted transesterification of C.Gly with DMC showed that higher yield of GC was attained at 95.41% than that of the conventional-heating method which the maximum yield of 63%. The yield of GC synthesized using ultrasonic-assisted method was found to be 51.44% better as compared to conventional-heating method. The transesterification reaction rate is closely associated with the value of activation energy. Theoretically, the lower the activation energy, the faster the reaction rate. Ultrasonic irradiation has the potential in enhancing the mass transfer characteristics for transesterification of C.Gly with reduction of activation energy, than that of mechanically stirring systems. Furthermore, ultrasonic technology has a beneficial impact, it produces fine emulsion between the non-miscible phases of the reactants. As a result, the interfacial area between the phases improves markedly, leading more kinetics reaction in the
heterogeneously catalyzed transesterification reaction. As shown in table 3, optimization study on conventional-heating method was also conducted in previous study [35], the yield of GC attained was 79% with (DMC:C.Gly) molar ratio at 3 and catalyst loading of 8.35 mol% at 80 °C for 105 min. In view of this study, the ultrasonic-assisted transesterification of C.Gly with DMC gave better performance than that of conventional heating. Higher GC yield was attained at 95.41% with a shorter reaction time and lower reaction temperature as compared to conventional-heating method at optimum condition.

Table 3. The comparison of conversion C.Gly, GC yield, selectivity in conventional transesterification and ultrasonic-assisted transesterification of industrial C.Gly.

| Method                | Grade of glycerol | Conversion of C.Gly (%) | Yield of GC (%) | Reference |
|-----------------------|-------------------|--------------------------|-----------------|-----------|
| Conventional-heatinga| Crude             | 94.6                     | 63.0            | [35]      |
| Conventional-heatingb| Crude             | 97.3                     | 79.2            | [35]      |
| Ultrasonic irradiationa| Crude             | 96.19                    | 95.41           | current work |

* Operating conditions: reaction temperature = 70 °C, reaction time = 90 min, molar ratio of (DMC:C.Gly) = 3:1 and catalyst loading 9 mol%

b Operating conditions (Optimization): reaction temperature = 80 °C, reaction time = 105 min, molar ratio of (DMC:C.Gly) = 3:1 and catalyst loading 8.35 mol%

4. Conclusion
The present study rendered an environmentally friendly route for transesterification of C.Gly using DMC. Moreover, the study has shown that C.Gly can be used directly without further pre-treatment to synthesis GC via transesterification reaction. The influence of critical parameters such as reaction temperature, reaction time, molar ratio of (DMC:C.Gly) and catalyst loading to transesterification were studied. The results showed that ultrasonic irradiation transesterification of C.Gly shows positive effect towards conversion of C.Gly and yield of GC. The maximum C.Gly conversion and GC yield achieved were at 96.19% and 95.41%, respectively under operating conditions: reaction temperature at 70 °C, reaction time at 90 min, molar ratio of (DMC:C.Gly) at 3 and 9 mol% of CaO. Ultrasonic favors the transesterification reaction since the yield of GC was higher in ultrasonic-assisted method as compared to conventional-heating method. Ultrasonic irradiation is more energy efficient due to shorter reaction time and high GC yield attained. Hence, ultrasonic-assisted transesterification is suitable to valorize the surplus C.Gly to synthesize GC.

Acknowledgement
The authors acknowledged the research grant (IPSR/RMC/UTARRF/2019-C1/L09) provided by the Universiti Tunku Abdul Rahman, Postgraduate Research Grant Scheme. The authors wish to express their gratitude to the Sime Darby Biodiesel Sdn. Bhd. through their generosity by sponsoring industrial grade crude glycerol in this work.

References
[1] Rodrigues A, Bordado J C and Santos R G dos 2017 Upgrading the Glycerol from Biodiesel Production as a Source of Energy Carriers and Chemicals—A Technological Review for Three Chemical Pathways Energies 10 18171–36
[2] Konwar L J, Mikkola J-P, Bordoloi N, Saikia R, Chutia R S and Kataki R 2018 Sidestreams From Bioenergy and Biorefinery Complexes as a Resource for Circular Bioeconomy Waste
Biorefinery (Elsevier) pp 85–125

[3] Wu Y, Song X, Cai F and Xiao G 2017 Synthesis of glycerol carbonate from glycerol and diethyl carbonate over Ce-NiO catalyst: The role of multiphase Ni. J. Alloys Compd. 720 360–8

[4] Wang D, Zhang X, Cong X, Liu S and Zhou D 2018 Influence of Zr on the performance of Mg-Al catalysts via hydrotalcite-like precursors for the synthesis of glycerol carbonate from urea and glycerol. Appl. Catal. A Gen. 555 36–46

[5] Wang S, Hao P, Li S, Zhang A, Guan Y and Zhang L 2017 Synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by calcined silicates. Appl. Catal. A Gen. 542 174–81

[6] Granados-Reyes J, Salagre P and Cesteros Y 2017 Effect of the preparation conditions on the catalytic activity of calcined Ca-Al layered double hydroxides for the synthesis of glycerol carbonate. Appl. Catal. A Gen. 536 9–17

[7] Wang J, Yong T, Yang J, Ouyang C and Zhang L 2015 Organosilicon functionalized glycerol carbonates as electrolytes for lithium-ion batteries. RSC Adv. 5 17660–6

[8] Shikhaliyev K, Okoye P U and Hameed B H 2018 Transesterification of biodiesel byproduct glycerol and dimethyl carbonate over porous biochar derived from pyrolysis of fishery waste. Energy Convers. Manag. 165 794–800

[9] Razali N A, Conte M and McGregor J 2019 The role of impurities in the La2O3 catalysed carboxylation of crude glycerol. Catal. Letters 149 1403–14

[10] Nguyen-Phu H, Park C and Shin E W 2018 Dual catalysis over ZnAl mixed oxides in the glycerolysis of urea: Homogeneous and heterogeneous reaction routes. Appl. Catal. A Gen. 552 1–10

[11] Algoufi Y T, Kabir G and Hameed B H 2017 Synthesis of glycerol carbonate from biodiesel by-product glycerol over calcined dolomite. J. Taiwan Inst. Chem. Eng. 70 179–87

[12] Lanjekar K and Rathod V K 2013 Utilization of glycerol for the production of glycerol carbonate through greener route. Biochem. Pharmacol. 1 1231–6

[13] Syamsuddin Y and Hameed B H 2016 Synthesis of glycerol free-fatty acid methyl esters from Jatropha oil over Ca−La mixed-oxide catalyst. J. Taiwan Inst. Chem. Eng. 58 181–8

[14] Parameswaram G, Rao P S N, Srivani A, Rao G N and Lingaiah N 2018 Magnesia-ceria mixed oxide catalysts for the selective transesterification of glycerol to glycerol carbonate. Mol. Catal. 451 135–42

[15] Liu Z, Wang J, Kang M, Yin N, Wang X, Tan Y and Zhu Y 2015 Structure-activity correlations of LiNO3/Mg4AlO5.5 catalysts for glycerol carbonate synthesis from glycerol and dimethyl carbonate. J. Ind. Eng. Chem. 21 394–9

[16] Silva L L, Alkimim I P, Meneghetti S M. and Cardoso D 2019 Catalytic evaluation of MCM-41 hybrid silicas in the transesterification reactions. Microporous Mesoporous Mater. 284 265–75

[17] Ochoa-Gómez J R, Gómez-Jiménez-Aberasturi O, Maestro-Madurga B, Pesquera-Rodríguez A, Ramírez-López C, Lorenzo-Ibarreta L, Torrecilla-Soria J and Villarán-Velasco M C 2009 Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification: Catalyst screening and reaction optimization. Appl. Catal. A Gen. 366 315–24

[18] Roschat W, Phewphong S, Kaewpuang T and Promarak V 2018 Synthesis of glycerol carbonate from transesterification of glycerol with dimethyl carbonate catalyzed by CaO from natural sources as green and economical catalyst. Mater. Today Proc. 5 13909–15

[19] Lu P, Wang H and Hu K 2013 Synthesis of glycerol carbonate from glycerol and dimethyl carbonate over the extruded CaO-based catalyst. Chem. Eng. J. 228 147–54

[20] Li J and Wang T 2010 Coupling reaction and azeotropic distillation for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. Chem. Eng. Process. Process Intensif. 49 530–5

[21] de Caro P, Bandres M, Urrutigoity M, Cecutti C and Thiebaud-Roux S 2019 Recent Progress in Synthesis of Glycerol Carbonate and Evaluation of Its Plasticizing Properties. Front. Chem. 7
[22] Gude V G 2015 Synergism of microwaves and ultrasound for advanced biorefineries Resour. Technol. 1 116–25
[23] Sajjadi B, Ashgarzadehahmadi S, Asaithambi P, Raman A A A and Parthasarathy R 2017 Investigation of mass transfer intensification under power ultrasound irradiation using 3D computational simulation: A comparative analysis Ultrason. Sonochem. 34 504–18
[24] Kojima Y, Takayasu M, Toma M and Koda S 2019 Degradation of cellulose in NaOH and NaOH/urea aqueous solutions by ultrasonic irradiation Ultrason. Sonochem. 51 419–23
[25] Safarifard V and Morsali A 2012 Sonochemical syntheses of a nanoparticles cadmium(II) supramolecule as a precursor for the synthesis of cadmium(II) oxide nanoparticles Ultrason. Sonochem. 19 1227–33
[26] Chemat F, Rombaut N, Sicai A G, Meullemiestre A, Fabiano-Tixier A S and Abert-Vian M 2017 Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review Ultrason. Sonochem. 34 540–60
[27] Poosumas J, Ngaosuwan K, Quitain A T and Assabumrungrat S 2016 Role of ultrasonic irradiation on transesterification of palm oil using calcium oxide as a solid base catalyst Energy Convers. Manag. 120 62–70
[28] Yüceer M and Caner C 2018 Ultrasound ; a Novel and Innovative Processing Method for Egg and Egg Products Preservation Keywords : Introduction J. Chem. Biol. Pharm. Chem. 1 3–5
[29] Trojanowska A, Tsibranska I, Dzhonova D, Wróbklewska M, Haponska M, Jovancic P, Marturano V and Tylkowski B 2019 Ultrasound-assisted extraction of biologically active compounds and their successive concentration by using membrane processes Chem. Eng. Res. Des. 147 378–89
[30] Marimuthu E and Murugesan V 2017 Ultrasonic condition boosts up the rate of phase transfer catalyzed polymerization of acrylonitrile in two-phase system Appl. Petrochemical Res. 7 85–96
[31] Kojima Y, Imazu H and Nishida K 2014 Physical and chemical characteristics of ultrasonically-prepared water-in-diesel fuel: Effects of ultrasonic horn position and water content Ultrason. Sonochem. 21 722–8
[32] Figueiredo M K K, Costa-Felix R P B, Maggi L E, Alvarenga A V. and Romeiro G A 2012 Biofuel ethanol adulteration detection using an ultrasonic measurement method Fuel 91 209–12
[33] Ishak Z I, Sairi N A, Alias Y, Aroua M K T and Yusoff R 2016 Production of glycerol carbonate from glycerol with aid of ionic liquid as catalyst Chem. Eng. J. 297 128–38
[34] Teng W K, Ngoh G C, Yusoff R and Aroua M K 2016 Microwave-assisted transesterification of industrial grade crude glycerol for the production of glycerol carbonate Chem. Eng. J. 284 469–77
[35] Tan C Y, Leong S Y and Lo P K 2018 Direct use of crude glycerol in synthesis of glycerol carbonate via transesterification AIP Conference Proceedings vol 2020 p 020063
[36] Chen J, Yan S, Zhang X, Tyagi R D, Surampalli R Y and Valéro J R 2018 Chemical and biological conversion of crude glycerol derived from waste cooking oil to biodiesel Waste Manag. 71 164–75
[37] Praikaw E, Kiatkittipong W, Kiatkittipong K, Laosiripojana N, Viriya-empikul N, Boonyasuwat S, Aiouache F, Najdanovic V and Assabumrungrat S 2018 Synthesis of glycerol carbonate from dimethyl carbonate and glycerol using CaO derived from eggshells MATEC Web Conf. 192 03045
[38] Li J and Wang T 2011 Chemical equilibrium of glycerol carbonate synthesis from glycerol J. Chem. Thermodyn. 43 731–6
[39] Islam A, Taufiq-Yap Y H, Chan E, Moniruzzaman M, Islam S and Nabi M N 2014 Advances in solid-catalytic and non-catalytic technologies for biodiesel production Energy Convers. Manag. 88 1200–18
[40] Okoye P U, Abdullah A Z and Hameed B H 2016 Glycerol carbonate synthesis from glycerol and dimethyl carbonate using trisodium phosphate J. Taiwan Inst. Chem. Eng. 68 51–8

[41] Waghmare G V., Vetal M D and Rathod V K 2015 Ultrasound assisted enzyme catalyzed synthesis of glycerol carbonate from glycerol and dimethyl carbonate Ultrason. Sonochem. 22 311–6

[42] Wang S, Wang J, Sun P, Xu L, Okoye P U, Li S, Zhang L, Guo A, Zhang J and Zhang A 2019 Disposable baby diapers waste derived catalyst for synthesizing glycerol carbonate by the transesterification of glycerol with dimethyl carbonate J. Clean. Prod. 211 330–41

[43] Okoye P U, Abdullah A Z and Hameed B H 2017 Stabilized ladle furnace steel slag for glycerol carbonate synthesis via glycerol transesterification reaction with dimethyl carbonate Energy Convers. Manag. 133 477–85

[44] Jamalluddin N A and Abdullah A Z 2011 Reactive dye degradation by combined Fe(III)/TiO$_2$ catalyst and ultrasonic irradiation: Effect of Fe(III) loading and calcination temperature Ultrason. Sonochem. 18 669–78

[45] Zhou M, Yu J, Cheng B and Yu H 2005 Preparation and photocatalytic activity of Fe-doped mesoporous titanium dioxide nanocrystalline photocatalysts Mater. Chem. Phys. 93 159–63