

Article

Process and Energy Intensification of Glycerol Carbonate Production from Glycerol and Dimethyl Carbonate in the Presence of Eggshell-Derived CaO Heterogeneous Catalyst

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Citation: Praikaew, W.; Kiatkittipong, W.; Aiouache, F.; Najdanovic-Visak, V.; Ngaosuwan, K.; Wongsawaeng, D.; Lim, J.W.; Lam, S.S.; Kiatkittipong, K.; Laosiripojana, N.; et al. Process and Energy Intensification of Glycerol Carbonate Production from Glycerol and Dimethyl Carbonate in the Presence of Eggshell-Derived CaO Heterogeneous Catalyst. *Energies* **2021**, *14*, 4249. <https://doi.org/10.3390/en14144249>

Academic Editors: Francis Verpoort and Luca Gonsalvi

Received: 31 May 2021

Accepted: 6 July 2021

Published: 14 July 2021

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Abstract: The process and energy intensifications for the synthesis of glycerol carbonate (GC) from glycerol and dimethyl carbonate (DMC) using an eggshell-derived CaO heterogeneous catalyst were investigated. The transesterification reaction between glycerol and DMC was typically limited by mass transfer because of the immiscible nature of the reactants. By varying the stirring speed, it was observed that the mass transfer limitation could be neglected at 800 rpm. The presence of the CaO solid catalyst made the mass transport-limited reaction process more prominent. Mass transfer intensification using a simple kitchen countertop blender as an alternative to overcome the external mass transfer limitation of a typical magnetic stirrer was demonstrated. A lower amount of the catalyst and a shorter reaction time were required to achieve 93% glycerol conversion or 91% GC yield, and the turnover frequency (TOF) increased almost 5 times from 1.5 to 7.2 min⁻¹ when using a conventional magnetic stirrer and countertop blender, respectively. In addition, using a simple kitchen countertop blender with 7200 rpm, the reaction temperature of 60 °C could be reached within approximately 3 min without the need of a heating unit. This was the result of the self-frictional heat generated by the high-shear blender. This was considered to be heat transfer intensification, as heat was generated locally (in situ), offering a higher homogeneity distribution. Meanwhile, the trend toward energy intensification was promising as the yield efficiency increased from 0.064 to 2.391 g/kJ. A comparison among other process intensification techniques, e.g., microwave reactor, ultrasonic reactor, and reactive distillation was also rationalized.

Keywords: process intensification; glycerol carbonate production; mass and heat transfer; biomass waste derived catalyst; fatty acid methyl ester (FAME)

1. Introduction

Nowadays, biodiesel is an alternative fuel to substitute for fossil fuels. Biodiesel can be produced from the transesterification of vegetable oil or animal fat with alcohol. Biodiesel with a target of 20% blending is expected to increase from 19.8 to 31.1 billion liters in 2020 and 2030, respectively [1]. The rapidly increasing demand for biodiesel has led to a high amount of glycerol, a low-value byproduct. Therefore, the use of glycerol is necessary for the biodiesel industry. There are several pathways to convert glycerol to value-added chemicals such as 1,3-propanediol, epichlorohydrin, glycidol, glycerol carbonate, etc. [2,3].

One of the most promising derivatives of glycerol is glycerol carbonate (GC), which has a market price greater than USD 6000/ton [4]. GC can be incorporated into various types and applications such as solvents, additives, monomers, and chemical intermediates that are highly used in several industries, for example, in detergents, cement, paints and coatings, plastics, etc. GC can be produced from glycerol via different reaction routes including carboxylation with CO₂ [5,6], oxidative carboxylation with CO and O₂ [7,8], phosgenation with phosgene, glycerolysis with urea [9,10], and transesterification with alkyl carbonate or dialkyl carbonate [11–14]. Among these reaction routes, the transesterification of glycerol with dimethyl carbonate (DMC) is an efficient route that is of interest due to its high conversion and selectivity, its reaction occurring at low temperatures, being free of solvent or toxic substances, and the simple separation and purification of the product.

With the ease of catalyst recovery, heterogeneous catalysts are known to improve the transesterification process while avoiding the additional downstream processing costs involved in homogeneous catalysis. Various solid base catalysts such as alkaline earth metal oxides [15], basic zeolites [16], and mixed metal oxides derived from hydrotalcite [17] have shown higher catalytic activity than the acidic catalyst used for the transesterification of glycerol with DMC. CaO, which is low cost and readily available, is one of the most promising catalysts for providing high catalytic activity. Ochoa-Gomez et al. [18] reported that CaO could achieve complete glycerol conversion and a > 95% GC yield in under 1.5 h of reaction time with a reaction temperature of 95 °C, a catalyst/glycerol molar ratio = 0.06, and a DMC/glycerol molar ratio = 3.5. In addition, Algoufi et al. [19] obtained 97% glycerol conversion and a 94% yield of GC at 75 °C for 90 min, a DMC/glycerol molar ratio of 3, and a 6 wt% catalyst dose.

Although the reaction could offer very high glycerol conversion and GC yield, it still required a prolonged reaction time or high catalyst loading due to a slow reaction rate. The reaction between the immiscible reactants of hydrophilic glycerol and a hydrophobic carbonate source, providing two-phase liquid system, and therefore starting with great excess of carbonate source, is necessary in order to increase miscibility and to overcome chemical reaction equilibrium. In addition, as is the nature of the endothermic reaction, the reactor relies largely on an external heat source to achieve the desired reaction temperature. To alleviate/eliminate the above limitations, some researchers have applied intensifying methods such as (1) alternative energy sources including microwave irradiation [20] and ultrasonic irradiation [21]; (2) multifunctional reactors such as coupling reaction and azeotropic distillation [22] and reactive distillation and extractive distillation [23]; and (3) others such as the non-catalytic supercritical process [24] of transesterification between glycerol and DMC.

However, as shown above, there is scarce assessment on the mass transfer intensification on glycerol carbonate production. Mass transfer limitations play a significant influential role in the rate of chemical reactions, especially in the case of this reaction, considering the immiscibility of the reactants and the heterogeneous catalytic system. In our recent work, a household fruit blender was first introduced as simple and low-cost

piece of equipment for biodiesel production from refined palm oil and waste cooking oil catalyzed by a sodium hydroxide homogeneous catalyst [25,26]. The results showed that a high methyl ester yield could be achieved within a very short reaction time and without an external heating source.

In this study, the household blender was used for the first time in a heterogeneous catalytic system. The transesterification between glycerol and DMC for GC production is associated with mass transfer limitations both at the immiscible glycerol–DMC liquid–liquid interface and/or at the solid-phase catalyst. Overcoming these limitations would significantly improve the rate of the reaction. This study elucidates these mass transfer limitations individually and illustrates what and how to eliminate/minimize them. Factors influencing the reaction using the countertop blender were also examined in order to approach the thermodynamic reaction equilibrium within rapid reaction time. Finally, the yield efficiencies among the process intensification technologies for the transesterification of GC production were calculated, summarized, and discussed as well.

2. Materials and Methods

2.1. Chemicals

Experiments were conducted using pure glycerol (purity $\geq 99.5\%$) from Ajax Finechem Ltd. (Taren Point, Australia), dimethyl carbonate (purity $> 99\%$) from Merck (Darmstadt, Germany). Butanol (Sigma Aldrich, Singapore, purity $\geq 99.8\%$) was used as the internal standard, and glycerol carbonate (Sigma Aldrich, Singapore, purity $> 99\%$) was used as a calibration standard for gas chromatography analysis.

2.2. Catalyst Preparation

CaO was derived from waste eggshells, which were initially washed with water several times and dried in an oven at $110\text{ }^{\circ}\text{C}$ overnight. They were then crushed and calcined at $900\text{ }^{\circ}\text{C}$ for 2.5 h under a N_2 atmosphere in order to transform CaCO_3 into CaO.

2.3. Catalyst Characterizations

Thermogravimetric analysis (TGA) analyzed the decomposition of the catalysts under airflow conditions with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from 25 to $1000\text{ }^{\circ}\text{C}$.

An X-ray diffraction (XRD) pattern of the CaO derived from the eggshells was performed to investigate the structure of the crystalline phases. SIEMENS D-5000 XRD of Cu $\text{K}\alpha$ connected with Diffract ZT version 3.3 for full control of the XRD analyzer was employed with a scanning rate of $2^{\circ}/\text{min}$ and recording within the range of 2θ from 10° to 80° .

The BET surface area, pore volume, and pore diameter were measured by the BEL-sorp mini, Japan. The pretreatments of the CaO derived from eggshells were carried out with $50\text{ mL}/\text{min}$ of helium at $180\text{ }^{\circ}\text{C}$ for 3 h.

A scanning electron microscopy (SEM) micrograph was obtained using MX2000s microscopy to observe the morphology of the catalyst.

Temperature programmed desorption of carbon dioxide (CO_2 -TPD) was employed to determine the basic properties of the catalysts. Before CO_2 adsorption, a catalyst (0.1 g) was pretreated under a helium atmosphere at $180\text{ }^{\circ}\text{C}$ for 60 min. After the temperature was reduced to ambient temperature, $30\text{ mL}/\text{min}$ CO_2 was subsequently introduced to the samples for 90 min. The system was flushed with helium for 60 min. CO_2 -TPD was carried out under a helium atmosphere at a flow rate of $30\text{ mL}/\text{min}$. The operating temperature was increased from 50 to $800\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and held at the final temperature for 60 min.

2.4. Evaluation of Catalytic Efficiency

2.4.1. Conventional Process

Conventional transesterification reaction of glycerol with DMC was carried out in a 250 mL three-necked batch reactor equipped with a magnetic stirrer, condenser, and water

bath. In a typical experiment, the initial amount of 46.05 g of glycerol (0.5 moles), 112.6 g of DMC (1.25 moles calculated as 2.5 times the amount of glycerol), the initial CaO catalyst loading based on the initial amount of glycerol of 4.8 wt%, and a reaction temperature of 60 °C were set as a standard condition [27].

2.4.2. Process Intensification Using a Kitchen Countertop Blender

GC synthesis was conducted in a kitchen countertop blender (OTTO brand, model: BE-127A, 1200W, capacity 2 L equipped with 6 stainless steel blades). A variac was employed to adjust the voltage to control the speed of the blender while thermocouple and product sampling tubes made of silicone were submerged into the reaction mixture [26]. The reaction was performed without an external heat source. In a typical experiment, 3 moles of glycerol were loaded with various initial amount of DMC (3–7.5 moles) and catalyst loadings (1.2–4.8 wt% of glycerol).

2.5. Product Analysis

The collected samples were analyzed using a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector and a BP-20WAX capillary column (30 m long, 0.32 mm, 0.5 µm). The oven temperature was initially set at 45 °C, then was increased at 15 °C/min up to 240 °C and was maintained for 30 min. The injector temperature was set at 300 °C in tandem with the detector temperature.

The conversion of glycerol, the yield of GC, the turnover frequency (TOF), and the Reynolds number were determined by following Equations (1)–(4), respectively.

$$\text{Conversion of glycerol (\%)} = \frac{\text{mole of glycerol, initial} - \text{mole of glycerol, final}}{\text{mole of glycerol, initial}} \times 100 \quad (1)$$

$$\text{Yield of glycerol carbonate (\%)} = \frac{\text{mole of GC, produced}}{\text{mole of glycerol, initial}} \times 100 \quad (2)$$

$$\text{TOF (min}^{-1}\text{)} = \frac{\text{mole of GC produced (g)}}{\text{amount of catalyst (g)} \times \text{reaction time (min)}} \quad (3)$$

While Reynolds number (N_{Re}) [26]

$$N_{Re} = \frac{n \times D^2}{\nu} \quad (4)$$

where n = impeller speed (rpm.), D = impeller diameter (m.) as 0.04 and 0.074 m in the case of the magnetic stirrer and the blender, respectively, and ν = kinematic viscosity of the feed mixture at a molar ratio of DMC to glycerol = 2.5 as $4.66 \times 10^{-5} \text{ m}^2/\text{s}$.

2.6. Energy Consumption and Yield Efficiency

Energy consumption is a significant factor to consider the feasibility of the process. Energy consumption was measured by an AC power meter. Yield efficiency, also known as energy efficiency or energy yield efficiency, is a parameter enabling the comparison of the economic competitiveness among various production methods [28]. The yield efficiency (g/kJ) was calculated by following Equation (5).

$$\text{Yield efficiency (g/kJ)} = \frac{\text{Amount of GC produced (g)}}{\text{Power supplied (}\frac{\text{kJ}}{\text{s}}\text{)} \times \text{reaction time (s)}} \quad (5)$$

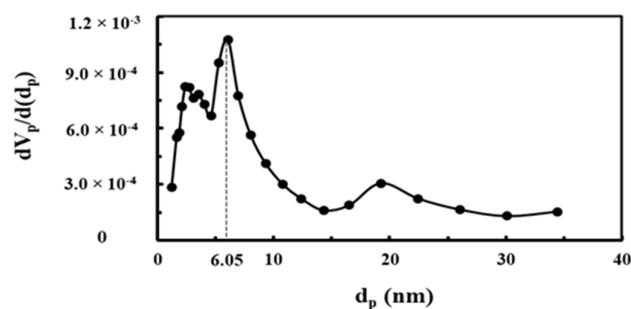
3. Results and Discussion

3.1. Characteristics of Catalyst

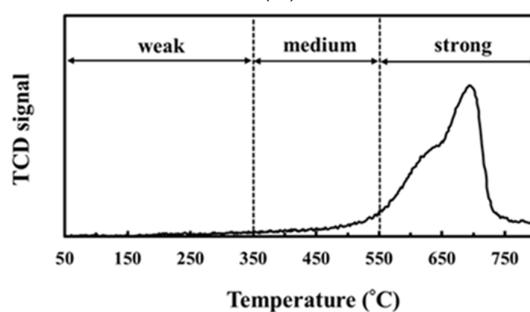
The thermogravimetric analysis (TGA) results of the eggshells exhibited two main weight losses. The first eggshell weight loss occurred at around 300–600 °C due to the decomposition of organic compounds, whereas the other weight loss occurred within the

range of 600–750 °C, resulting from the loss of carbon dioxide from the conversion of CaCO_3 into CaO [29]. This supported the transformation of CaCO_3 to CaO , which could be completed at 900 °C, as confirmed by the XRD pattern [27].

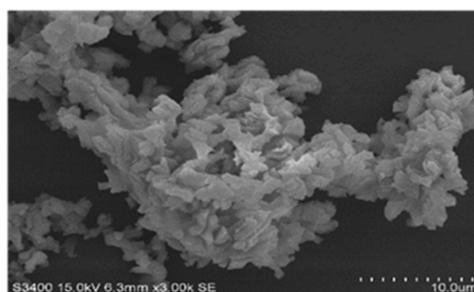
The BET surface area and pore volume were attained at $3.77 \text{ m}^2/\text{g}$ and $0.0115 \text{ cm}^3/\text{g}$, respectively. The pore size distribution of eggshell-derived CaO is shown in Figure 1A. The pore diameter, which was based on the Barrett–Joyner–Halenda (BJH) method, deposited the 6.05 nm of the mesoporous materials (pore diameter 2–50 nm.) to promote catalytic activity [3].



(A)



(B)



(C)

Figure 1. Characterization of CaO derived from eggshells; (A) the pore size distribution, (B) CO_2 -TPD curve, and (C) SEM micrograph.

CaO derived from eggshells was characterized by CO_2 -TPD, which presented a distinct basic site with the peak between 500–750 °C, which can be attributed to strong basicity leading to high catalytic activity for transesterification [30], as shown in Figure 1B. The concentration of the basic site was determined from area under the CO_2 -TPD curve, and was found to be $215 \mu\text{mol}/\text{g}$. Furthermore, the SEM micrograph represents an irregular catalyst shape and an aggregate on the surface with a size ranging from 1–10 μm , as shown in Figure 1C [31].

3.2. Effect of Stirring Speed of Conventional Magnetic Stirrer on Mass Transfer Limitation

The transesterification reaction between the hydrophilic glycerol and hydrophobic DMC presents a biphasic system [32]. This immiscibility of the two reactants typically

leads to a mass transfer limitation, which influences the rate of transesterification. To investigate the external mass transfer limitation, the reaction rate resulting from variation in stirring speed (500–1000 rpm) is illustrated in Figure 2. The reaction rates increased when the stirring speed increased, and glycerol conversion at 3 h increased from 71% to 83% and 97% with stirring speeds of 500, 600, and 800 rpm, respectively. However, by increasing stirring speed from 800 rpm to 1000 rpm (the maximum speed of the magnetic stirrer), reaction rates equal to the glycerol conversion profile were attained, indicating the external mass transfer limitation due to the fact that the immiscibility of the reactants was negligible above 800 rpm. In other words, with the stirring speed of the magnetic stirred set at 800 rpm, the mass transfer limitation problem from the presence of two liquid phases at the initial stages of the reaction could be minimized. However, this plateau as a result of stirring speed could not confirm that other mass-transfer limitations such as the external mass transfer resistance of solid catalysts, and this could not be neglected. The need to be aware of the external mass transfer resistance depends on the flow regime, which the magnetic stirrer cannot offer, as will be shown in the next section.

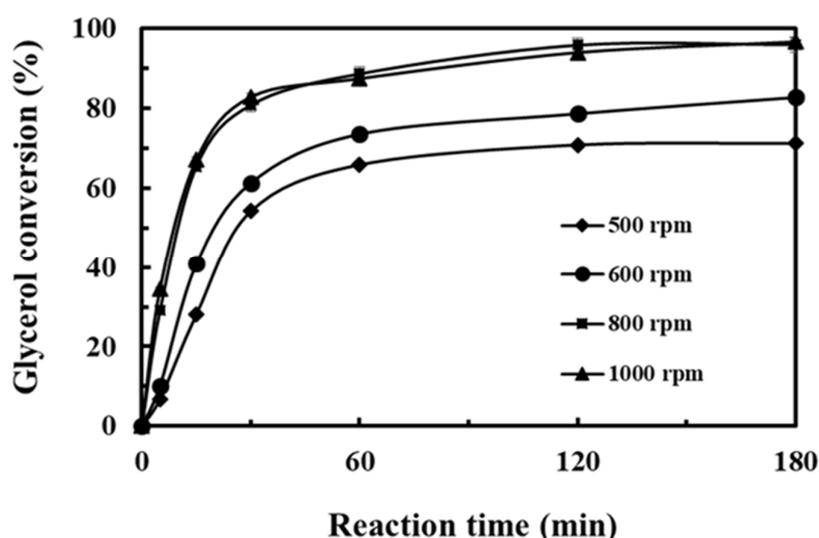


Figure 2. Effect of stirring speeds of conventional magnetic stirrer on glycerol conversion. Reaction condition: molar ratio of DMC: glycerol = 2.5, catalyst loading = 4.8 wt%, reaction temperature = 60 °C, reaction time = 180 min.

3.3. Performance Comparison between Kitchen Countertop Blender and Conventional Process

The kitchen countertop blender successfully enhanced the performance of GC synthesis, as a high glycerol conversion of 93% could be achieved within 15 min, while the conventional stirrer needed a prolonged reaction time of 90 min. It was noted that the catalyst loading of 4.8 wt% was used during the conventional process because at lower catalyst loading i.e., 2.4 wt%, glycerol conversion could not reach 93%, even after long reaction time of 180 min. However, 2.4 wt% loading is found to be suitable to achieve high conversion when using the countertop blender, which will be detailed in the following section. This was due to the high speed of the countertop blender, leading to an effective mixing of the glycerol and DMC. The immiscibility of the reactants could be overcome by using a high-speed countertop blender, which consisted of a suitable impeller with a small blade area rotating at high rpm. The Reynolds number (N_{Re}) was calculated following Equation (4), and the N_{Re} of 450 could be obtained from the conventional process, representing a laminar flow ($N_{Re} < 2000$) [33]. The obtained N_{Re} value to avoid initial mass transfer controlled by the immiscibility of reactants was aligned with the previous research [32] that reported an optimum agitator speed of 1500 rpm (calculated N_{Re} ca. 960), in which both reactants represented a laminar flow regime. It is worthy to note that Esteban et al. [32] employed a K_2CO_3 homogeneous catalyst, thus there was no concern

of the interphase diffusion (as also called external-, film- diffusion) of reactant molecules through the catalyst particles.

On the other hand, using a countertop blender presented $N_{Re} = 14,000$ and provided turbulence flow regime ($N_{Re} \geq 4000$ as turbulence flow) [33]. The appearance of the turbulence flow had been reported to result in cavitation, which provided a large area of the active zone and improved the exchange rate between the active and passive zone, overcoming the mass transfer limitation [34]. The result of using a high-speed countertop blender as shown in Figure 3 is that it essentially promoted the rate of reaction as it facilitated the enhancement of the overall mass transferring rate of the system. The liquid film diffusion (interphase diffusion) through the catalyst particles was hypothesized to be enhanced by using a countertop blender since this external mass transfer rate was dependent upon the flow conditions at the catalyst surfaces. TOFs at the initial stage (5 min) of the kinetic profile presented 7.2 and 1.5 min^{-1} when using the countertop blender and conventional process, respectively, which shows a five-fold increase. From the above observation, it can be concluded here that mass transfer resistance at the liquid–liquid interface played a minor role that could be eliminated by operating the conventional magnetic stirrer at a higher stirring speed, while the mass transfer resistance at the solid–liquid interface was found to play a major role under the conditions employed.

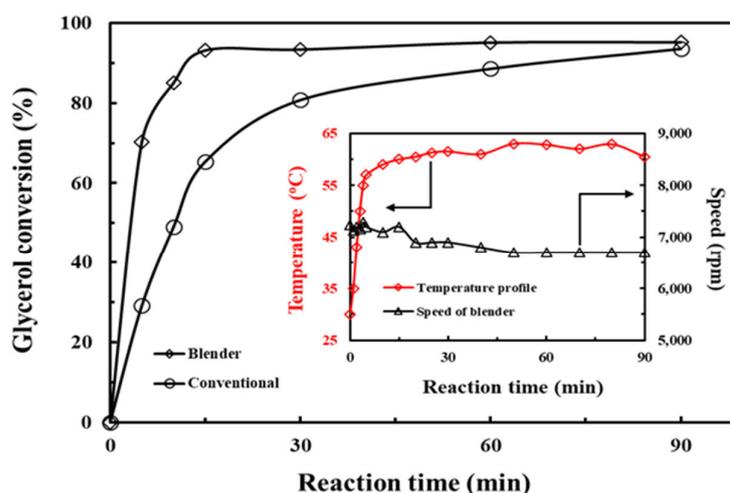


Figure 3. Comparison performance of kitchen countertop blender vs. conventional process on glycerol conversion. Reaction condition: molar ratio of DMC: glycerol = 2.5, reaction temperature = 60 °C, reaction time = 90 min. The inset is the reaction temperature history and blender speed history.

Apart from mass transfer intensification, when using a countertop blender, no external heat source was required, as in situ heat generation resulting from frictional heat had led to the self-sufficiency to sustain the endothermic reaction. Accordingly, the reaction temperature could reach the desired reaction temperature of 60 °C. The raise from room temperature (ca. 30 °C) to 60 °C was very fast (within 3 min), as the heat was generated locally (in situ), offering higher homogeneity distribution. The temperature was controlled by installing two fans (100 W each) adjacent to the blender to help disperse the generated thermal energy from the motor during prolonged runs as well as to decrease the temperature of the liquid mixture during some runs. Moreover, the blender speed was decreased slightly to maintain the constant temperature of around 60 °C. The reaction temperature history and the blender speed history are shown inset of Figure 3. Thus, the process could be considered to be heat transfer intensification. It is worth noting that indeed the generated heat was higher than the required heat for the endothermic reaction, as the system was intently performed without any insulation to release the excess heat in order to control the desired reaction temperature. Therefore, performance at a higher blender speed was

possible, but the cooling system for transferring the heat from the enclosure was necessary. However, this would not be beneficial if heat recovery was not adopted.

3.4. Effect of Molar Ratio of DMC to Glycerol

Although the reactants are presented in an equimolar stoichiometric ratio of DMC to glycerol for the transesterification reaction, excess DMC is typically used to increase the equilibrium conversion and miscibility between the hydrophilic glycerol and hydrophobic dimethyl carbonate reactants. Based on the activity coefficients from the theoretical Rozicka–Domalski functional group method reported by Wang et al. [35], the equilibrium of the glycerol conversion is dependent on the DMC: glycerol feed ratio and can be calculated as indicated by the dashed line as shown in Figure 4. Increasing the initial DMC: glycerol feed ratio from 1.0 to 1.5 and 2.5 led to higher equilibrium conversions of 70.5%, 82.9%, and 92.4%, respectively. The 98.6% selectivity of the obtained GC was very high with insignificant changes when the molar ratio of DMC to glycerol was increased due to the reaction operating at a low temperature. A side product such as glycidol or glycerol dicarbonate could occur under a high reaction temperature and large amount of excess DMC, respectively [2,16].

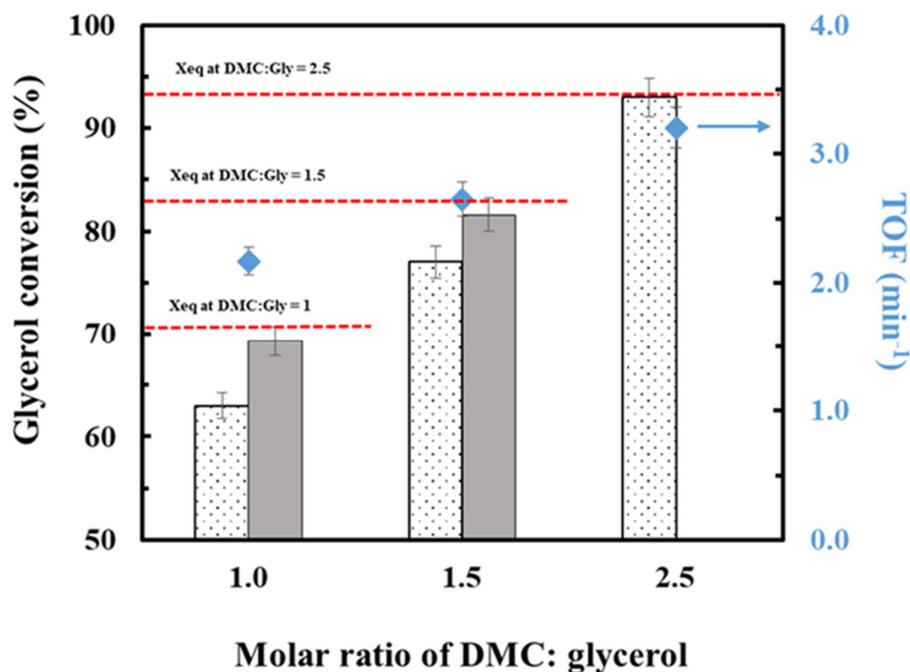


Figure 4. Effect of molar ratio of DMC: glycerol on glycerol conversion and TOF using kitchen countertop blender. Reaction condition: catalyst loading = 2.4 wt%, reaction temperature = 60 °C, blender speed = 7200 rpm, □ reaction time = 15 min, ■ reaction time = 120 min.

As shown in Figure 4, only the DMC to glycerol ratio of 2.5 could achieve the equilibrium conversion within 15 min of the reaction time (denoted as white bars), while the other ratios needed 120 min (denoted as grey bars) in order to be close to their equilibrium conversion. The results demonstrated that excess DMC that is 2.5 times the concentration of glycerol was necessary for obtaining a high enough reaction rate to achieve a high equilibrium conversion (approximately 93%) with a rapid reaction time of 15 min. This obviously resulted in the increase of TOF with an excess of DMC.

Indeed, this intrinsic reaction rate of glycerol to GC in terms of TOF monotonically increased with the addition of the excess DMC. This behavior suggested that the TOF was first order in DMC, which was consistent with the phenomenological kinetic model proposed by Esteban et al. [32]. However, excess DMC higher than 2.5 times the original concentration was not recommended, as glycerol dicarbonate could be formed as a side

reaction [27]. Consequently, the mass transfer limitations between the two immiscible reactants and the external mass transfer resistance that had taken place on the CaO solid catalyst can be assumed to be minimized when the molar ratio of DMC: glycerol = 2.5.

3.5. Effect of Catalyst Loading

The effect of the catalyst loadings on the glycerol conversion and TOF is shown in Figure 5. The glycerol conversion increased with increasing catalyst loading. The catalytic activity was improved due to the increase in the concentration of the active basic sites that were essential to catalyze the transesterification reaction. However, as the catalyst loading increased to 4.8%, the glycerol conversion improved slightly during the first 10 min of reaction time, indicating that the excess amount of catalyst could not further improve the glycerol conversion, as the reaction had reached equilibrium within a short time of approximately 15 min. Therefore, a superfluous amount of catalyst would result in the decrease of TOF (Figure 5 inset). On the other hand, a much slower reaction rate was observed in the case of 1.2 wt% loading, indicating that there were not enough active sites to achieve the desired conversion of glycerol. This led to a low TOF of 1.2% loading (Figure 5 inset). The CaO loading of 2.4 wt% was, therefore, chosen as the optimum condition when using a countertop blender.

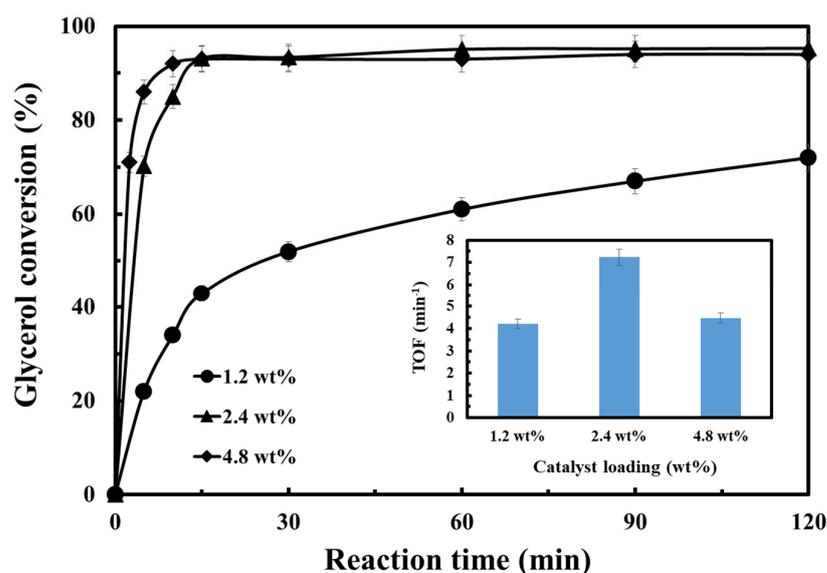


Figure 5. Profiles of glycerol conversion with reaction time at different catalyst loadings under the reaction condition: molar ratio of DMC: glycerol = 2.5, reaction temperature = 60 °C, using kitchen countertop blender at 7200 rpm. The inset is TOF at 5 min of different catalyst loadings.

It is worthy to note that for catalyst reusability, our previous work found that the re-calcination of the used CaO catalyst produced glycerol conversion similar to that of fresh CaO catalyst. Therefore, the leaching of an active site was less likely to occur in the CaO catalyzed transesterification of glycerol and DMC. The catalyst deactivation mechanism and alternative monitoring of the deactivation were also proposed in our previous work [27].

3.6. Comparison of High Speed of Kitchen Countertop Blender with Other Intensification Processes Using CaO as a Catalyst

Several researchers have reported on the transesterification for GC synthesis catalyzed by CaO using conventional reactor stirring with a magnetic stirrer and heated by the electrical hot plate. There were certainly different details regarding experimental setup and protocol, therefore, leading to the deviation in the suitable operating conditions that they reported. However, as summarized in Table 1, without any process intensification, long reaction time (more than ca. 90 min) and high catalyst loading (ca. 5 wt%) with excess

DMC (ca. 2.5 times or higher) were usually employed to achieve a reasonable yield of approximately 90%. It is noted that changing other parameters such as using crude glycerol (glycerol content 71% *w/w*) have been reported as having other possible positive benefits on impurities (methanol and sodium methylate) [20]. It was found that the lower molar ratio of DMC to glycerol was required compared to using pure glycerol, thus, lowering the DMC to glycerol ratio to 2.0 and catalyst loading to 1 wt%. However, the evaluation of yield efficiency showed that all of these conventional processes exhibited low indexes of yield efficiency, as the values were mostly in the range of 0.02–0.06 g/kJ.

Microwave irradiation has gained more attention in recent years as an alternative heating technology. Microwave-assisted transesterification had been reported to show a fast reaction rate and low energy consumption with a GC yield of 90.1% within 15 min under temperature constant mode (TCM) at 95 °C, and a 92.1% yield within only 50 s under power constant mode (PCM) at 175 W [36]. From the reported energy consumption and GC production, the yield efficiency could be calculated as 0.118 g/kJ and 0.125 g/kJ for TCM and PCM, respectively. The significantly shorter reaction time would result in higher yield efficiency compared to the conventional process. Furthermore, Teng et al. [20] also presented the advantages of using crude glycerol for microwave-assisted transesterification. The highest GC yield of 93.4% from crude glycerol could be obtained within 5 min of the reaction time. Based on the reported value, a calculated yield efficiency of 0.766 g/kJ could be achieved, which showed much higher than the yield efficiency of 0.023 g/kJ achieved by the conventional process [19]. Therefore, the microwave-assisted transesterification of GC carbonate production enhanced the heat transfer rate and decreased the reaction time and energy consumption, leading to a high yield efficiency. However, several studies have discussed limitations of the microwave technique, such as the inability to penetrate on large scale [36].

Ultrasound irradiation has been used in transesterification reactions and enhances the interaction between the immiscible reactants due to the cavitation phenomenon caused by sonication [37,38]. Recently, Leong et al. [39] reported a high glycerol conversion of 95.41% at 70 °C after 90 min using crude glycerol for GC production. However, the intensification process was not obvious and was much less pronounced than the microwave reactor.

An alternative intensification process based on the multifunctional reactor is reactive distillation, in which the reaction and distillation are integrated within one unit. As the reaction products can be removed continuously from the reactive section through distillation, high conversion and shift reaction equilibrium can be achieved. Li and Wang [22] used the method of coupling reaction and azeotropic distillation. The impressive results of a high yield of GC (98%) could be obtained under a stoichiometric ratio of DMC to glycerol (1:1). However, the evaporation of the azeotropic agent required consumption energy, and regeneration of the azeotropic agent was difficult due to the azeotrope of the methanol–benzene mixture [23].

The non-catalytic supercritical dimethyl carbonate technique was performed by Ilham and Saka [24]. They determined a high GC yield of 98% under a reaction temperature of 300 °C, 20–40 MPa, and 15 min of reaction time. Operation under supercritical dimethyl carbonate conditions can decrease the reaction time substantially without the use of catalyst. However, the supercritical dimethyl carbonate condition technique requires high operating conditions, leading to a high cost of experimental equipment for control and safety. Although the yield efficiency could not be calculated, as energy consumption was not reported in the study, it was difficult to expect a high value of yield efficiency under supercritical fluid conditions.

Table 1. Comparison of kitchen countertop blender with other process intensifications and conventional processes.

Reactor System	Heat Source	Advantages	Disadvantages/Limitations	Reaction Condition				Y _{GC} or X _{Gly} (%)	Yield Eff. (g/kJ)	Ref.
				DMC: Gly	CaO load. (wt %)	T (°C)	t (min)			
Conventional										
Atmospheric pressure reactor	electrical hot plate			2 ^a	1	65	120	Y _{GC} = 84.3	0.023	[20]
Atmospheric pressure reactor	electrical hot plate	-	- Long reaction time and/or high catalyst loading	5	6.1	75	90	Y _{GC} = 64.1	0.018	[20]
Autogenously pressure reactor	electrical hot plate		- Low yield efficiency	4	5	95	80	X _{Gly} = 97.0	0.003	[36]
Atmospheric pressure reactor	electrical hot plate			2.5	4.8	60	120	Y _{GC} = 94.0	0.064	This work
Process intensification										
Microwave reactor	microwave irradiation	- Improve heat transfer rate		4	5	95 ^b	15	Y _{GC} = 90.1	0.118	[36]
Microwave reactor	microwave irradiation	- Low energy consumption	- Inability to penetrate in large reaction volumes [36]	4	1	< 200 ^c	0.83	Y _{GC} = 92.1	0.125	[36]
Microwave reactor	microwave irradiation	- Short reaction time		2 ^a	1	65	5	Y _{GC} = 93.4	0.766	[20]
Ultrasonic reactor	ultrasonic irradiation	- Fast heating time - Improve mass transfer	- Difficult for using in Large-scale [39] - High cost ultrasound equipment [21]	3 ^a	5.4	70	90	Y _{GC} = 95.4	n/a	[40]
Batch distillation tower	electric heating mantle	- Stoichiometric feed ratio is possible	- High energy consumption [23] - Benzene as azeotropic agent is needed	1	1.2	85	n/a	Y _{GC} = 98.0	n/a	[22]
Reactive and Extractive distillation	electric heating mantle	- When CaO reused, the reduction of catalytic activity is less than the conventional process	- Difficult to control and scale-up	4	3	85	n/a	Y _{GC} = 99.0	n/a	[23]

Table 1. Cont.

Reactor System	Heat Source	Advantages	Disadvantages/Limitations	Reaction Condition				Y _{GC} or X _{Gly} (%)	Yield Eff. (g/kJ)	Ref.
				DMC: Gly	CaO load. (wt %)	T (°C)	t (min)			
Supercritical tube reactor	electric heating jacket	- Absence catalyst - Simple to separation due to the absence of the catalyst	- Severe operating condition - High cost of operating equipment	10	-	300	15	Y _{GC} = 98.0	n/a	[24]
Countertop blender	in situ heat generation	- Intensive mixing, improve mass transfer - No external heat source as <i>in situ</i> heat generation and thus rapid heat transfer rate - Enhance reaction rate	- Balance heat to maintain the desired temperature	2.5	2.4	60	15	Y _{GC} = 91.3	2.391	This work

^a The experiment using crude glycerol (glycerol content 71 %w/w). ^b The experiment was investigated under the temperature constant mode (TCM) at 95 °C. ^c The experiment was investigated under the power constant mode (PCM) at 175W.

For the countertop blender in this study, 135 kJ of energy was consumed during 15 min of reaction time to achieve a 91.3% yield of GC, which corresponds to a yield efficiency of 2.391 g/kJ. Compared to available values from other intensification techniques, the countertop blender exhibited outstanding yield efficiency. This value was higher than the conventional process (0.064 g/kJ) by approximately 40 times, indicating energy intensification superiority.

4. Conclusions

The transesterification reaction between hydrophilic glycerol and hydrophobic DMC using CaO solid catalysts have led to a mass transfer limitation, lowering the reaction rate. Accordingly, reactor designs need to accommodate heat intensification and mass transfers. Process intensification using a simple kitchen countertop blender was successfully applied in a heterogeneous catalytic system of transesterification between glycerol and DMC for GC synthesis using an eggshell-derived CaO catalyst. A glycerol conversion and GC yield of 93% and 91%, respectively, could be achieved within 15 min of reaction time. Moreover, external heating was not required because the effect of the high-speed stirring could generate sufficient self-frictional heating for the high-shear blender, which transferred the kinetic energy from the rapidly rotating blades to the fluid through friction. The reaction mixture could automatically be heated to 60 °C within a few minutes. The study found that the mass transfer resistance at the liquid–liquid interface played a minor role that could be eliminated by operating a conventional magnetic stirrer at a higher stirring speed, even under laminar flow regime. The mass transfer resistance at the solid–liquid interface was instead found to play a major role under the employed conditions. A high-speed countertop blender operating at 7200 rpm provided a turbulent flow, with $N_{Re} = 14,000$. This presumably resulted from cavitation, which provided a large area of the active zone and improved the exchange rate between the active and passive zones thereby lessening the solid–liquid mass transfer limitation. In addition, the countertop blender energy offered a much higher GC yield efficiency production than the conventional process, an outstanding emergence from other intensification techniques. Consequently, the synergy among mass, heating, and energy intensification had enhanced the miscibility of the reactants, decreased the amount of catalyst, and increased the rate of reaction faster than the conventional approach thus lowering the required reaction time, which is crucial in the industry.

Author Contributions: Conceptualization, W.P. and W.K.; methodology, W.P.; validation, W.P. and W.K.; formal analysis, W.P.; investigation, W.P. and W.K.; data curation, W.P. and W.K.; writing—original draft preparation, W.P.; writing—review and editing, W.K., F.A., V.N.-V., K.N., D.W., J.W.L., S.S.L., K.K., N.L., S.B., and S.A.; visualization, W.P.; supervision, W.K.; funding acquisition, W.K. and S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Thailand Research Fund (Research and Researchers for Industrials PhD Program: Grant No. PHD 57I0078) and Verasuwan Co., Ltd.

Acknowledgments: The financial support provided by the Thailand Research Fund (Research and Researchers for Industrials PhD Program: Grant No. PHD 57I0078) and Verasuwan Co., Ltd. is gratefully acknowledged. W. Kiatkittipong and S. Assabumrungrat also would like to acknowledge the Research Chair Grant supported by the National Science and Technology Development Agency (NSTDA).

Conflicts of Interest: The authors declare no conflict of interest.

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