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# SYNTHESIS OF GLYCERYL CARBONATE VIA MICROWAVE IRRADIATION

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## ABSTRACT

*Supported by increasing awareness for environment and sustainability, glyceryl carbonate (Gly-C) has gained much interest over the last 20 years because of its versatile reactivity and as a way to valorise waste glycerol. In this study, synthesis of Gly-C via microwave irradiation was conducted as an alternative method to synthesise the glycerol derivative. Reaction parameters which include the type of carbonating agent, glycerol to carbonating agent mole ratio, reaction temperature as well as the reaction time have been examined. By setting microwave power at the lowest power (100 W), results from this study show that the synthesis of Gly-C under microwave irradiation is best carried out using ethylene carbonate as the carbonating agent with glycerol to ethylene carbonate molar ratio of 3:1 for 10 min at 80°C under atmospheric pressure. Gly-C was successfully obtained with 62% yield and purity of 96%. This study implies the significant use of microwave technique in the synthesis of Gly-C.*

**Keywords:** glycerol, glyceryl carbonate, microwave irradiation, oleochemical.

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## INTRODUCTION

The utilisation of glycerol for the synthesis of value-added chemicals is important because glycerol is produced abundantly as a co-product during the production of basic oleochemical and biodiesel. Biodiesel is well-known as promising alternative and renewable fuels. However, one of the challenges for further development of the biodiesel industry is the large amount of glycerol produce as co-product, with around 10% of the weight of the feedstock (Coombs, 2007). It was projected that the world biodiesel market would reach 49 million tonnes by 2016; resulting in approximately 5 million tonnes of crude glycerol would be produced (Yang *et al.*, 2012).

The surplus of glycerol not only causes storage and waste treatment problems but also substantially influences the glycerol price. The price of glycerol may decrease further with the increase of biodiesel production and thus, the economic viability of biodiesel production will be reduced; this has already limited the development of the biodiesel industry (Wu *et al.*, 2013). Making profit from glycerol will be an important factor to solve the economic and environmental challenges of biodiesel production. This has attracted extensive research interest with efforts focused on production of valuable products from glycerol (Cho *et al.*, 2010; Sonnati *et al.*, 2013).

Gly-C is a cyclic carbonate that can be easily derived from glycerol. The molecule presents a structural duality that bears a hydroxyl group and 2-oxo-1,3-dioxolane group that makes Gly-C to have wide reactivity. It has low toxicity, good biodegradability and high boiling point (Sonnati *et al.*, 2013). Gly-C was proposed as a promising biobased alternative in both direct and indirect applications. It was described to have potential application as a solvent in various applications (Kreutzberger, 2000; Schaffner *et al.*, 2010), in development of rechargeable lithium batteries (Baril *et al.*, 1997; Britz *et al.*, 2007), a part of membrane component for gas separation

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(Kovvali and Sirkar, 2002), as a component of surfactants and detergents (Ghandi *et al.,* 2007; Iaych *et al.,* 2011) and as monomer of polycarbonate and polyurethane (Kob *et al.,* 2007).

Various synthesis pathways for Gly-C have been studied, such as carbonation; the process to obtain Gly-C by reacting glycerol with carbon monoxide or carbon dioxide (Aresta *et al.,* 2006; Hu *et al.,* 2010). Another method is the carbonate exchange reaction between alcohols and carbonate source such as phosgene, alkylene carbonate (ethylene carbonate or propylene carbonate) and dialkyl carbonate (dimethyl carbonate, diethyl carbonate) (Climent *et al.,* 2010; Cho *et al.,* 2010). In addition, the synthesis of Gly-C from glycerol and urea is another alternative method (Climent *et al.,* 2010; Li *et al.,* 2006).

Despite all the studies on the synthesis of Gly-C that have been reported, however only a few studies mention about microwave-assisted synthesis of Gly-C. Microwave-assisted reactions have been highlighted due to their short reaction time as compared to those of conventionally heated reaction (Kappe *et al.,* 2009). The objectives of this research is to synthesise Gly-C via microwave irradiation at atmospheric pressure and optimisation of the process parameters such as reaction temperature and reaction time, type of carbonating agent, type of catalyst and mole ratio of carbonating agent to glycerol.

## MATERIALS AND METHODS

### Materials

Refined glycerol (99.8% purity) as the platform chemical for the synthesis of Gly-C was obtained from a local oleochemical company. Ethylene carbonate, dimethyl carbonate (DMC) and urea used in the screening test in this study were purchased from Merck, Germany. All carbonating agent were 99% purity. Glycidol and catalysts used in this study namely molecular sieve, calcium oxide, zinc chloride, sodium carbonate, ammonium carbonate, potassium carbonate, lithium carbonate, sodium acetate, calcium acetate, montmorillonite, calcium hydroxide and dibutyltin oxide were obtained from Sigma Aldrich USA. Magnesium oxide and aluminium oxide were purchased from Merck, Germany. All the reagents were used without further purification. Gly-C standard was purchased from Tokyo Chemical Industry Co., Ltd, Tokyo, Japan.

### Methods

***Synthesis of glyceryl carbonate.*** The transesterification of glycerol with a particular carbonating agent was carried out in batches using MARS Synthesis microwave reactor from CEM, USA. The microwave power was set at 100 W. Typically, a 125 ml round-bottom flask was charged with 9.21 g of glycerol and desired amount of specific carbonating agent followed by addition of a specified catalyst (5% w/w to glycerol). The reagents were calculated according to the desired molar ratio for each reaction. The reaction mixture was stirred at 80°C for 3 min. The reaction was conducted at atmospheric pressure without any solvent. For all the reaction conducted, all ramping time from ambient to the desired reaction temperature was set to 7-8 min.

***Separation and distillation of reaction mixtures.*** Once the reaction has been completed, filtration of the catalyst from the reaction mixture was carried out using Büchner funnel and Wattman filter paper No. 5 equipped with aspirator pump to reduce the pressure. Purification of crude Gly-C was conducted via vacuum distillation. The best purity of Gly-C was obtained when the crude was distilled in an oil bath at 120°C – 130°C and pressured at $7.0 \times 10^{-1}$ - $8.0 \times 10^{-1}$ mbar. Under such condition, the separation step yielded 62% Gly-C with 96.01% purity, which was isolated as residue from the distillate. The distillation time was approximately 7 hr. The purified Gly-C was slightly yellowish. The yield of Gly-C was calculated by using the formula below:

% Yield = (actual yield/theoretical yield) x 100

### Characterisation

***Fourier transform infrared (FTIR).*** A convenient analytical method for determining the functional group of the Gly-C was conducted using Spectrum 100 FT-IR Spectrometer Perkin Elmer. Samples were scanned between 4000-650 $cm^{-1}$ wavenumbers.

***Gas chromatography (GC/MS) analysis.*** Qualitative analysis of the reaction mixture was conducted using gas chromatography (GC). The GC (Agilent System 6890N Network GC System) was equipped with a HP-Innowax (30 m x 0.25 mm x 0.2 μm) capillary column and flame ionisation detector. The following temperature programming was used: oven temperature: 80°C, initial temperature: 80°C, heating rate at 10°C $min^{-1}$, final temperature: 260°C, injector temperature: 250°C, detector temperature: 260°C, carrier gas: helium at 40.0 ml $min^{-1}$. Composition of Gly-C, unreacted glycerol and glycidol was determined according to the percent area under respective peak from the GC analysis chromatogram of the crude glycerol carbonate sample. Pure glycerol, Gly-C and glycidol were used for the product qualitative evaluation.

GC-MS spectroscopy analysis was determined using GC 7890A series equipped with auto-injector 7683B series. Inert MSD 5976C series was used to ascertain the molecular weight of Gly-C. Chromatographic separation was accomplished using a rugged high temperature GC capillary column HP-Innowax (30 m; 0.25 mm; 0.25 µm), a split injection mode with ratio of 80:1 at 250ºC and helium as a mobile phase at a flow rate of 0.8 ml min$^{-1}$. The oven temperature was initially set at 80ºC, then increased to 240ºC at a ramping rate of 10ºC per minute and held at the final temperature for 14 min. The MS temperature was set at 230ºC for the ion source and 150ºC for the MS quadrupole magnet. Electron impact spectra were obtained at acceleration energy of 70 eV. As for sample preparation, the sample was dissolved in methanol. Fragment ions were analysed over 0-150 m/z mass range in the full scan.

***Proton nuclear magnetic resonance ($^1$HNMR) analysis.*** The $^1$H NMR analysis of Gly-C was analysed using Bruker FT-NMR 600 MHz spectrometer Advanced III 600, in which 600 MHz for $^1$H and 150 MHz for $^{13}$C. Tetramethylsilane was used as internal standard. Samples were dissolved in deuterated chloroform ($CDCl_3$) prior to analysis.

## RESULTS AND DISCUSSION

### Effect of Carbonating Agent

The type of carbonating agent used in the synthesis of Gly-C plays a significant role in microwave-assisted reaction. Selecting carbonating agent with high polarity may assist the reaction because high polarity substance absorbs microwave irradiation more readily (Kappe *et al.*, 2009).

*Table 1* illustrates the effect of carbonating agent on Gly-C formation. Ethylene carbonate gave the highest Gly-C composition (31.81%) and low unreacted glycerol (25.47 %) as compared to dimethyl carbonate (Gly-C composition, 2.22%; unreacted glycerol, 94.78%) and urea (Gly-C composition, 0.26%; unreacted glycerol 99.39%). The conversion of glycerol to product was determined based on the corresponding amount of unreacted glycerol. The result can be attributed to the strong polar nature of ethylene carbonate, which makes it an ideal reaction medium under microwave irradiation. As reported by Hoz *et al.* (2005), the magnitude of heating via microwave depends on the dielectric properties of the molecules. By comparing the dipole moment, which indicates the polarity of the compounds, ethylene carbonate has the highest dipole moment of 4.87 D (Naejus *et al.*, 1998) as compared to urea (4.56 D) (Kumler *et al.*, 1942) and dimethyl carbonate (0.91 D) (Naejus *et al.*, 1998). Among the carbonating agents, dimethyl carbonate has the lowest dipole moment and it also gave lowest Gly-C composition. These comparisons were made to select the most suitable carbonating agent for the preparation of Gly-C under microwave irradiation.

In addition, glycerolysis reaction mechanism of urea to form Gly-C proposed by Aresta *et al.* (2006) and Li *et al.* (2006) reported that initial conversion of urea into isocyanic acid had taken place before direct attack of isocyanic acid on glycerol to form Gly-C. The isocyanic acid is an acid having boiling point of 23.5°C. Due to the reaction temperature that was set at 80°C, there would be a possibility of this acid to be liberated out of the reaction before the set temperature was reached. This would lead to low Gly-C composition when urea was used as carbonating agent. Ethylene carbonate was later used as the carbonating agent for succeeding studies.

Synthesis of Gly-C using ethylene carbonate as the carbonating agent is often conducted at reduced pressure (Sonnati *et al.*, 2013). This is to remove the by-product ethylene glycol, and thus shifts the chemical equilibrium towards Gly-C formation. *Figure 1* depicts the mechanism of Gly-C synthesis from ethylene carbonate using base catalyst.

### Effect of Catalyst

It was reported that transcarbonation process of glycerol and alkylene carbonate proceeds well with basic catalyst (Hu *et al.*, 2010; Li and Wang, 2010). Various types of heterogeneous catalysts

TABLE 1. EFFECT OF CARBONATING AGENT ON THE SYNTHESIS OF GLY-C*

| Carbonating agent | Gly-C composition in crude product (%) | Unreacted glycerol (%) |
|---|---|---|
| Urea | 0.26 | 99.39 |
| Ethylene carbonate | 31.81 | 25.47 |
| Dimethyl carbonate | 2.22 | 94.78 |

Note: * Reaction conditions: temperature, 80°C; molar ratio ethylene carbonate:glycerol, 1:1; catalyst loading, 5% (w/w) of glycerol; reaction time, 20 min.

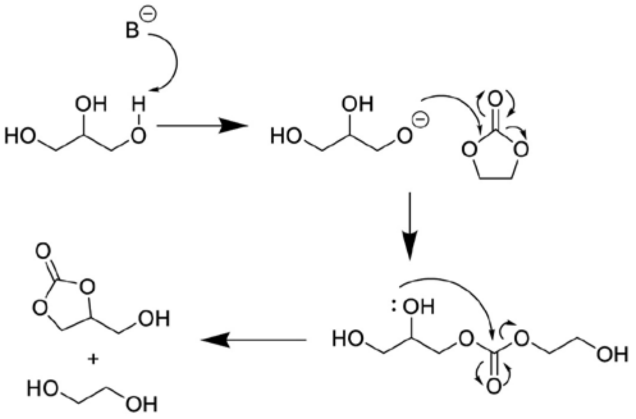

*Figure 1. The typical base-catalysed mechanism for Gly-C synthesis from ethylene carbonate and glycerol by transesterification.*

were evaluated mainly from Lewis base, Lewis acid and amphoteric type of catalyst. A control reaction without catalyst was also carried out. As shown in *Table 2*, control reaction gave 21.78% Gly-C composition and almost 30% of unreacted glycerol. Transcarbonation is a similar process to transesterification (Sonnati *et al.*, 2013) that can proceed without catalyst. The reaction was able to form Gly-C without addition of catalyst, however it suffered low Gly-C yield (Ma *et al.*, 1999). For all catalysed reactions, the compositions of Gly-C were from 37% to 41% except for montmorillonite that gave Gly-C composition below 5%. The highest Gly-C composition (41%) was obtained when calcium acetate was used. However, calcium acetate was among the catalysts that produce certain amount of glycidol in the crude product. It was reported that glycidol can be obtained from Gly-C over a basic catalyst (Malkemus *et al.*, 1958; Climent *et al.*, 2010).

Furthermore, it was reported that compounds containing magnesium and zinc can enhance the formation of glycidol (Liu *et al.*, 2009; Claude *et al.*, 2000). But the experimental results showed that, reaction catalysed with magnesium oxide, zinc chloride, and aluminum oxide did not produce any glycidol. Magnesium oxide was chosen as the catalyst in further experiments as it is relatively cheaper than zinc chloride and aluminum oxide.

**TABLE 2. CATALYST SCREENING FOR GLY-C SYNTHESIS UNDER MICROWAVE IRRADIATION AT ATMOSPHERIC PRESSURE***

| Type of catalyst | Gly-C composition in crude product (%) | Unreacted glycerol (%) | Glycidol composition (%) |
|---|---|---|---|
| Control | 21.78 | 29.96 | 0.00 |
| Calcium oxide | 38.39 | 18.64 | 1.41 |
| Sodium carbonate | 37.09 | 21.38 | 7.92 |
| Potassium carbonate | 39.66 | 15.94 | 11.88 |
| Lithium carbonate | 38.51 | 18.38 | 4.48 |
| Ammonium carbonate | 39.03 | 17.27 | 1.00 |
| Sodium acetate | 39.62 | 16.03 | 3.04 |
| Calcium acetate | 41.43 | 12.20 | 2.61 |
| Calcium hydroxide | 38.87 | 17.61 | 1.00 |
| Magnesium oxide | 38.75 | 17.88 | 0.00 |
| Dibutyltin oxide | 40.09 | 15.03 | 2.72 |
| Zinc chloride | 39.68 | 15.91 | 0.00 |
| Montmorillonite | 4.76 | 89.90 | 0.00 |
| Molecular sieve | 38.94 | 17.48 | 1.97 |
| Aluminium oxide | 37.68 | 20.15 | 0.00 |

Note: *Reaction conditions: temperature, 80°C; molar ratio ethylene carbonate:glycerol, 1:1; catalyst loading, 5% (w/w) of glycerol; reaction time, 20 min.

### Effect of Temperature

The influence of reaction temperature on the formation of Gly-C was studied at various temperatures between 40°C and 180°C (*Figure 2*). *Figure 2* shows the composition of Gly-C in crude product increased as the reaction temperature increased. Gly-C composition was the highest (38.77%-39.31%) at reaction temperature between 80°C to 140°C. Further increased in reaction temperature (160ºC-180ºC) had decreased the Gly-C composition. Unreacted glycerol showed decreasing trend between 50°C to 140°C, and increased when reaction temperature was increased from 140°C to 180°C. Results from Gly-C composition and unreacted glycerol percentage suggested that the optimum reaction temperature is between 80°C to 140°C. Ochoa-Gómez *et al.* (2012) and Bai *et al.* (2013) have described, formation of glycidol will occur at temperature 90°C and above. At said temperature, base catalyst can extract a proton from the hydroxyl moiety of Gly-C resulting in the formation of the strong nucleophile 1,3-dioxolan-2-one-4-methoxide that leads to the formation of glycidol. In order to avoid glycidol formation and high reaction temperature, 80°C was used as the optimum temperature for the following studies. This process can be considered energy efficient due to low reaction temperature. The ramping time to achieve 80°C when power of microwave was set at 100 W was approximately 3-5 min.

### Effect of Reaction Time and Percentage of Catalyst

Effect of reaction time was studied from 1 to 25 min with different percentage of catalyst loading tested which were 0.5%, 1% and 3%. A control reaction was conducted without addition of catalyst. As plotted in *Figure 3*, for all reaction with addition of 0.5%, 1% and 3% of MgO, Gly-C composition in crude product increased as the reaction time increased. This showed that formation of Gly-C was dependent on the dosage of the catalyst. Increasing the catalyst amount (from 0.5% to 3%) increased Gly-C composition because of the increased numbers of active sites. On the other hand, increasing the

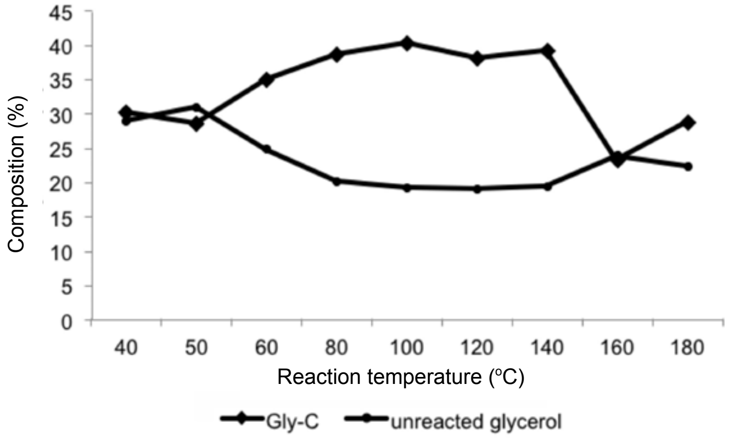

*Figure 2. Effect of reaction temperature on the crude Gly-C composition and glycerol conversion. Reaction conditions: molar ratio ethylene carbonate:glycerol, 1:1; catalyst loading, 5% (w/w) of glycerol; reaction time, 20 min.*

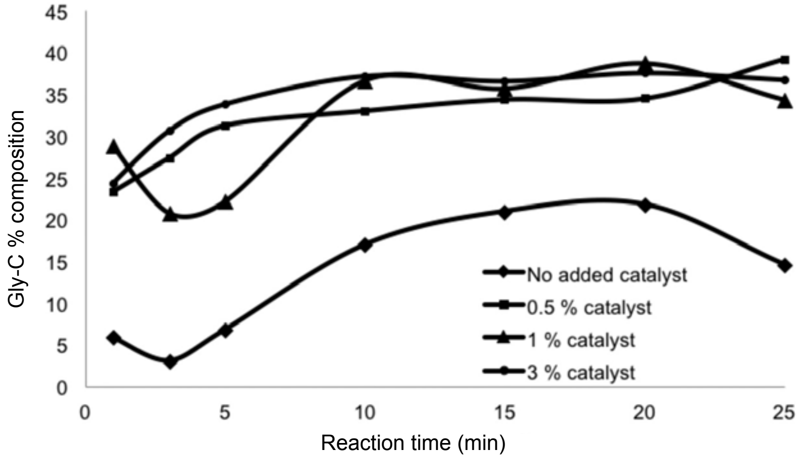

*Figure 3. Effect of microwave irradiation time and catalyst loading on Gly-C composition. Reaction conditions: temperature, 80°C; molar ratio ethylene carbonate:glycerol, 1:1.*

catalyst amount also increased the opportunity for contact between the catalyst and the reactant, which could directly influence the reaction rate. This statement also supported by Bai *et al.* (2013). For all percentage of catalyst tested, Gly-C composition in crude product had reached the plateau value after 10 min of reaction. The Gly-C composition in crude product obtained was between 33%-39%. Increase in MgO loading from 0.5% to 3% showed insignificant improvement in Gly-C composition.

As for unreacted glycerol percentage (*Figure 4*), addition of catalyst 0.5%, 1.0%, 3%, had decreased the amount of unreacted glycerol gradually as the reaction time increased, which indicated that more glycerol was converted to form Gly-C. For all three catalysts loading, unreacted glycerol percentage had reached plateau value after 10 min of reaction. No further decrease of unreacted glycerol after 10 min. The result above suggests that 0.5% addition of catalyst with 10 min of reaction time is adequate to give optimum amount of Gly-C composition with low amount of unreacted glycerol. This value of catalyst loading and reaction time were used for the next study.

### Effect of Mole Ratio

Transcarbonation which is similar to transesterification is a reversible reaction; therefore excess of ethylene carbonate was expected to shift the chemical equilibrium towards Gly-C formation. In this work, effect of ethylene carbonate to glycerol molar ratio on formation of Gly-C and percentage of unreacted glycerol was investigated and the results are shown in *Figure 5*. The Gly-C composition in crude product increased from 31% to 51% when the molar ratio of ethylene carbonate to glycerol was increased from 1:1 to 3:1. The percentage of unreacted glycerol had decreased when molar ratio of ethylene carbonate to glycerol increased. The result showed that 3 moles of ethylene carbonate had converted almost 100% of glycerol to product. Therefore, sample from this study was subjected to purification via vacuum distillation process.

### Purification and Qualitative Analysis on Synthesised Gly-C

Purification process was conducted on the crude Gly-C obtained from the optimised reaction parameters. After the purification process, the yield of Gly-C was 62% with purity of 96%. Later qualitative analysis such as FTIR, $^{1}H$ and $^{13}C$ NMR and GC/MS were conducted on the crude and purified Gly-C for further confirmation.

***FTIR spectra.*** The main characteristic band of synthesised Gly-C was shown by the absorption band at 3427 cm$^{-1}$ (O-H stretching). Absorption bands at 2943 and 2881 cm$^{-1}$ can be assigned to $CH_2$ and CH stretching of the O-methylene and O-methylidyne groups of the cyclic carbonate; 1773 cm$^{-1}$ assigned to C=O stretching of the five-membered cyclic carbonate; and 1169 and 1047 cm$^{-1}$ are assigned to C–C, and C–O stretching respectively. The absorptions are in agreement with the spectrum of Gly-C standard as reported by Calvino-Casilda *et al.* (2011).

***$^{1}H$ NMR analysis.*** Verification of the prepared Gly-C structure was determined using $^{1}H$ and $^{13}C$ NMR spectra and the results as illustrated in *Figure 6*. For the prepared Gly-C, the chemical shifts was observed at δ 4.88-4.85 for the $CH_2C\underline{H}CH_2OCOO$ while for $CH_2CHC\underline{H}_2OCOO$ was observed at δ 4.54-4.33. These results were supported by the reported Gly-C $^{1}H$ NMR by Fleischer *et al.* (2013) which showed chemical shifts at δ 4.89 for the proton at

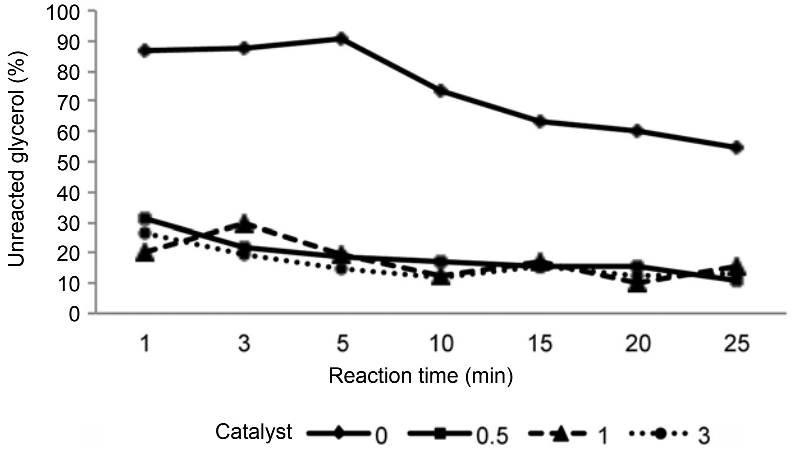

*Figure 4. Effect of microwave irradiation time and catalytic loading on percentage of unreacted glycerol. Reaction conditions: temperature, 80°C; molar ratio ethylene carbonate:glycerol, 1:1.*

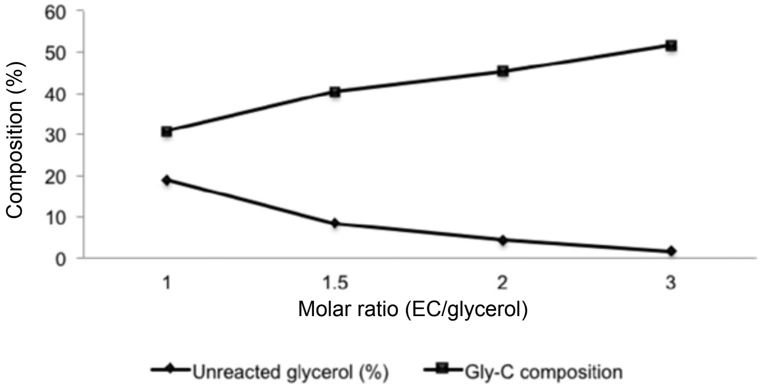

*Figure 5. Effect of mole ratio of ethylene carbonate:glycerol on Gly-C composition and percentage of unreacted glycerol. Reaction conditions: temperature, 80°C; catalyst loading, 0.5% (w/w) of glycerol; reaction time, 10 min.*

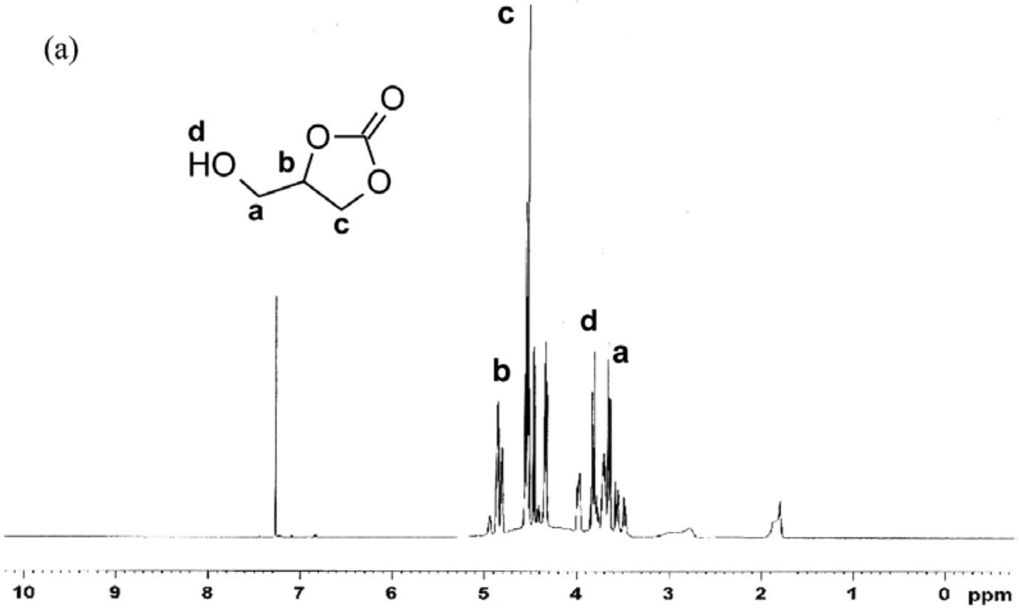

*Figure 6. The $^1H$ NMR spectrum of purified Gly-C.*

$CH_2C\underline{H}CH_2OCOO$ and δ 4.57-4.29 for proton at $CH_2CHC\underline{H}_2OCOO$.

***GC/MS.*** *Figure 7* shows GC chromatogram for crude, purified and standard Gly-C. Gly-C peak can be detected at retention time of 22 min for all samples. For confirmation of mass analysis, purified and standard Gly-C was analysed using GC/MS. *Figure 8* shows the appearance of identical peak at retention time 20.5 min for both purified and standard Gly-C. This was further confirmed by the strong matching of fragment ion at retention time 20.5 min (*m/z* 87, 44, 31 and 15) in purified and standard Gly-C.

## CONCLUSION

It can be concluded from this study; under microwave irradiation Gly-C is best synthesised with ethylene carbonate as the carbonating agent and the reaction accelerated by magnesium oxide at 0.5% (w/w) of glycerol. Molar ratio of ethylene carbonate to glycerol at 3:1 was found suitable to give high yield of Gly-C. Optimum reaction time was found to be 10 min and temperature at 80°C. Vacuum distillation was used as the purification technique and the percent yield of Gly-C obtained was 62% with purity of 96%.

It was observed that for microwave assisted reaction, the selection of carbonating agent with high dipole moment is crucial to give optimum amount of Gly-C composition percentage. The transesterification of glycerol and ethylene carbonate via microwave assisted synthesis enable the rise of reaction temperature from ambient to 80ºC (selected reaction temperature) to be achieved in less than 5 min. Furthermore with reaction time of 10 min, glycerol conversion to product has reached almost

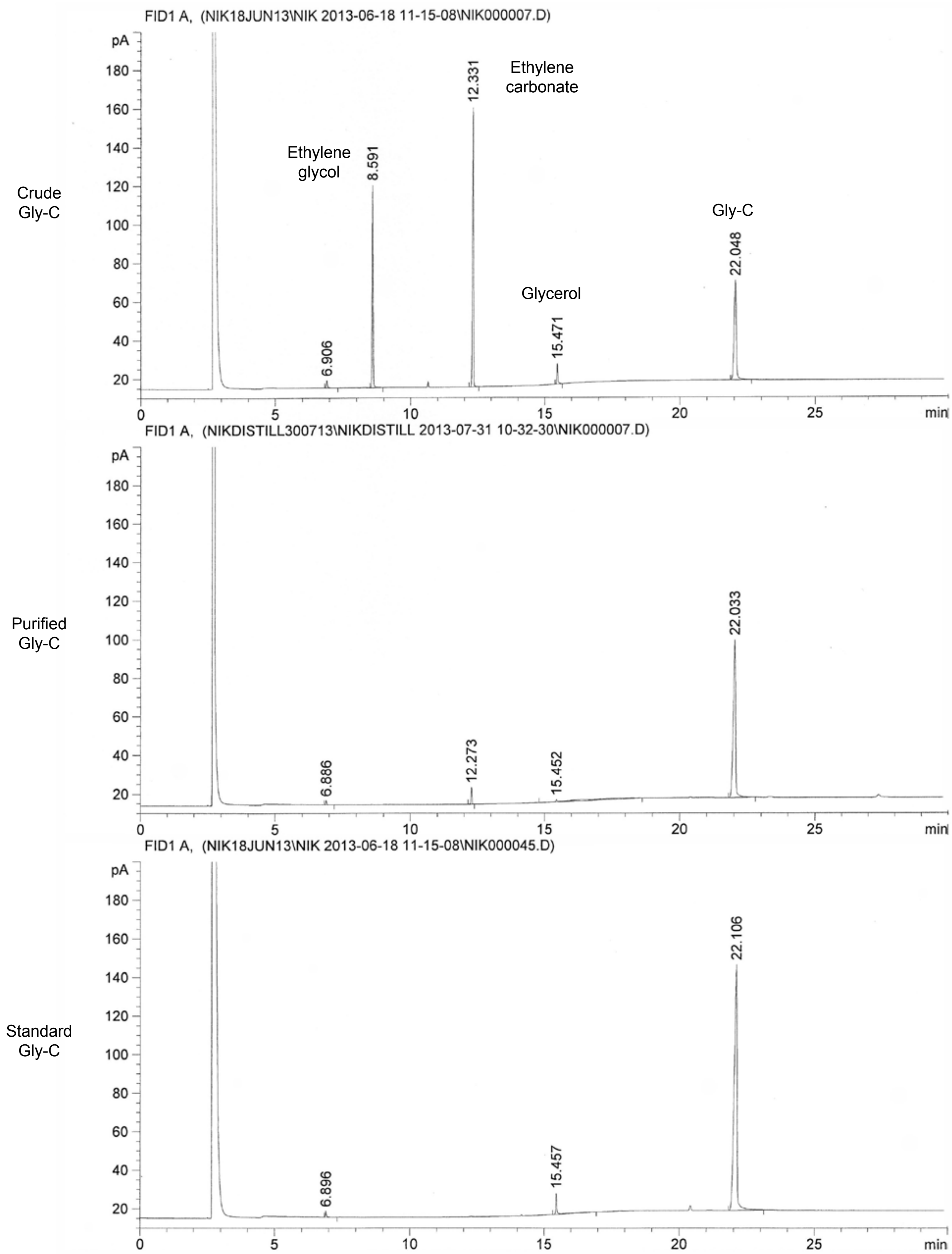

*Figure 7. Gas chromatography (GC) chromatograms for crude, purified and standard Gly-C.*

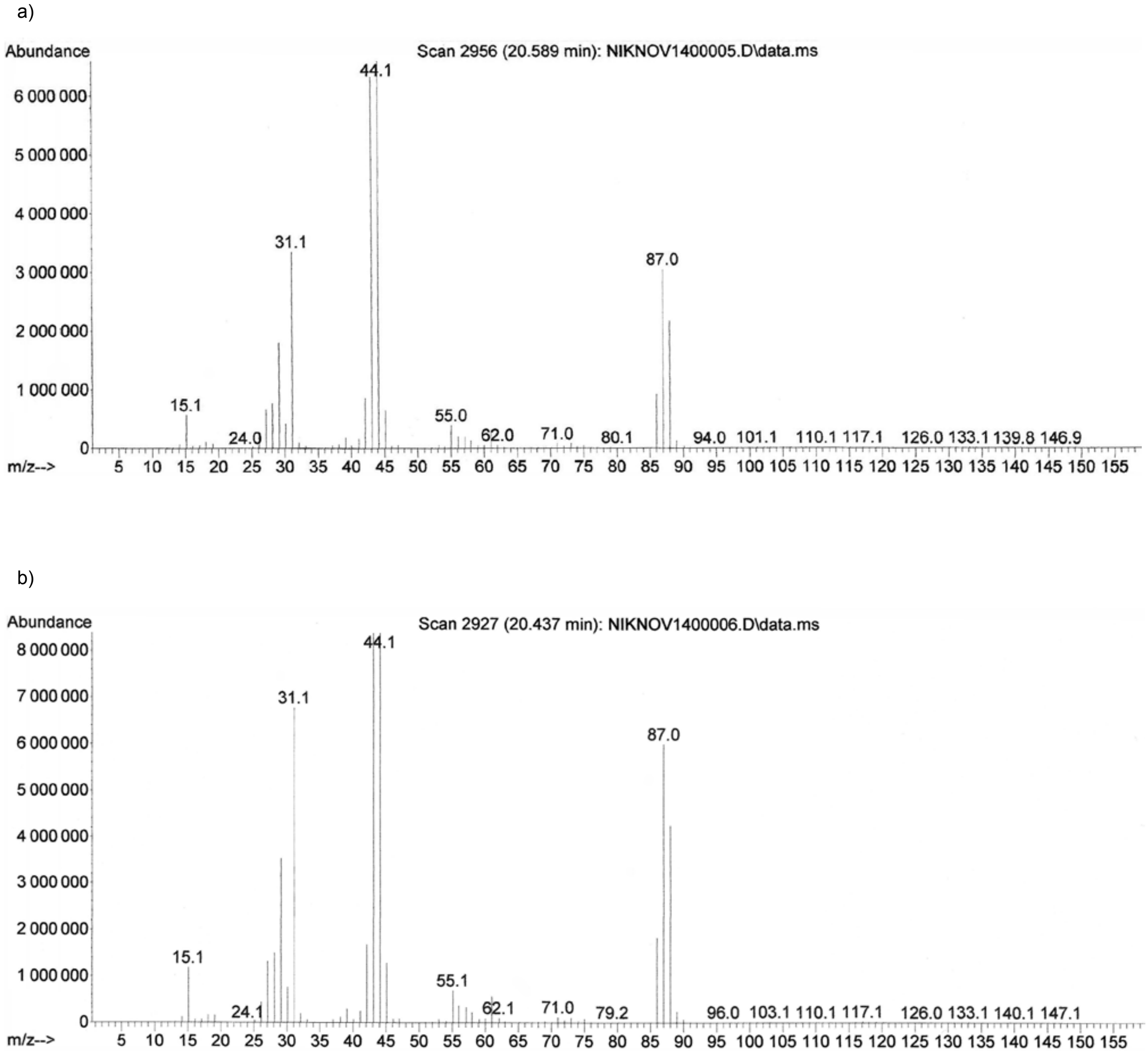

*Figure 8. Gas chromatography/mass spectrometry (GC/MS) spectrums for (a) purified and (b) standard Gly-C.*

100% conversions. Therefore, the method given in this study can be considered time efficient that can lead to economic advantages. Therefore, it can be concluded that this study implies the noteworthy use of microwave technique in the synthesis of Gly-C which gave good yield of Gly-C in relatively short reaction time.

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