# BOILER ASH AS CATALYST FOR THE CATALYTIC SYNTHESIS OF ORGANIC CARBONATES

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DOCTOR OF PHILOSOPHY (INDUSTRIAL CHEMISTRY)
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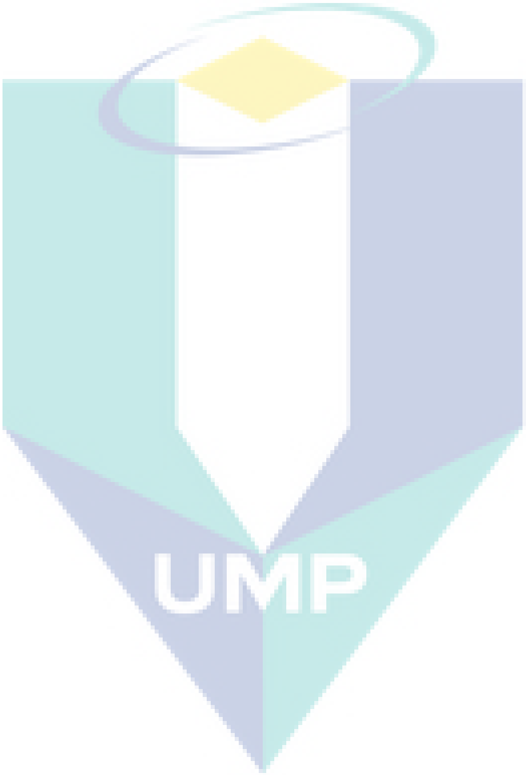

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# BOILER ASH AS CATALYST FOR THE CATALYTIC SYNTHESIS OF ORGANIC CARBONATES

VIDHYAA A/P PAROO INDRAN

Thesis submitted in fulfilment of the requirements
for the award of the degree of
Doctor of Philosophy (Industrial Chemistry)

Faculty of Industrial Sciences & Technology
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AUGUST 2016

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***I specially dedicate this dissertation to my respected parents;***

*Mr. Paroo Indran Krishnan and Mrs. Vijayaletchumy Ramakrishna Pillay*

***Beloved husband;***

*Mr. Puspanathan Subramaniam*

***Dearest mentor;***

*Prof. Dr. Mashitah Mohd. Yusoff*

***Supportive families and friends***

***For their love, guidance, support, sacrifices and best wishes.***

# ACKNOWLEDGEMENTS

The completion of this thesis would not have been possible without the guidance and help from several individuals who in one way or another have contributed and extended their valuable assistance. First and foremost, I would like to extend my utmost gratitude to Dr. Mohd. Hasbi Ab. Rahim, Deputy Dean (Research & Postgraduate Studies) of Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang whose sincerity and encouragement I will never forget. Dr. Mohd. Hasbi Ab. Rahim has been my supervisor and inspiration as I hurdle all the obstacles in the completion of this research work. I value his guidance and appreciate all his support throughout this journey of education and character building.

My heartiest gratitude also extends to my co-supervisor Assoc. Prof. Dr. Gaanty Pragas Maniam who has in all way guided and corrected my mistakes in the completion of this study. I would also want to take this opportunity to thank all FIST technical and administrative staffs who have been very helpful and motivating throughout the completion of this research work. I also feel privileged to acknowledge Prof. Dr. Taufiq-Tap Yun Hin from Universiti Putra Malaysia for lending a helping hand when I needed to use some technical instruments for analysis in Putracat. I also would like to take this space to specially thank my friend Thenmoli Tharamalingam who has been supportive throughout this journey of knowledge gathering. Last but not the least, my FIST lecturers, central laboratory staffs, Putracat Staffs and friends whose names have not been mentioned and the one above all of us, the omnipresent God, for answering my prayers, for giving me the strength to plod on despite my constitution wanting to give up and throw in the towel. Thank you all.

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# ABSTRACT

Over the years production of crude glycerol has been in an increasing pattern due to the rapid growth of biodiesel industry. Therefore, the market value of glycerol has dropped drastically in recent years. To overcome this problem, the conversion of glycerol into fine chemical such as glycerol carbonate through an economical catalytic synthesis route using boiler ash as catalyst was carried out in this study. Besides, Malaysia is the second largest oil palm producer in the world and about 4 million tons of boiler ash is produced annually from incineration of palm fruits, palm kernels, palm shells and palm fibres which contains variety of interesting metal elements. A series of catalysts were prepared using various calcination temperatures and through catalytic testing, the boiler ash calcined at 900 $^{o}$C under static air (BA 900) was identified as the most active catalyst. The highest catalytic activity obtained resulted in an average of 93.6 ± 0.4 % conversion of glycerol, 90.1 ± 1.0 % selectivity of glycerol carbonate and 84.3 ± 1.1 % yield of glycerol carbonate at optimum reaction conditions of 150 °C, 4 h, molar ratio of 1:1.5 (glycerol: urea) plus stirring rate of 340 rpm. Potassium silicate ($K_2SiO_3$) present in boiler ash subsequently promoted the selective conversion of glycerol carbamate intermediate to glycerol carbonate at an accelerated manner in which $K^+$ acted as weak Lewis acid while the $SiO_3^{2-}$ as conjugated basic site. It was found that, $K^+$ activates the carbonyl group of urea while the conjugated basic $SiO_3^{2-}$ activates the hydroxyl group of glycerol to form glycerol carbonate. The turnover frequency (TOF) value calculated for both BA 900 (126.5 mmol/ g.cat.h$^{-1}$) and $K_2SiO_3$ (125.6 mmol/ g.cat.h$^{-1}$) were comparable, thus confirming similar active sites responsible for catalytic reaction. Although, studies using direct utilisation of industrial crude glycerol revealed that the catalyst is feasible to produce glycerol carbonate, the presence of impurities at certain amount in crude glycerol affected the catalytic activity. Boiler ash is also a versatile catalyst to synthesise ethylene carbonate and propylene carbonate. It was evidently proven that boiler ash showed similar catalytic pathway in synthesis of the three different carbonates. The current study pioneers in introducing catalyst derived from waste for the production of organic carbonate. It also proposes new scheme of mechanistic pathway at an accelerated manner for the synthesis of organic carbonates while proposing direct utilisation of crude glycerol without prior purification. In concise, the studies employed is near to a complete green synthesis approach as it suggests proper utilisation of waste boiler ash as catalyst and crude glycerol as feedstock.

# ABSTRAK

Sejak kebelakangan ini, pertumbuhan pesat industri biodiesel menyebabkan pengeluaran gliserol mentah sebagai produk sampingan semakin meningkat. Oleh itu, nilai pasaran gliserol telah menurun secara drastik sejak beberapa tahun yang lalu. Bagi mengatasi masalah ini, kaedah yang mempunyai nilai ekonomi bagi penghasilan gliserol karbonat menggunakan gliserol dan urea dengan kehadiran mangkin abu dandang telah dijalankan dalam kajian ini. Selain itu, Malaysia juga merupakan pengeluar minyak sawit kedua terbesar di dunia dan kira-kira 4 juta tan abu dandang dihasilkan setiap tahun sebagai sisa dari pembakaran buah kelapa, isirung sawit, tempurung kelapa dan gentian sawit yang mengandungi pelbagai unsur logam yang berguna. Sehubungan dengan itu, satu siri pemangkin berasaskan abu dandang telah disediakan berdasarkan perbezaan suhu pengkalsinan, didapati bahawa pengkalsinan pada suhu 900 $^{o}$C (BA 900) menghasilkan pemangkin yang mempunyai aktiviti pemangkinan yang optimum. Aktiviti pemangkin yang optimum diperoleh dengan purata penukaran gliserol sebanyak 93.6 ± 0.4 %, pemilihan gliserol karbonat sebanyak 90.1 ± 1.0 % dan hasil gliserol karbonat sebanyak 84.3 ± 1.1 % dalam keadaan tindak balas bersuhu 150 °C selama 4 jam dengan nisbah molar gliserol kepada urea (1:1.5) serta kadar putaran media tindakbalas selaju 340 rpm. Aktiviti pemangkin abu dandang didapati dipengaruhi oleh kandungan kalium silikat yang menyebabkan perubahan gliserol “carbamate” kepada gliserol karbonat dalam kadar yang cepat. Selain itu, nilai keaktifan pemangkinan berdasarkan TOF bagi kedua-dua BA 900 (126.5 mmol/ g.cat.h$^{-1}$) dan $K_2SiO_3$ (125.6 mmol/ g.cat.h$^{-1}$) adalah hampir sama menunjukkan kedua-dua pemangkin dipengaruhi pusat tindak balas yang sama di mana $K^+$ merupakan asid Lewis yang lemah dan $SiO_3^{2-}$ merupakan alkali berkonjugat. $K^+$ memainkan peranan untuk mengaktifkan kumpulan karbonat daripada urea manakala $SiO_3^{2-}$ mengaktifkan kumpulan hidroksil daripada gliserol dalam kajian ini. Selain itu, kajian menggunakan gliserol mentah yang diperoleh daripada industri biodiesel tempatan telah dijalankan untuk menganalisis kebolehan BA 900 dalam penghasilan gliserol karbonat. Melalui kajian tersebut, didapati bahawa BA 900 boleh digunakan sebagai pemangkin dalam penghasilan gliserol karbonat secara terus dari gliserol mentah. Namun begitu, kandungan lain dalam gliserol mentah dalam komposisi yang tertentu boleh mengurangkan aktiviti pemangkin. Mangkin berasaskan abu dandang juga telah terbukti sebagai pemangkin untuk proses penghasilan etilena karbonat dan propilena karbonat. Secara umumnya, abu dandang didapati mempunyai laluan mekanistik pemangkin yang sama bagi ketiga-tiga sintesis sebatian karbonat tersebut. Kepentingan kajian ini terbukti di mana kajian ini menjadi perintis dalam memperkenalkan pemangkin daripada sisa untuk penghasilan organik karbonat. Kajian ini turut mencadangkan skim laluan mekanistik yang pantas untuk menghasilkan gliserol karbonat disamping mencadangkan penggunaan gliserol mentah secara terus tanpa melalui proses pra-rawatan. Kajian ini juga adalah suatu pendekatan sintesis berkonsep hijau yang lengkap kerana menggunakan pemangkin dan gliserol mentah yang berasaskan bahan buangan industri setempat.

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# LIST OF SYMBOLS

| | |
|---|---|
| - | Subtract |
| % | Percentage |
| ~ | Tilde |
| + | Add |
| < | Less-than |
| = | Equals |
| > | Greater-than |
| ± | Plus-minus |
| ≤ | Less than or equal to |
| ≥ | More than or equal to |
| °C | Degree Celsius |
| °C/min | Degree Celsius per minute |
| µg/mL | Micrograms per milliliter |
| µL/mL | Microliter per milliliter |
| µm | Micrometre |
| atm | Atmospheric Pressure |
| cm | Centimetre |
| $cm^{-1}$ | Reciprocal centimetre |
| g | Gram |
| $g/cm^3$ | Gram per cubic centimetre |
| g/g | Gram per gram |
| g/kg | Gram per kilogram |
| g/mol | Gram per mol |
| h | Hour |

| | |
|---|---|
| kPa | Kilopascal |
| L | Litre |
| lb | Pound |
| m | Metre |
| M | Molarity |
| *m/z* | Mass-to-charge ratio |
| mg | Milligram |
| mg/mL | Milligram per millilitre |
| MHz | Megahertz |
| min | Minutes |
| mL | Millilitre |
| mL/min | Millilitre per minute |
| mm | Millimetre |
| N | Normality |
| nm | Nanometre |
| ppb | Parts per billion |
| ppm | Parts per million |
| wt % | Weight percentage |
| x | Multiple |
| δ | Delta |
| λ | Gamma |
| $p/p^o$ | Relative pressure |

# LIST OF ABBREVATIONS

| | |
|---|---|
| $^{13}C$-NMR | Carbon Nuclear Magnetic Resonance |
| AOAC | Association of Analytical Chemists |
| AOCS | American Oil Chemists' Society |
| ATR-FTIR | Attenuated Total Reflectance-Fourier Transform Infrared |
| BA 110 | Boiler Ash 110 |
| BA 500 | Boiler Ash 500 |
| BA 700 | Boiler Ash 700 |
| BA 900 | Boiler Ash 900 |
| BA 1100 | Boiler Ash 1100 |
| BET | Brunauer Emmett Teller |
| CA | Compress Air |
| CaCO3 | Calcite |
| CaO | Calcium Oxide |
| $CO_2$-TPD | Carbon dioxide-Temperature Programmed Desorption |
| DMC | Dimethyl carbonate |
| DEC | Diethyl carbonate |
| EC | Ethylene Carbonate |
| EDXRF | Energy Dispersive X-Ray Fluorescence |
| EG | Ethylene Carbonate |
| FESEM-EDX | Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray |
| FTIR | Fourier Transform Infrared |
| GC | Gas Chromatography |
| GC-FID | Gas Chromatography-Flame Ionisation Detector |
| GC-MS | Gas Chromatography-Mass Spectroscopy |

| | |
|---|---|
| Gly | Glycerol |
| Gly C | Glycerol Carbonate |
| Gly KM | Crude Glycerol Potassium Methylate |
| Gly NaM | Crude Glycerol Potassium Methylate |
| ICP-MS | Inductively Coupled Plasma-Mass Spectroscopy |
| ISO | International Standard Organisation |
| $K_2SiO_3$ | Potassium Silicate |
| $K_2CO_3$ | Potassium carbonate |
| KCl | Sylvite |
| KOH | Potassium Hydroxide |
| $N_2$ | Nitrogen Gas |
| NIST | National Institute of Standards and Technology |
| MgO | Magnesium Oxide |
| MPOB | Malaysian Palm Oil Board |
| NMR | Nuclear Magnetic Resonance |
| PC | Propylene Carbonate |
| PG | Propylene Glycol |
| rpm | Revolutions Per Minute |
| RSD | Relative Standard Deviation |
| USDA | United States Department of Agriculture |
| WHO | World Health Organisation |
| XRD | X-ray Diffraction |

# LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

In this chapter, the main aim is to introduce the thesis in general which includes the background of research, problem statement, objectives, scope of study and its significance. In precise, the chapter will provide the necessary platform towards developing further depth in the current research.

## 1.2 Background of the Research

In the recent years, syntheses of cyclic organic carbonates (i.e. glycerol carbonate) have interest many researchers in the field of chemistry across the world due to their interesting chemical properties. Glycerol carbonate is a fundamental cyclic organic carbonate with low toxicity, low volatility, high boiling point, high flash point and biodegradability (Aresta, Dibenedetto, Nocito, & Ferragina, 2009; Sonnati et al., 2013). This essential carbonate being a versatile compound gained much attention of researchers due to their myriad applications in many major industries directly and indirectly (Pagliaro, Ciriminna, Kimura, Rossi, & Della Pina, 2007; Ochoa-Gómez, Gómez-Jiménez-Aberasturi, Ramírez-López; Belsue, 2012 and (Sonnati et al., 2013). The promising applications include in polymers (Mizuno, Nakai, & Mihara, 2010a), cosmetics and pharmaceuticals (Plasman, Caulier, & Boulos, 2005), paints, coatings, surfactants, gas separation membranes as well as anti-explosive additives (Pacheco & Marshall, 1997;

Aresta et al., 2009; Dibenedetto et al., 2011; Hammond et al., 2011). This vast application of glycerol carbonate as a key material in industries has been one of the main reasons to study the synthesis of organic carbonates using bio-renewable feedstock with the presence of catalyst.

There are various routes of producing glycerol carbonate as reported by researchers over the years. In conventional method, organic carbonates are synthesised via phosgenation of glycerol, however, phosgene is a toxic chemical and corrodes the reactor (Aresta, Dibenedetto, Nocito, & Pastore, 2006; Kim, D.-W. et al., 2014); hence the phosgene route has been gradually replaced by oxidative carbonylation of an alcohol in the presence of carbon monoxide and oxygen in recent years (McKetta & Cunningham, 1984; Claude, Mouloungui, Yoo, & Gaset, 2000; Yoo & Mouloungui, 2003). Other synthesis method includes the use of propylene and ethylene carbonate which is largely used by Huntsman Corporation but ethylene carbonate was reported as a non-cost effective chemical which needed replacement (Mouloungui, Yoo, Gachen, Gaset, & Vermeersch, 1996). Therefore, to overcome this issue, direct carbonylation of glycerol was suggested with aid of carbon dioxide gas which was adopted by UBE Industries. However, this reaction suffered from thermodynamic limitations which lead to poor yield and the need for high pressure reactions which was contributed to high operational cost (Vieville, Yoo, Pelet, & Mouloungui, 1998; Aresta et al., 2006; George, Patel, Pillai, & Munshi, 2009). On the other hand, the use of dimethyl carbonate (DMC) with glycerol to produce glycerol carbonate was also introduced as a solution but this reaction involved usage of higher ratio of DMC to glycerol and was limited to the use of expensive catalyst as well as shift in the chemical equilibrium to form glycerol carbonate at higher temperatures (Li & Wang, 2011a). Alternatively, favoured route of synthesis opted in this research involved the use of glycerol and urea under solvent-free condition as reported by Rahim et al., (2012). These feedstock are readily available, cheap and bio-renewable (Aresta et al., 2009 and Fujita, Yamanishi, & Arai, 2013). The industrial approach towards synthesising glycerol carbonate and other organic carbonates such as propylene carbonate as well as ethylene carbonate in larger scale has been established by Huntsman Corporation (Jeffsol ® Glycerine Carbonate Bulletin, 2010) through direct carbonylation route. However, their main feedstock associated with non-renewable and petroleum based sources.

In addition, most catalyst employed in the research contained rare earth element which is relatively expensive (Wang, L., Ma, Wang, Liu, & Deng, 2011; Rahim et al., 2012; Jagadeeswaraiah, Kumar, Prasad, Loridant, & Lingaiah, 2014). Thus, the possibility to utilise cheaper catalyst derived from abundantly available industrial waste or side product is considerably crucial for both economic and environmental preservation perspectives. As example, boiler ash from palm oil mill has been used to catalyst several chemical process, *i.e.* biodiesel production and in waste water treatment. Malaysia was affirmed as the world second largest palm oil producer by Foreign Agricultural Service, Production, Supply and Distribution Online, United States Department of Agriculture (USDA) with 4 million tons of boiler ashes produced yearly from this industry (Lee, K. T., Zainudin, & Mohamed, 2004; Zainudin, Lee, Kamaruddin, Bhatia, & Mohamed, 2005; Ooi, Ismail, Bakar, & Teoh, 2014). Therefore, there were rising questions and researches to ensure proper disposal of this boiler ash (Shuit, Tan, Lee, & Kamaruddin, 2009).

Up to date, only few limited studies focused on the direct utilisation of crude glycerol from biodiesel industry into synthesis of value added products (Johnson & Taconi, 2007; Nguyen & Demirel, 2011; Hu et al., 2012; Tudorache, Negoi, Tudora, & Parvulescu, 2013; Phin, Lim, Low, Low & Tan, 2015). Nonetheless, Nguyen and Demirel, (2013) focused on direct utilisation of the crude glycerol by glycerolysis with urea to produce glycerol carbonate but others indulge on purifying the crude glycerol to the purest possible form before transforming them to value added chemicals. The disadvantage of the work reported by Nguyen and Demirel in 2013 involved use of synthetic catalysts sourced from lanthanum for the synthesis of glycerol carbonate. On the other hand, the reported study is a modelling to propose co-production of biodiesel and glycerol carbonate which has not been tested. The report is also based on theoretical evaluation. Besides, crude glycerol typically contains moisture, methanol, soap, ash, oil and matter of organic non-glycerol (MONG) (Hazimah, Ooi, & Salmiah, 2003; Hu et al., 2012) apart from glycerol in the by-product which potentially inhibits the synthesis of desired product. It is reported that for every 10 kg of biodiesel produced 1 kg of glycerol is produced (Thompson & He, 2006; Johnson & Taconi, 2007). Besides, the increasing amount of waste glycerol generated yearly has impacted the price of the glycerol to drop drastically over the years (Johnson & Taconi, 2007; Quispe, Coronado, & Carvalho Jr., 2013). Figure 1.1 suggests the global glycerol production from biodiesel plant to be increasing since 2013 and is expected to grow until 2023. This may result in significant drop in price of glycerol. Previously, the production of glycerol in industries is reported to be increasing at the rate of 2.8 % yearly contributing to about 160 thousand tons of glycerol waste (Pagliaro & Rossi, 2008). Currently, in Malaysia Biofuel Annual, reported that the total biodiesel production is approximately 500 000 tons in 2015 which is equivalent to 50000 tons of crude glycerol (10 % w/w ratio) (Wahab, 2014). Therefore, employing crude glycerol, urea and catalyst derived from industrial waste is a benchmark towards near green synthesis approach (Figure 1.2).

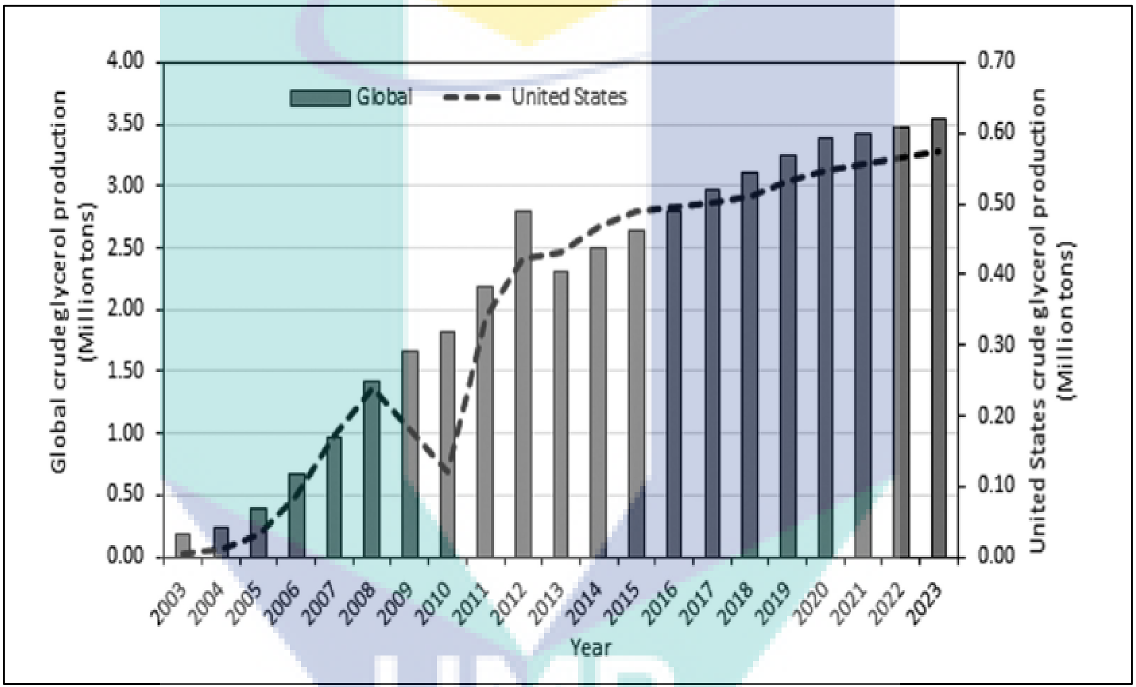


*Figure 1.1.* Projection of global glycerol production from biodiesel industry.

Source: Ye and Ren, (2014).

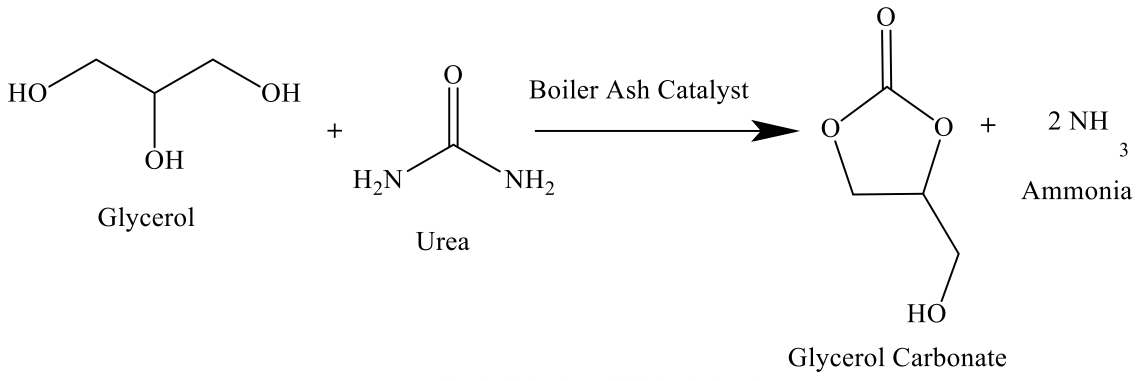


*Figure 1.2.* Synthesis of glycerol carbonate using boiler ash.

In addition to glycerol carbonate, other carbonates based chemical such as ethylene and propylene carbonate shared considerable value in chemical market. Thus, the ability to utilise similar catalytic system for the production of different carbonates based chemical will essentially be beneficial for the industry point of view. Until now, there is no available data reported on the feasibility of using similar catalytic synthesis approach for the production of different organic carbonates.

In general, the synthesis approach used in this study is novel as it uses bio-renewable sources and real wastes from industry as feedstock. Besides, it offers a simple and economical route of transforming polyols to desired cyclic organic carbonates under solvent-free conditions. The aim of the research also clearly illustrates that the use of real waste from industry will benefit both industry and environment fundamentally. This is because there are many biodiesel manufacturing plant and palm oil plant in worldwide that generates significant amount of wastes yearly. Hence, this approach can aid in transforming the wastes into useful substances that will be useful for the future generation in major industries. Thus, the value added product is expected to be commercialized by industry in relatively cheaper and safe procedure. In concise, the research is built on the idea of waste into wealth generation platform.

## 1.3 Problem Statement

Over the years, production of glycerol as a by-product of the biodiesel making industry has rampantly increased and directly affected the market value of glycerol to drop considerably. In aspect of utilising this glycerol, studies has been conducted by many researchers to tune them into fine chemicals such as glycerol carbonate which has variety of applications directly and indirectly. However, the approach to transform glycerol into glycerol carbonate was based on the use of synthetically derived catalyst which is in some cases expensive and more importantly based on reactions that operated under high pressure with aid of solvents. Besides, the industrial approach also used non-renewable feedstock that would also deplete over time. Therefore, this research was directly aimed at synthesising glycerol carbonate at suitable conditions using bio-renewable feedstock glycerol along with urea. Alternatively, there have been many recent studies on the use of this bio-renewable feedstock for the synthesis of glycerol carbonate but all catalyst used were synthetically derived or contained rare earth minerals which were relatively expensive. Hence, for the first time catalyst from waste and natural source was introduced in this research. Nevertheless, no research testified the feasibility of the reaction to synthesise other organic carbonates using different polyol sources under similar synthesis approach using the same catalysts. Thus, this gap was an opening door to our research to do a proof of concept study on formation of other organic carbonates using waste as catalyst as well as other polyol sources along with urea. The research did not stop there but expanded into using real waste glycerol for the first time for glycerolysis reaction with urea from local biodiesel industry to proof the feasibility of the reaction using the waste catalyst without any purification. This is essential as there are only few previously reported studies on direct utilisation of crude glycerol for glycerolysis with urea without purification due to interferences of other substances in crude glycerol which alters the conversion to be poor. Nevertheless, none of the study suggested use of both catalyst and feedstock derived from waste. In short, the use bio-renewable feedstock crude glycerol, urea and waste boiler ash is an advantage for waste into wealth generation seeking industry besides being an environmentally friend process to the nature.

## 1.4 Objectives

The objectives of the present study are;

i. To synthesise glycerol carbonate from glycerol in the presence of waste boiler ash as a catalyst under suitable reaction conditions and propose scheme of mechanistic pathway as well as establish the catalyst active sites.

ii. To investigate the direct utilisation of industrial crude glycerol in synthesis of glycerol carbonate.

iii. To propose proof of concept study on utilisation of boiler ash as a feasible catalyst for the synthesis of other organic carbonates such as ethylene carbonate and propylene carbonate.

## 1.5 Scope of Study

As a way to achieve the objectives of the research, the scope of the study focuses on synthesis of glycerol carbonate using bio-renewable feedstock glycerol and urea commercially purchased. This feedstock was later loaded for reaction with aid of catalyst boiler ash collected from local palm oil industry. The catalysts were subjected to calcination treatment in order to obtain a range of catalyst with different metal phases existing predominantly. The cyclic carbonylation reaction of glycerol with urea are conducted under various reaction condition parameters including temperature, molar ratio of glycerol to urea, mass of catalyst loaded, duration of reaction, stirring rate and different type of flowing gas. From these parameters studied, the suitable reaction conditions for the synthesis of glycerol carbonates were confirmed. The catalyst which achieves the highest yield based on selectivity and conversion are selected as the most active catalyst. The catalyst was later subjected to various catalyst characterisation techniques to identify the characteristic responsible for the catalytic behaviour of boiler ash. The dominant metal elements present in boiler ash especially potassium in various forms were subjected to catalyst testing. The products obtained were analysed using Gas Chromatography- Flame Ionized Detector (GC-FID).

The mechanistic pathway of glycerol transformation to glycerol carbonate was confirmed from time online analysis (TOL) study. The product formation, intermediate compound formation, by-product formation and product decomposition were studied using GC-FID and validated using Nuclear Magnetic Resonance (NMR) as well as Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy (ATR-FTIR) instrumentation techniques for the synthesis of glycerol carbonate. For all three glycerol carbonate, ethylene carbonate and propylene carbonate synthesis the by-products formed were also detected using Gas Chromatography-Mass spectrometry (GC-MS). The active sites and element responsible for the catalytic behaviour of waste boiler ash are studied using a series of catalyst characterisation technique which involves use of Fourier Transform Infrared Spectroscopy (FTIR), Hammett test, Temperature Programmed Desorption-Carbon Dioxide (TPD-$CO_2$), X-Ray Diffraction (XRD), Energy Dispersive - X-Ray Fluorescence (EDXRF), Inductively Couple Plasma- Mass Spectroscopy (ICP-MS), Brunauer Emmett Teller (BET), Thermogravimetry (TGA) and Field Emission Scanning Microscopy-Energy Dispersive X-ray (FESEM-EDX). The element in its existing phase in boiler ash was introduced as a catalyst for the synthesis of glycerol carbonate.

The feasibility of the reaction was studied using crude glycerol collected from local biodiesel industry in Malaysia as a way to accomplish the second objective of this research. The crude glycerol was directly employed for the synthesis of glycerol carbonate without removal of impurities under suitable parameters using waste boiler ash as catalyst. To study the level of interference of impurities in the crude glycerol, an array of reactions were conducted by simulating the presence of each substance in commercial glycerol. The simulated glycerol was prepared accordingly based on the certificate of analysis (COA) data of crude glycerol. The final products of reaction were analysed using GC-FID based on calibration of standard glycerol and glycerol carbonate.

To meet the final objective of the study, the study is also aimed at the viability of the similar reaction approach for the synthesis of other organic carbonate such as ethylene carbonate and propylene carbonate. To prove the concept study, similar synthesis approach was employed but instead of glycerol, the feedstock was replaced to ethylene glycol and propylene glycol respectively. Similarly, GC-FID was used to analyse the product formation and product validations were conducted using NMR, ATR-FTIR and GC-MS.

## 1.6 Significance of Study

The major aim of the research is to introduce a suitable catalyst from waste source for the synthesis of organic carbonates. Therefore, the novelty of the research lies in the introduction of boiler ash from local palm oil industry in Malaysia as a suitable catalyst.

The identified element potassium silicate ($K_2SiO_3$) in it is phase in boiler ash was also reported as a new catalyst for the synthesis of glycerol carbonate for the first time which also added to the significance of the research.

Consecutively, a new scheme of mechanistic pathway was also proposed for the synthesis of glycerol carbonate using waste boiler ash as catalyst. This scheme suggested that glycerol carbonate was formed at an accelerated manner whereby the decomposition of intermediate product was not directly proportional to the product formation. Thus, this result showed that the glycerol carbonate was formed at a faster rate than most study reported earlier using glycerol and urea as feedstock while offering an economical synthesis route due to the usage of catalyst from waste.

To add on, the feasibility study of the suitable reaction conditions and use of waste catalyst with crude glycerol with no initial stages of purification is another innovative finding of this research. The reaction is feasible and will significantly reduce overall operational cost for producing value added fine chemical glycerol carbonate.

The robustness of the synthesis approach was also an important remark of the study whereby the synthesis route with the same catalyst was used to study synthesis of other organic carbonates from different polyol sources. There is no research to date that reports on similar catalyst and reaction route used for the synthesis of different organic carbonates. Therefore, this study can be a platform for further development of synthesis of other organic carbonates in future using waste boiler ash as catalyst.

Organic carbonates specifically glycerol carbonate; propylene carbonate and ethylene carbonate have myriad applications in many major industries. These fine chemicals are used in industries involving polymer, pharmaceuticals, agricultural, semiconductor, personal care products and chemicals. Therefore, this research will significantly impact these industries in general whereby the organic carbonates can be synthesised at a lower operational cost and will be available for use by these industries at a cheaper price.

In concise, the possibility of using direct waste for synthesis of value added product can benefit both industry and environment fundamentally whereby the disposal of these wastes can be reduced over time.

## 1.7 Summary of the Thesis

In general, chapter 1 discuss about the background of the research along with the overall problem statement to the reason the research was conducted. The background of the study is an overview of the reported results and facts that support the aim of the study. The objectives of the research are clearly underlined to meet the problems discussed in the background of research and addressed using the scope of research. Finally, the significance of the research is deliberated in terms of novelty, innovation and contribution of the research towards industry and environment.

On the other hand, chapter 2 is compilation of literatures related to the research carried out. The chapter discusses detailed statistic, values, results and facts reported previously in other study. Several reviews on organic carbonates and its applications, boiler ash from palm oil industry and its uses, glycerol from biodiesel industry, conventional method, modern methods and industrial methods of glycerol carbonate synthesis as well as parameters of synthesis approach are elaborated in this chapter. The chapter also discusses the different mechanistic pathway route that has been reported accordance to the current study of glycerol carbonate (Gly C), ethylene carbonate (EC) and propylene carbonate (PC).

In chapter 3, the research methodology of the study is elucidated. The research methodology is subdivided into five main sections which includes catalyst preparation, catalyst testing, catalyst characterisation, crude glycerol analysis, product analysis and validation. The overall research methodology is portrayed in the research flow chart based on the five subsections. All complete calculation formulas of conversion, selectivity, yield and turnover frequency are discussed in this chapter as well.

Chapter 4 of this research includes results and discussion based on the first objective which is to synthesise glycerol carbonate using waste boiler ash from local palm oil industry under suitable reaction conditions with bio-renewable feedstock. In this chapter critical review and evaluation of the findings on synthesis of glycerol carbonate using boiler ash as catalyst are discussed in the form of graphs and tables, in which it involves various reaction condition parameters, product identification techniques, quantification as well as validation. Next, the chapter aims to identify the active element responsible for the catalytic behaviour of boiler ash and propose scheme of mechanistic pathway. The results and discussion includes graphs, table and scheme that related to the catalyst characterisation, and proposed scheme of mechanistic pathway of reaction as well as the catalyst mechanism. The catalyst reusability study and the characterisation of spent catalyst are also elaborated in this chapter.

Chapter 5 of the thesis covers related results and discussion to meet the second objective of the study which is to utilise the boilers ash directly in crude glycerol. The chapter also focuses on studying the effect of interferences such moisture, methanol and catalyst content in the crude glycerol.

Chapter 6 of this thesis discusses the feasibility of catalytic process of boiler ash in converting other polyols (ethylene glycol and propylene glycol) into their respective organic carbonates. This chapter also elaborates finding on the mechanistic pathway of reaction and catalyst mechanism in the synthesis of ethylene carbonate and propylene carbonate.

In summary, chapter 7 in this thesis is the concluding chapter of the research. The most prominent findings and results of the research are summarised briefly in this chapter in accordance to the research objectives. In concise, the limitation of the study and further recommendations for future work are also suggested in this chapter.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

This chapter is an elaboration of related literatures reviewed in an order to meet the main objectives of the study. The study cover reviews on organic carbonates and its applications, boiler ash from palm oil industry and its uses, glycerol from biodiesel industry, conventional method, modern methods and industrial methods of glycerol carbonate synthesis as well as parameters of synthesis approach including their reaction pathways are elaborated in this chapter.

## 2.2 Organic Carbonates

Organic carbonates are also known as carbonate esters where it contains a carbonyl group attached two alkoxy group (Shaikh & Sivaram, 1996). There are aliphatic organic carbonates (i.e. dimethyl carbonate (DMC) and diethyl carbonate (DEC)) and cyclic forms of organic carbonates (i.e. glycerol carbonate (Gly C), ethylene carbonate (EC) and propylene carbonate (PC)) which are well used in the industry. In this research, the syntheses of cyclic organic carbonates as mentioned in the examples are focused due to their interesting chemical properties and vast application in many major industries.

### 2.2.1 Glycerol Carbonate

4-hydroxymethyl-2-oxo-1,3-dioxolane is an alkylene carbonate also known as glycerol carbonate which bears two hydroxyl group and 2-oxo-1,3-dioxolane group (ODO) (Figure 2.1). This compound has the molecular weight of 118.09 g $mol^{-1}$ with low toxicity, low volatility (vapor pressure is 8 mbar at 177 °C), high boiling point(110–115 °C at 0.1 mmHg and  353.9 °C at 760 mmHg), high flash point (190 °C) and noble biodegradability (Aresta et al., 2009; Sonnati et al., 2013) . This essential chemical properties of glycerol carbonate has been the fundamental criteria in whereby it possess many potential applications (Sonnati et al., 2013).

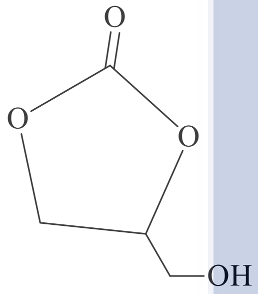


*Figure 2.1.* Structure of glycerol carbonate (4-hydroxymethyl- 2-oxo-1,3-dioxolane).

Looking at the industrial point of view, (Gly C) is reported to be one of the most celebrated products in the last five years. Schols reported in 2014 that the price of glycerol carbonate is about 8141 USD/ton (Schols, Schuurbiers, & Zevenbergen, 2014) and market demand for glycerol carbonate is reported to be few kilo tons per year. This market value was significantly higher than market value of glycerol which was reported to be 240 USD/ton in 2014 (Ciriminna, Pina, Rossi, & Pagliaro, 2014). Glycerol carbonate in general has various applications directly and indirectly as proposed by Pagliaro et al., (2007) and Ochoa-Gómez et al., (2012). Glycerol is directly used as solvent, as plant vitaliser, as blowing agent, as detergent, in batteries, in cement and concrete as well as in cosmetics. The indirect use of glycerol carbonate involves transformation of glycerol carbonate into its derivatives for further applications as surfactants, chemical intermediates and polymers. In addition, glycerol carbonate has also vast potential applications in many major industry as grouped by Teng, Ngoh, Yusoff, and Aroua, (2014) in Figure 2.2. The industry includes polymers and plastic industry, cosmetic and personal care industry, agricultural industry, building and construction industry, pharmaceutical industry, chemical industry as well as semiconductor industry (Plasman et al., 2005; Mizuno et al., 2010a; Jeffsol ® Glycerine Carbonate Bulletin, 2010; Ochoa-Gómez et al., 2012; Sonnati et al., 2013; Ang, Tan, & Lee, 2014).

The synthesis of glycerol carbonate as a fine chemical of interest has been established by Huntsman Corporation and UBE Industries Limited (Ochoa-Gomez, Gomez-Jimenez-Aberasturi, Ramirez-Lopez, & Maestro-Madurga, 2012). Previously, Huntsman Corporation used either propylene carbonate or ethylene carbonate along with glycerol  for the synthesis of glycerol carbonate (Gly C) as reported by Jung, Kim, Hee, and Kim, (2012). Moreover, major glycerol carbonate producing industry Huntsman Corporation have introduced the use of glycerol by-product from the biodiesel industry as the processing raw material for synthesis of glycerol carbonate but the synthesis route is still expected to use ethylene carbonate and propylene carbonate as the carbonate source with synthetic catalyst (Huntsman News). Besides, the crude glycerol may also involve purification procedures before being used. Therefore, a cheaper source of carbonate such as urea can be more economical to these industries in general.

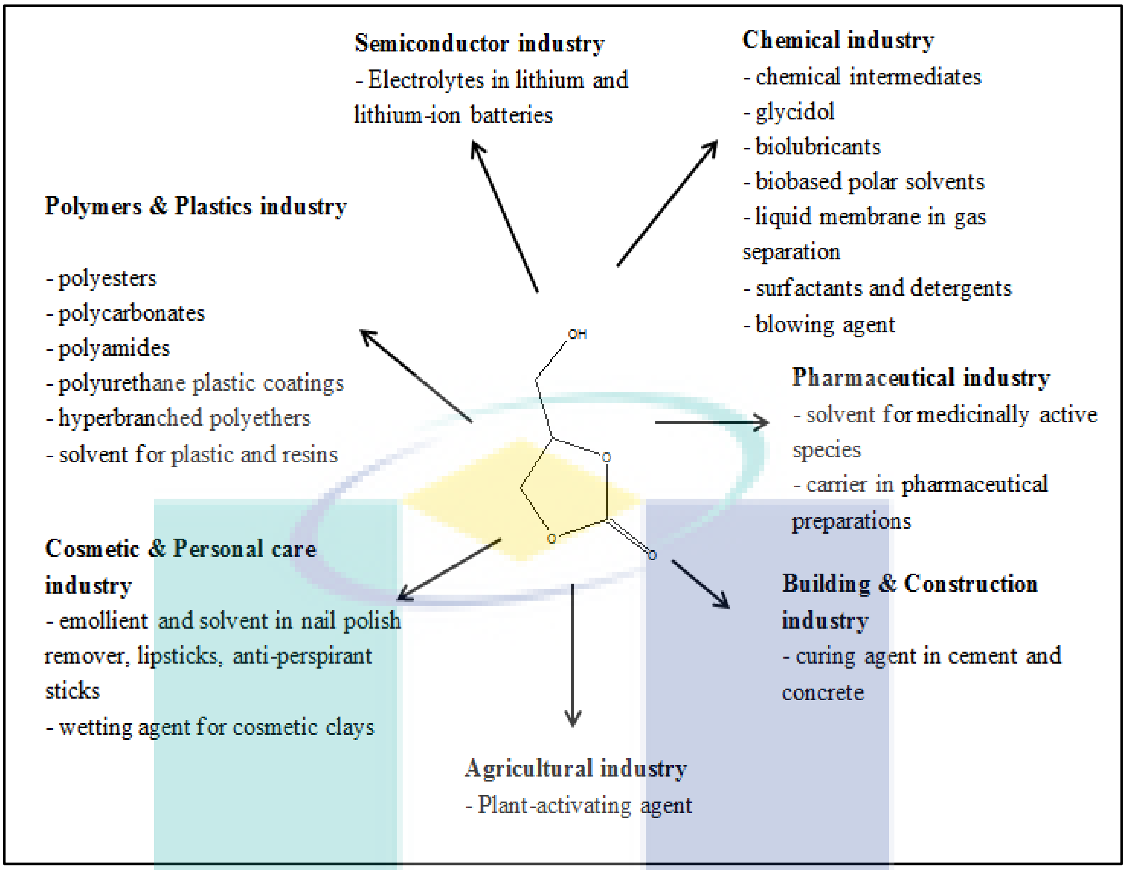


*Figure 2.2.* Glycerol carbonate applications in industries.

Source: Teng et al., (2014).

### 2.2.2 Ethylene Carbonate

1,3-dioxolan-2-one is also known as ethylene carbonate (Figure 2.3) or carbonate ester of ethylene glycol. The properties physical and chemical property of ethylene carbonate include having molar mass of 88.06 g·mol$^{-1}$, boiling point of 260.7 °C, flash point of 150 °C, while being odourless, colourless and being in state of crystalline solid at room temperature. Similarly like glycerol carbonate, ethylene carbonate is also a desired chemical product to many industries due to its interesting chemical properties (Perricone et al., 2013).

Ethylene carbonate acts as an interesting solvent in organic and in organic material where it is used for surface coatings, dyes, fibers, plastics, and batteries. It is also functions as an excellent intermediate for selective alkoxylation, transesterification, and carbamate formation (Jeffsol ® Ethylene Carbonate Bulletin, 2008). Furthermore, ethylene carbonates in industries include in polymers, gas separation membranes, paints, agrochemicals and in batteries as well as supercapacitor (BASF Safety Data, 2012; Perricone et al., 2013)

In recent times, several studies have been reported on production of ethylene carbonate using ethylene glycol and urea as feedstock but the reactions were conducted under reduced pressure and synthetically derived catalyst such as $La(NO_3)_3$ and Zn/Y mixed oxide (Qiu, Jiang, Kang, & Yang, 2012; Wang, P. et al., 2014). In industry, synthesis of ethylene carbonate is focussed using ethylene glycol with direct carbonylation reaction with carbon dioxide using high temperatures and pressures (Clements, 2003). The synthesis of ethylene carbonate through this technique is limited to thermodynamic limitations and it is an expensive cost operations. Besides, previous reports states that the use of ethylene oxide needs much attention due to the risk assessment associated to the toxic nature of ethylene oxide (Liteplo, Meek, & Lewis, 2003). Therefore, the study to use non-toxic feedstock such as ethylene glycol is favoured. In china, industrial grade ethylene carbonate is priced at USD 1,221 - 1,983 per metric ton by Anhui Eaperal Chemical Co. Limited.

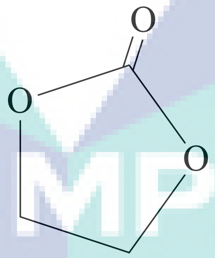


*Figure 2.3.* Structure of ethylene carbonate (1, 3-dioxolan-2-one).

### 2.2.3 Propylene Carbonate

4-Methyl-1,3-dioxolan-2-one is also known as propylene carbonate (Figure 2.4). It has the molecular mass of 102.09 g/mol, boiling point of 242 °C, density of 1.205 $g/cm^3$, non-corrosive, low viscosity and exists as colourless liquid at room temperature.

Propylene carbonate similarly like glycerol carbonate and ethylene carbonate have vast applications in many industries. The use of propylene carbonate as polar solvent is widely known in chemical laboratories and chemical engineering applications (Trivedi, Sarkar, & Pandey, 2009). Their application also include in lithium ion batteries (Wagner et al., 2014), pharmaceutical industry (Tache, Udrescu, Albu, Micăle, & Medvedovici, 2013) and in polymer industry (Barreto, Hansen, & Fredriksen, 2012) and in cosmetics (US Department of Health & Human Services, Household Product Database, 2015). However, the industrial approach of propylene carbonate synthesis route similar to ethylene carbonate uses direct carbonylation of propylene oxide into propylene carbonate by Huntsman corporation (Clements, 2003; Demire, 2015). The current price of propylene carbonate is more than USD 1440 per metric ton (Demire, 2015).

The synthesis is limited to thermodynamic limitations and involves use of toxic propylene oxide which may cause hazard (Institute for Health and Consumer Protection European Chemicals Bureau, 2002). Therefore, similar to ethylene carbonate synthesis, the use of non-hazardous chemical is important to reduce risk of danger industry. The synthesis of propylene carbonate from propylene glycol and urea have been studied by many researchers. However, the temperature of the reactions were relatively higher than the current study and proposed use of synthetics catalysts such as zinc-chromium mixed metal oxide and magnesium titanate (Wu, Guo, Geng, & Xia, 2013; Du et al., 2014).

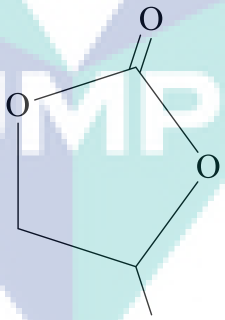


*Figure 2.4.* Structure of Propylene carbonate (4-Methyl-1, 3-dioxolan-2-one).

## 2.3 Bio-renewable Feedstock

Bio-renewable resources are defined as sustainable resources derived naturally. Sustainable denotes that the resources renew at a rate that it will be available for use by the future generation. Bio-renewable resources or feedstock is often referred as substance of biomass generally derived from organic matter of biological origin. They are usually classified as wastes or dedicated energy crops (Brown, 2003).

### 2.3.1 Crude Glycerol

Globally, the production of biodiesel as an alternative energy source is been growing due to demand from depletion of fossil fuel (Nanda, Yuan, Qin, Poirier, & Chunbao, 2014). Biodiesel is a product from transesterification of vegetable oils or animal fats using methanol catalysed by potassium hydroxide or sodium hydroxide (Ma & Hanna, 1999; Chien, Lu, Chai, & Boreo, 2009). Crude glycerol is the major by-product formed from biodiesel production (Hájek & Skopal, 2010). It is believed that for every 100 wt % of biodiesel produced 10 wt % of glycerol is produced as by-product (Thompson & He, 2006) as well as (Johnson & Taconi, 2007). Over the years, production of glycerol as by-product was linearly proportional to the growing biodiesel industry (Johnson & Taconi, 2007; Pagliaro et al., 2007), which resulted in shutdown of many traditional glycerol production plants (Mccoy, 2006).

In recent report by Wahab, (2014) in Malaysia Biofuels Annual 2014 report, there are only 10 operating biodiesel plants in Malaysia out of 31 registered plants. Biodiesel production increased from 140,983 tons in 2012 to 330,032 tons in 2013, of which 175,032 tons was for export and 155,000 tons for domestic use. The jump in production was due to increase in demand for exports markets and expansion of B7 (7% palm methyl ester and diesel) in 2014 as well as B10 (10% palm methyl ester and diesel) starting 2015 which was distributed domestically. On the other hand, exports of biodiesel jumped 6 fold in 2013 with strong demand from the European Union (EU) and China. Collectively the EU and China imported 161,864 tons or 92 % of the exports. The increase in exports to the EU in 2013 was due to a relative decline in the competitiveness of supplies from

Indonesia. Exports during the first 5 months of 2014 were 30,755 tons, which was well off the pace of the previous year. Therefore, an increase in the crude glycerol production from local biodiesel industries in Malaysia is expected. It is estimated that by the year 2016, an excess of 4 billion gallons of crude glycerol will be produced (Rahmat, Abdullah, & Mohamed, 2010). Besides, recent statistical results reported by Nanda and co-researchers in 2014 (Figure 2.5) has shown the production of crude glycerol is in an increasing trend. The increasing by-product has definitely alarmed many researchers across the globe to propose synthesis of value added substances from glycerol as also done in this current study. The current price of crude glycerol is reported to be USD 0.24 per kilogram by the Oil Price Information Service, (OPIS) (Ciriminna et al., 2014).

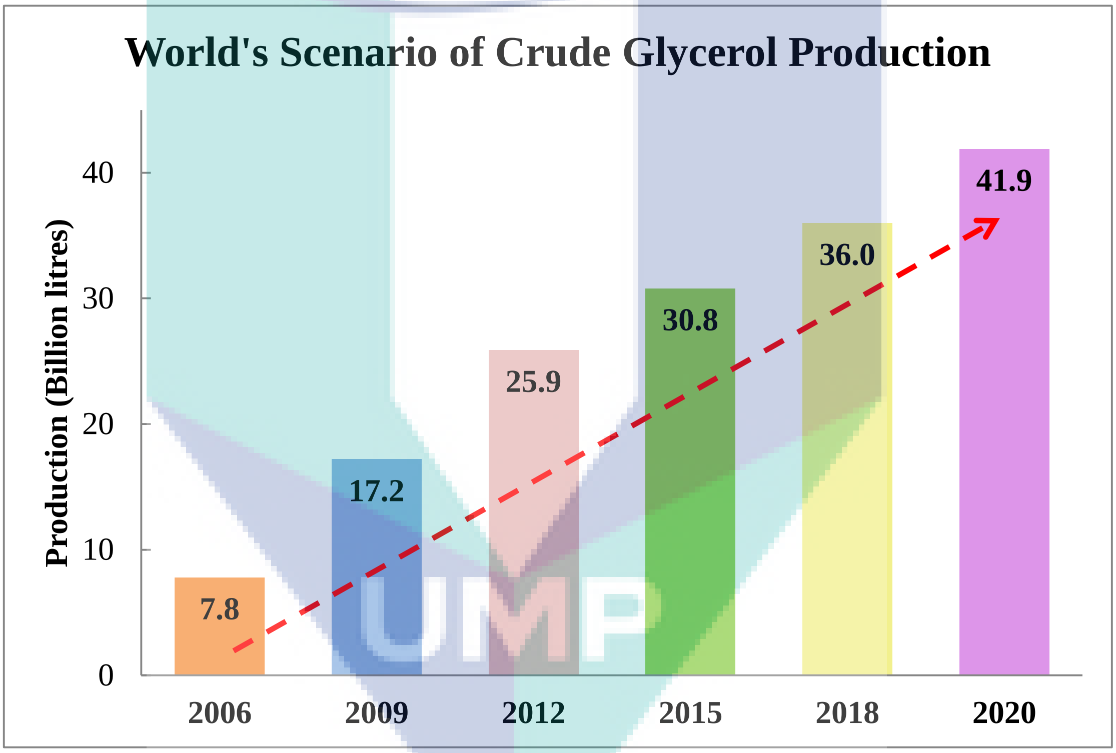


*Figure 2.5.* World’s scenario of crude glycerol production.

Source: Nanda et al., (2014).

The scenario is due to presence of various impurities such as methanol, soap, fatty acid methyl esters (FAMEs, i.e., biodiesel), and alkaline catalyst residues (Santibáñez, Varner, & Bustamante, 2011; S. Hu et al., 2012; Tan, Abdul Aziz, & Aroua, 2013). Over the years, production of glycerol as a by-product has been increasing to an extend where glycerol mounting beyond amount needed for application in industry have created a glut in the glycerol market (Johnson & Taconi, 2007). Therefore, a number of research have been conducted to convert crude glycerol into its value added derivative (Johnson & Taconi, 2007; Behr, Eilting, Irawadi, Leschinski, & Lindner, 2008; Zhou, Beltramini, Fan, & Lu, 2008; Santibáñez et al., 2011). Even though, there are several studies that reports synthesis of value added products from crude glycerol, none of the reports really uses actual waste as feedstock without purification (Ochoa-Gómez, Gómez-jiménez-aberasturi, Ramírez-lópez, & Nieto-mestre, 2011; S. Hu et al., 2012; Tudorache et al., 2013). Therefore, the ability to utilise crude glycerol without any pretreatment and purification steps will simplify the overall process which later on contributes to the reduction of the total production cost.

### 2.3.2 Glycerol and Its Applications

Propane-1, 2, 3-triol or glycerine is also known as glycerol (Figure 2.6). It is an odorless, colorless and non-toxic liquid with molecular mass of 92.09 g/mol and a very high boiling point of 290 °C. It is also a viscous solution with density 1.261 g/cm$^3$. Glycerol having extensive hydrogen bonding within the molecule causes glycerol to have high density and high boiling point. Glycerol is relatively stable when is brought to contact with air where it is believed to have the ability to attract and sustain moisture from environment without being altered (The Soap and Detergent Association, 1990).

*Figure 2.6.* Structure of glycerol (Propane-1, 2, 3-triol).

Glycerol has various applications in many industries as reported by Katryniok, Paul, Bellière-Baca, Rey, and Dumeignil, (2010) (Figure 2.7). Currently, glycerol is reported with having about two thousand applications (Centi & Santen, 2007). The major application of glycerol includes in the drugs and pharmaceutical industry where they are used as solubilizing agents as well as viscosity adjusters where it is used as carrier for antibiotics, antiseptics and plasticizers of medicine capsules (Singhabhandhu & Tezuka, 2010). Besides, they are also used vastly in personal car products where one third of the market of glycerol is controlled by application of glycerol in toothpaste. Glycerol in toothpaste avoids drying and hardening of the paste in the tube (Speight, 2002). Application of glycerol also include in the paper industry and textile industry as lubricant and softeners (The Soap and Detergent Association, 1990).

Even though, there are various applications of glycerol in many areas, still there is rising consciousness to transform glycerol into value added products. This is because the demand towards glycerol need in industry is lower than the amount of glycerol discharged as by-product (Ahmed & Papadias, 2010; Schill, 2012; Viana, Freitas, Leitão, Pinto, & Santaella, 2012). Therefore, the research clearly focuses on transformation of glycerol into glycerol carbonate which an important value added substance to the industry. To add on, crude glycerol purified into glycerol can be also transformed into various products such as propylene oxide, malonic acid, pyruvic acid, propylene glycol, lactic acid, glyceraldehydes, dihydroxy acetones, ketomalonic acid, glyceric acid, glycidol, proponic acid, isopropanol, acetone and acrolein as reviewed by Johnson and Taconi (2007).

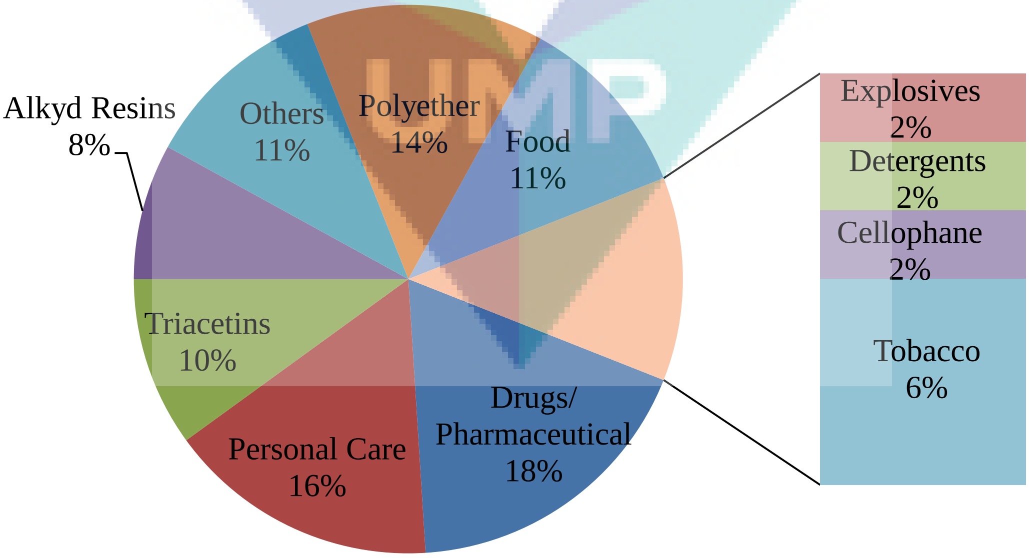


Figure 2.7. Industrial applications of glycerol.

Source: Katryniok et al., (2010).

## 2.4 Other Feedstock

### 2.4.1 Polyols

Polyols are generally classified as alcohols containing more than one hydroxyl group. They have wide range of applications such as bulking agents, emulsifiers, stabilisers, humectants, thickeners, texturisers, glazing agents and anti-caking agents. The general concern is also that they have wide range of application as solvents and as ingredient in the pharmaceutical industry (European Association of Polyol Producers, 2013).

#### 2.4.1.1 Ethylene Glycol

Ethane-1,2- diol or ethylene glycol (Figure 2.8) is an odorless, colorless and sweet tasting liquid. It has the molecular weight of 62.07 g/mol and density of 1.1132 g/cm$^3$. It has a boiling point of 197.3 °C and is moderately toxic. Ethylene glycol has various applications such as they are used in alcohol fuel cells (Livshits, Philosoph, & Peled, 2008), used for the synthesis of acetal and fructones (Song, Zello, Boehman, & Waller, 2004; Shylesh, Sharma, Mirajkar, & Singh, 2004), used as a mediator for the synthesis of nanomaterial (Kim, M. H., Lim, Lee, & Xia, 2008), used as antifreeze, coolant and heat transfer fluid (Staples, 2001; Perkas, Zhong, Chen, Besson, & Gedanken, 2005), used as precursors for polymers (Meyer & Hoelderich, 1999) as well as used for synthetic waxes, separations for aromatic and paraffinic hydrocarbons, detergents for equipment cleaning, and inks for ball-point pens (MEGlobal, 2008). The global market volume for ethylene glycols was 16,511 kilo tons in 2013 and is expected to reach 22,815.4 kilo tons by 2020, growing at a Compound Annual Growth rate (CAGR) of 4.7% from 2014 to 2020. In which Asia-Pacific accounted for 66.5 % of the total market value. The global market for ethylene glycol is expected to reach USD 33.36 billion by 2020, according to a new study by Grand View Research, 2014.

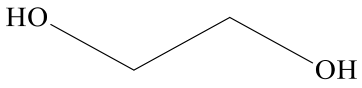


*Figure 2.8.* Structure of ethylene glycol (Ethane-1, 2- diol).

#### 2.4.1.2 Propylene Glycol

Propane-1,2-diol is also known as propylene glycol (Figure 2.9). It has the boiling point of 188.2 °C and density of 1.04 g/cm³ with molecular mass of 76.09 g/mol. It is a compound reported with multipurpose functions where it is used as anti-freeze agent, used in chemical applications, consumer products food and drugs as well as in pharmaceuticals (U.S. Food and Drug Administration, 2014; Cameron, Altaras, Hoffman, & Shaw, 1998; Saxena, Anand, Saran, Isar, & Agarwal, 2010) as well as in polymer resins (Bennett & San, 2001). The propylene glycol market is projected to witness a CAGR of 5.7% between 2014 and 2019, and is expected to generate a global market value of USD 4,194.59 million by 2019 (Propylene Glycol, Global Trends and Forecasts to 2019).

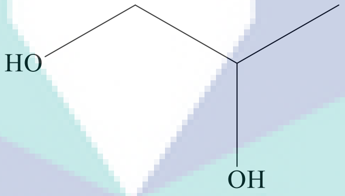


***Figure 2.9.*** Structure of propylene glycol (Propane-1, 2-diol).

### 2.4.2 Urea

Urea or carbamide is an organic compound with two $–NH_2$ groups and one carbonyl (C=O) functional group (Figure 2.10). The molar mass of urea is 60.06 g/mol with density 1.32 g/cm$^3$. Urea is a major component in agricultural industry whereby it is vastly used as fertilizers for crops. The global urea production is about seventy million metric tons per year and is estimated to exceed 200 million metric tons in 2020 (Glibert, Harrison, Heil, & Seitzinger, 2006). In the commercial production of glycerol 2 molecule of ammonia is reacted with one molecule of carbon dioxide under high pressure and temperature to produce urea in a two-step process (Copplestone & Kirk, 1998). In recent times the increase in demand for urea has been growing. Major exporters of commercial urea in Asia includes to China and Indonesia. Total exports of urea is been increasing since 2011 to 2013 from 18057 to 20630 metric tons in Asia. In 2014 global urea demand was about 179800 metric tons and capacity for supply was 212600 metric tonnes. Urea used as non-fertilizers were more than 30000 metric tons (Agrium, 2014). On the other hand, due to increase in number of exporters and production of urea in excess the price of urea is relatively low and declining over the years. The current price of urea is about 187.22 USD per metric ton (IRM, 2016).

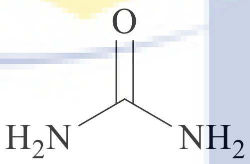


*Figure 2.10.* Urea.

## 2.5 Synthesis Routes of Cyclic Organic Carbonates

There are various routes of synthesis of cyclic organic carbonates and it was divided into three main section consisting conventional, modern and industrial synthesis route. The conventional route involves use of toxic phosgene gas while the modern route includes transcarbonation, direct carbonylation, enzymatic catalysis and oxiranes. On the other hand, industrial synthesis route is adapted from modern synthesis route which favours the use of transcarbonation route.

### 2.5.1 Conventional Synthesis Route through Phosgenation

The conventional synthesis route which typically used for synthesis of cyclic carbonate involved the use of phosgene an essential carbonate source. Nemirowsky in the year 1883 and Franklin in 1948 introduced the synthesis of glycerol carbonate with glycerol and phosgene (Sonnati et al., 2013). Synthesis of organic carbonates using phosgene involves reaction with alcohol and release of by-product hydrochloric (HCl) gas (Vriet & Mouloungui, 2005). Subsequently, researchers proposed synthesis of cyclic organic carbonates since then which bears a 2-oxo-1,3-dioxolane group (ODO) (Figure 2.11) (Burk & Roof, 1993; Seki et al., 2011). In the beginning, the use of phosgene as a carbonate source for the synthesis of organic carbonates was favoured due to the simple and effective reaction steps, but the toxicity and hazard problem related to phosgene caused decline in use of the chemical over the years (Rousseau et al., 2009; Li, J. & Wang, 2011a). Thus, there were rising need for substitution of the conventional method.

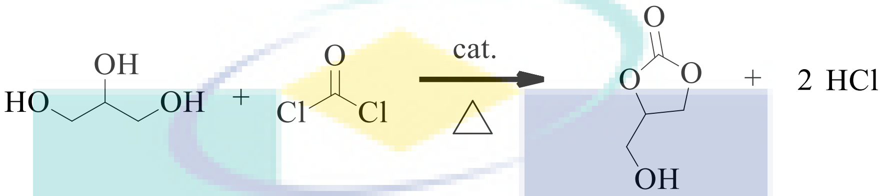


*Figure 2.11.* Synthesis of organic carbonates using phosgene.

### 2.5.2 Modern Synthesis Routes

In order to overcome the toxicity problem related to synthesis of organic carbonates using phosgene as a carbonate source, several synthesis approaches to replace phosgenation has been introduced in the modern era which involved transcarbonation, direct carbonylation, enzymatic catalysis route and oxirane route. Details explanation on each synthesis route is elaborated in the following sub-sections.

#### 2.5.2.1 Transcarbonation

Transcarbonation is also known as the carbonate exchange reaction with carbonate sources and alcohol to produce organic carbonates (Vriet & Mouloungui, 2005).

#### i. Dimethyl carbonate (DMC)

Dimethyl carbonate synthesis reaction with methanol and urea was studied as a suitable carbonate source for the synthesis of glycerol carbonate. Glycerol and dimethyl carbonate is reacted to produce glycerol carbonate and methanol is removed as a by-product (Figure 2.12) (Singh, Reddy, Ganesh, & Mahajani, 2014). However, these reaction uses synthetically derived catalyst. The reaction in some cases requires use of solvents such as benzene and dimethylformamide, use of pressure and larger molar ratio of DMC to glycerol. The authors reported the use of $ZnO/La_2O_3$ mixed oxides as catalyst in their study. The reaction was also limited to decomposition of Gly C to glycidol due to the presence of methanol.

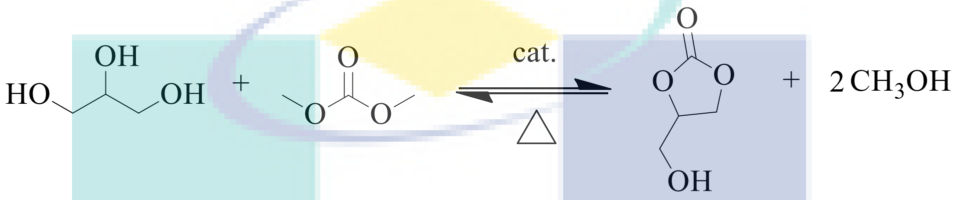


*Figure 2.12.* Synthesis of glycerol carbonate using DMC and glycerol.

**ii. Diethyl carbonate (DEC)**

Similarly like dimethyl carbonate an alkyl carbonate source, diethyl carbonate is also used for the synthesis of glycerol carbonate (Figure 2.13). In this reaction ethanol is removed as by-product Álvarez, Plíšková, Segarra, Medina and Figueras, (2012). In this synthesis approach Álvarez and co-workers proposed use of hydrotalcites supported on α and γ-$Al_2O_3$ which are also synthetically derived catalyst.

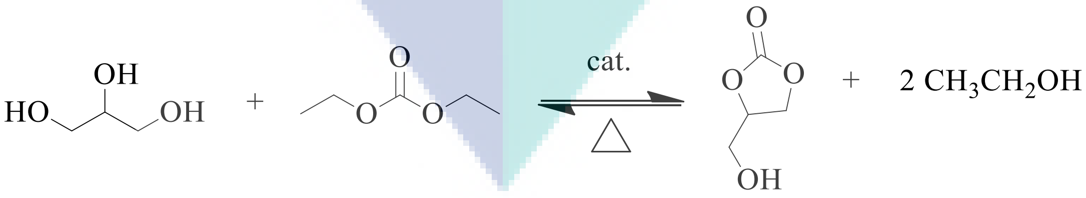


*Figure 2.13.* Synthesis of glycerol carbonate using DEC and glycerol.

Even though, there are many researches that have been carried out using DMC and DEC as a carbonate source for the synthesis of glycerol carbonate, the reported researches used larger ratio of DMC or DEC to glycerol (refer Table 2.1 in section 2.6.4).

Thus, this would significantly impact the price of the carbonate produced as it requires huge amount of carbonate source.

### 2.5.2.2 Direct Carbonylation

#### i. Carbon monoxide (CO)

Synthesis of glycerol carbonate is possible through direct carbonylation of glycerol using carbon monoxide followed by oxidation (Figure 2.14). However, due to toxicity associated with carbon monoxide the reaction is limited where to safety of handling carbon monoxide is a fatal risk both in normal laboratories and industrial scales (Teles, Rieber, & Harder, 1994; J. Li & Wang, 2011a). The synthesis routed used higher pressures and took longer reaction durations. In the study by Teles and co-researchers in 1994 found that salts of mercury and copper were employed as catalyst in which these catalyst are synthetically derived and mercury containing catalyst is known to be hazardous.

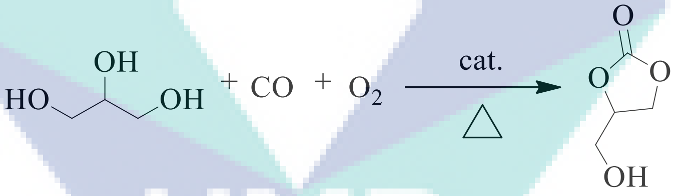


*Figure 2.14.* Carbonylation of glycerol using carbon monoxide.

#### ii. Carbon dioxide ($CO_2$)

Synthesis of organic carbonates (i.e. glycerol carbonate) can be conducted using glycerol and carbon dioxide with aid of catalyst (Figure 2.15) (George et al., 2009). However, the feasibility of the reaction was limited thermodynamically resulting in poor yield in most reactions in which higher temperature and pressure was required to solubilize carbon dioxide gas into the liquid phase of glycerol (Li, J. & Wang, 2011a). The reaction was also limited to use of excess carbon dioxide gas and in some cases longer reaction time. Besides, the formation of water causes decomposition of glycerol carbonate into glycerol where the reaction is reversible (Nohra, Candy, Blanco, Raoul, &

Mouloungui, 2012). George and co-researchers reported use of dibutyltin (IV) oxide as catalyst which is relatively expensive and synthetically derived.

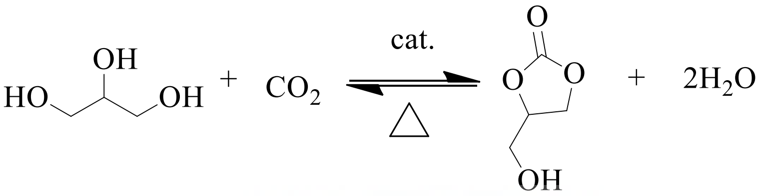


*Figure 2.15.* Carbonylation of glycerol using carbon dioxide.

### 2.5.2.3 Enzymatic catalysis

Several studies report the use of enzymes as catalysts are positive towards glycerol carbonate formation. This enzymes in forms of lipases can be used to synthesise glycerol carbonate by reacting glycerol and dimethyl carbonate (Figure 2.16) (Min & Lee, 2011**;** Seong et al., 2011)**.** It is very important to control the reaction parameters as enzymes are very sensitive to the phase of environment (humidity and moisture) as well as temperature. The denaturation of enzymes at higher temperature results in the enzyme deactivation that enhances yield of glycerol carbonate formation.

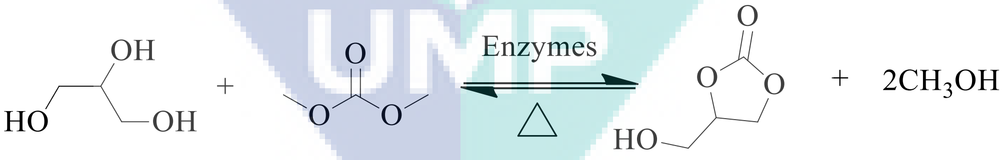


*Figure 2.16.* Enzymatic catalysis synthesis route of glycerol carbonate.

### 2.5.2.4 Oxirane route

In the synthesis route involving oxirane, carbon dioxide is reacted with oxirane to form cyclic carbonate (Figure 2.17) (Webster, 2003; Hwang, Son, Park, Park, & Oh, 2009). In the glycerol carbonate synthesis the glycidol is used as an oxirane. Kossev, Koseva, & Troev (2003) suggested the use of calcium chloride as catalyst for the cycloaddition of carbon dioxide into oxirane for the synthesis of glycerol carbonate which is a 5-membered (hetero) cycles.

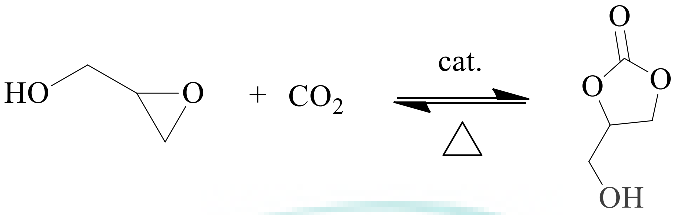


*Figure 2.17.* Synthesis of organic carbonates using oxirane.

### 2.5.3 Industrial Synthesis Route

The industrial synthesis approach of organic carbonates specifically glycerol carbonate is controlled majorly by the Huntsman Petrochemical Corporation. Previously, the typical synthesis route of glycerol route in the industry uses petrochemical derivative ethylene carbonate or propylene carbonate along with glycerol under optimised conditions (Figure 2.18) (Clements, 2003; Jung et al., 2012). However, the reaction is a two-step reaction where ethylene carbonate is synthesised from reaction of ethylene oxide and carbon dioxide followed by the transcarbonation of ethylene carbonate and glycerol (Figure 2.19) (Behr et al., 2008). On the other hand, UBE Industries produce glycerol carbonate using transcarbonation method with DMC as illustrated in Figure 2.12 (UBE Group, 2014). Similar to UBE Group, major glycerol carbonate producing industry, Huntsman Corporation have introduced the use of glycerol by-product from the biodiesel industry as the processing raw material for synthesis of glycerol carbonate but the synthesis route is limited to the use of synthetically derived catalyst and expensive source of carbonate such as ethylene carbonate and propylene carbonate as aforementioned.

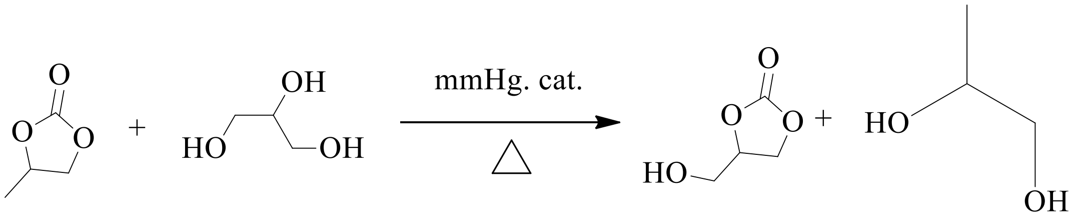


*Figure 2.18.* Glycerol carbonate synthesis route by Huntsman Petrochemical Corporation.

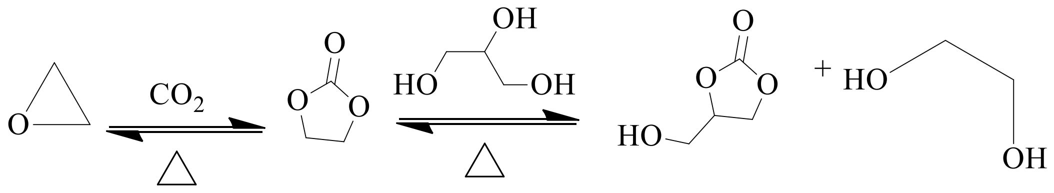


*Figure 2.19.* Two step synthesis of glycerol carbonate by Behr et al., (2008).

### 2.5.4 Glycerolysis of Urea

Synthesis of glycerol carbonate using bio-renewable feedstock glycerol and urea is considered an environment friendly approach (Figure 2.20). Study by Li, J. and Wang (2011a) suggest that the calculation of chemical equilibrium constant of glycerol and urea favoured lower pressure and higher temperature for the synthesis of glycerol carbonate. Catalyst bearing Lewis acidic sites seemed to produce better yield as reviewed by Sonnati et al., (2013).

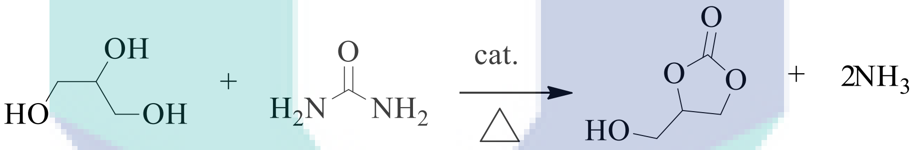


*Figure 2.20.* Synthesis of glycerol carbonate using glycerol and urea.

Synthesis of glycerol carbonate using glycerolysis of urea has interested many researchers in recent time due to the economical synthesis approach using low cost, and abundant urea as carbonate source. Besides, the reaction is also environment friendly as review by Sonnati et al., (2013).

## 2.6 Summary of Synthesis Approaches, Advantages and Disadvantages of Different Synthesis Routes.

Table 2.1 is a summary of synthesis approaches of glycerol carbonate which includes transcarbonation reaction of glycerol using dimethyl carbonate (DMC) and diethyl carbonate (DEC).Other routes of glycerol carbonate synthesis include direct carbonylation reaction using glycerol along with carbon monoxide and carbon dioxide.

Besides, enzymatic catalysis for glycerol carbonate synthesis is also summarised in this table. Direct carbonylation reaction using oxirane and carbon dioxide is also discussed in brief. On the other hand, synthesis of glycerol carbonate using glycerol and ethylene carbonate is also tabulated in table 2.1. The final section of the table discusses the glycerolysis reaction with urea to produce glycerol carbonate. Table 2.2 discusses the advantages and disadvantages of different synthesis route of glycerol carbonate.

Table 2.1
*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| **Reactants mol ratio** | **Solvent** | **Temperature (°C)** | **Pressure (MPa)** | **Reaction time (h)** | **Gly C Yield (%)** | **Catalyst** | **References** |
|---|---|---|---|---|---|---|---|
| | | | **Glycerol + Dimethyl Carbonate (DMC)** | | | | |
| 2:1 DMC: Glycerol | Free | 120 | 0.1 | 6 | 92 | Tetra-n-butlyammonium bromide | (Grey, 1992) |
| 3:1 DMC: Glycerol | Free | 75 | 0.1 | 3 | 97 | $K_2CO_3$ | (Rokicki, Rakoczy, Parzuchowski, & Sobiecki, 2005) |
| 1:1 DMC: Glycerol | Free | 180 | 5 | 1.5 | 65 | n-$Bu_2Sn(OMe)_2$ | (Aresta et al., 2006) |
| 2.5:1 DMC: Glycerol | Benzene | 60 | 0.1 | 2 | 95 | CaO | (Li, J. & Wang, 2011b) |
| 5:1 DMC: Glycerol | Dimethylformamide | 100 | 0.1 | 1 | 75 | Uncalcined Mg-Al hydrotalcite | (Takagaki, Iwatani, Nishimura, & Ebitani, 2010) |
| 2:1 DMC: Glycerol | Free | 78 | 0.1 | 1 | 99 | KF/hydroxyapatite | (Bai, Wang, Mei, Li, & Li, 2011) |
| 5:1 DMC: Glycerol | Free | 75 | 0.1 | 1.5 | 95 | Mg/Al/Zr | (Malyaadri, Jagadeeswaraiah, Prasad, & Lingaiah, 2011) |
| 5:1 DMC: Glycerol | Dimethylformamide | 100 | 0.1 | 0.5 | 79 | Calcined hydrotalcite-hydromagnesite | (A. Kumar, Iwatani, Nishimura, Takagaki, & Ebitani, 2012) |
| | | | **Glycerol + Diethyl Carbonate (DEC)** | | | | |
| 4:1 DEC: Glycerol | Free | 85 | 0.1 | 1 | 83 | Mg-La Oxide | (Simanjuntak et al., 2013) |

Table 2.1 continued

*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| **Reactants mol ratio** | **Solvent** | **Temperature (°C)** | **Pressure (MPa)** | **Reaction time (h)** | **Gly C Yield (%)** | **Catalyst** | **References** |
|---|---|---|---|---|---|---|---|
| | | | **Glycerol + Diethyl Carbonate (DEC)** | | | | |
| 6:1 DEC: Glycerol | Free | 150 | 0.1 | 2 | 96 | Zinc/Lanthanum Mixed-Oxide | (Singh et al., 2014) |
| 5:1 DEC: Glycerol | Free | 100 | 0.1 | 2 | 99 | 1,3-dichlorodistannoxanes | (Patel, George, Pillai, & Munshi, 2009) |
| 17:1 DEC: Glycerol | Free | 130 | 0.1 | 60 | 97 | Mg/Al hydrotalcite-like | (Alvarez et al., 2010) |
| 21:1 DEC: Glycerol | Dimethyl Sulfoxide | NR | 0.1 | 8 | 84 | Hydrotalcites supported on $Al_2O_3$ | (Álvarez et al., 2012) |
| | | | **Glycerol + Carbon Monoxide (CO)** | | | | |
| Excess CO and $O_2$ | Free | 110 | 0.6 | 63 | 47 | CuCl | (Teles et al., 1994) |
| Excess CO and $O_2$ | Nitrobenzene | 130 | 0.8 | 20 | 96 | CuCl | |
| Excess CO and $O_2$ | Dimethylformamide | 140 | 3 | 2 | 85 | $PdCl_2$(phen) + KI | (Hu, J. et al., 2010) |

Table 2.1 continued

*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| **Reactants mol ratio** | **Solvent** | **Temperature (°C)** | **Pressure (MPa)** | **Reaction time (h)** | **Gly C Yield (%)** | **Catalyst** | **References** |
|---|---|---|---|---|---|---|---|
| **Glycerol + Carbon Monoxide (CO)** | | | | | | | |
| 5: 1.5: 3: 1 $Et_3N$: $CuBr_2$: S: Glycerol | DMF or DMSO | 80 | 1 | 21 | 92 | None | (Mizuno, Nakai, & Mihara, 2010b) |
| 5:1:5 $K_2CO_3$:Se: Glycerol | DMF | 20 | 0.1 | 6 | 83 | None | (Mizuno et al., 2010a) |
| **Glycerol + Carbon Dioxide ($CO_2$)** | | | | | | | |
| Excess $CO_2$ | Free | 180 | 5 | 15 | 7 | n-$Bu_2Sn(OMe)_2$ | (Aresta et al., 2006) |
| Excess $CO_2$ | Methanol | 80 | 3.5 | 4 | 35 | n-$Bu_2SnO$ | (George et al., 2009) |
| Excess $CO_2$ | Methanol | 140 | 5 | 59 | 0.24 | $RhCl_3$ + $PPh_3$ +KI | (Ezhova et al., 2012) |
| 1:3:3 $K_2CO_3$: HCl: Glycerol | Free | 80 | 0.1 | 30 | 80 | KOH then HCl | (Gómez-Jiménez-Aberasturi et al., 2010) |
| 1.5:1:1 $[N(CH_2CH_3]_3$: HCl: Glycerol | Free | 100 | 2.5 | 1 | 90 | None | (Ochoa-Gómez, Gómez-Jiménez-Aberasturi, et al., 2011) |
| Excess $CO_2$ | Acetonitrile | 150 | 7 | 3 | 17 | Cu/Mg-Al-Zr | (Zhang & He, 2014b) |

Table 2.1 continued

*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| Reactants mol ratio | Solvent | Temperature (°C) | Pressure (MPa) | Reaction time (h) | Gly C Yield (%) | Catalyst | References |
|---|---|---|---|---|---|---|---|
| | | | **Enzymatic Catalysis** | | | | |
| 3:1 DEC: camellia oil | Free | 50 | 0.1 | 24 | 95 | Lipases (Lipozyme TL IM and Novozym 435) | (Wang, Y. & Cao, 2011) |
| 1:1 DMC: Glycerol | Tetrahydrofuran | 60 | 0.1 | 30 | 99 | Lipase (Novozyme 435) | (Kim, S. C., Kim, Lee, Yoon, & Song, 2007) |
| 10:1 DMC: Glycerol | Free | 70 | 0.1 | 48 | 90 | Lipase (Novozyme 435) | (Lee, K. H., Park, & Lee, 2010) |
| 10:1 DMC: Glycerol | Free | 60 | 0.1 | 4 | 59 | Lipase (Aspergillus niger) | (Tudorache, Protesescu, Coman, & Parvulescu, 2012) |
| 10:1 DMC: Corn oil | Free | 60 | 0.1 | 15 | 62 | Lipase (Novozyme 435) | (Min & Lee, 2011) |
| 6:1 DMC: Soybean oil | tert-Butanol | 60 | 0.1 | 48 | 92 | Lipase (Novozyme 435) | (Seong et al., 2011) |
| | | | **Oxirane + (Carbon Dioxide) $CO_2$** | | | | |
| Ethylene oxide + excess $CO_2$ | Dichloromethane | 25 | 0.1 | 24 | NR | (Porphinato)aluminum alkoxide | (Aida & Inoue, 1983) |

Table 2.1 continued

*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| **Reactants mol ratio** | **Solvent** | **Temperature (°C)** | **Pressure (MPa)** | **Reaction time (h)** | **Gly C Yield (%)** | **Catalyst** | **References** |
|---|---|---|---|---|---|---|---|
| **Oxirane + (Carbon Dioxide) $CO_2$** | | | | | | | |
| Propylene oxide + excess $CO_2$ | Free | 40 | 4.9 | 1 | 100 | $Bu_3SnI + Bu_4PI$ | (Baba, Nozaki, & Matsuda, 1987) |
| Propylene oxide + excess $CO_2$ | Free | 170 | 4 | 4 | 97 | $TEBACl + CaCl_2$ | (Kossev et al., 2003) |
| Poly(glycidyl methacrylate) + excess + excess $CO_2$ | Dimethylformamide | 100 | 0.1 | 24 | 100 | $NaI + Ph_3P$ | (Kihara & Endo, 1992) |
| Allyl glycidyl ether + excess $CO_2$ | Free | 100 | 3.45 | 48 | 98 | 1-hexyl-3-methylimidazolium chloride | (Hwang et al., 2009) |
| **Glycerol + Ethylene Carbonate** | | | | | | | |
| 2 : 1<br>EC: Glycerol | Free | 80 | 0.1 | 1 | 88 | Amberlyst A26 $HCO_3^-$ | (Mouloungui et al., 1996) |
| 2 : 1<br>EC: Glycerol | Free | 80 | 0.1 | 2 | 81 | Zeolite | |

Table 2.1 continued

*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| Reactants mol ratio | Solvent | Temperature (°C) | Pressure (MPa) | Reaction time (h) | Gly C Yield (%) | Catalyst | References |
|---|---|---|---|---|---|---|---|
| | | | **Glycerol + Ethylene Carbonate** | | | | |
| 2 : 1<br>EC: Glycerol | Free | 50 | 0.1 | 5 | 82 | Al/MgO hydrotalcite | (Climent et al., 2010) |
| 2 : 1<br>EC: Glycerol | Free | 50 | 0.1 | 5 | 78 | MgO | |
| 2 : 1<br>EC: Glycerol | Free | 50 | 0.1 | 5 | 68 | Al/Mg hydrotalcite | |
| 2 : 1<br>EC: Glycerol | Free | 80 | 0.1 | 1.5 | 92 | RNX-MCM41 | (Cho, Kwon, Tharun, & Park, 2010) |
| 1.5 : 1<br>EC: Glycerol | Supercritical $CO_2$ | 40 | 10 | 1 | NR | Amberlyst A26 OH | (Vieville et al., 1998) |
| | | | **Glycerol + Urea** | | | | |
| 1 : 1 (Urea: Glycerol) | Free<br>150 | 150 | $4.0 \times 10^{-3}$ | 2 | 61 | Calcined manganese sulfate | (Claude et al., 2000) |
| 1 : 1 (Urea: Glycerol) | Free | 140 | $3.0 \times 10^{-3}$ | 2 | 86 | Zinc Sulfate | (Yoo & Mouloungui, 2003) |

Table 2.1 continued

*Summary of different synthesis routes of glycerol carbonate (Gly C)*

| **Reactants mol ratio** | **Solvent** | **Temperature (°C)** | **Pressure (MPa)** | **Reaction time (h)** | **Gly C Yield (%)** | **Catalyst** | **References** |
|---|---|---|---|---|---|---|---|
| | | | **Glycerol + Urea** | | | | |
| 1 : 1 (Urea: Glycerol) | Free | 145 | $3.9 \times 10^{-3}$ | 5 | 72 | Calcined Zn hydrotalcite | (Climent et al., 2010) |
| 1 : 1 (Urea: Glycerol) | Free | 145 | 0.1 | 4 | 69 | $Co_3O_4$/ZnO nanodispersion | (Rubio-Marcos, Calvino-Casilda, Bañares, & Fernandez, 2010) |
| 1.5 : 1 (Urea: Glycerol) | Free | 150 | 0.1 | 4 | 55 | Gold, gallium, and zinc supported on oxides and zeolite ZSM-5 | (Hammond et al., 2011) |
| 1 : 3 (Urea: Glycerol) | Free | 140 | $3.0 \times 10^{-3}$ | 1 | 91 | $La_2O_3$ | (Wang, L. et al., 2011) |
| 1 : 1 (Urea: Glycerol) | Free | 140 | $1.4 \times 10^{-2}$ | 6 | 46 | Ionic liquids immobilized onto a structurally modified Merrifield peptide resin Green | (Kim, D.-W. et al., 2011) |
| 1.5 : 1 (Urea: Glycerol) | Free | 150 | $4.0 \times 10^{-3}$ | 7 | 75 | Metal monoglycerolates | (Turney, Patti, Gates, Shaheen, & Kulasegaram, 2013) |

NR= not reported

Table 2.2

*Advantages and disadvantages of different synthesis routes of glycerol carbonate*

| **Synthesis route** | **Advantages** | **Disadvantages** |
|---|---|---|
| Glycerol + Phosgene ($COCl_2$) | -Effective synthesis route<br>-Two step synthesis route | • Environmentally toxic chemical<br>• Hazardous chemical that causes fatal death upon consumption |
| Glycerol + Dimethyl carbonate (DMC) | -Two step synthesis route | • Higher ratio of DMC to glycerol<br>• Some requires use of solvent<br>• Higher temperature allows chemical shift towards Gly C formation |
| Glycerol + Diethyl carbonate (DEC) | -Two step synthesis route | • Higher ratio of DMC to glycerol<br>• Some reactions requires use of solvent<br>• Higher temperature allows chemical shift towards Gly C formation |
| Glycerol + Carbon monoxide (CO) | -Two step synthesis route | • Hazardous chemical reaction<br>• Require oxygen gas<br>• Thermodynamic limitation |
| Glycerol + Carbon dioxide ($CO_2$) | - One step synthesis | • Thermodynamic limitation<br>• Expensive catalysts |
| Enzymatic catalysis | - Two step synthesis route | • Highly intense parameters monitoring due to enzyme denaturation |

Table 2.2
*Advantages and disadvantages of different synthesis routes of glycerol carbonate*

| **Synthesis route** | **Advantages** | **Disadvantages** |
|---|---|---|
| Oxirane + $CO_2$ | - One step synthesis route | • Thermodynamic limitation |
| Glycerol + Ethylene Carbonate/ Propylene carbonate | - Two step synthesis route | • Use of expensive catalyst<br>• More than two stages of synthesis route<br>• Expensive feedstock derived from petroleum sources |
| Glycerol + Urea | - One pot synthesis<br>- Bio-renewable feedstock<br>- Abundant<br>- Cheap<br>- Solvent-free | |

## 2.7 Catalyst

### 2.7.1 Influence of Acidic and Basic Property of Catalyst towards Glycerolysis with Urea

There are several studies on acidic and basic catalysts that have been conducted to understand the catalytic activity of glycerolysis with urea. Based on these studies, it was found that basic catalyst relatively suited the reaction to support better selectivity and higher activity of catalyst as reported by Wang, L. et al., (2011) and Hammond et al., (2011). Mixed oxide catalysts are reported to be stable form of catalyst with promising role of activity in acid catalysed reaction. However, they do not show higher selectivity towards glycerol carbonate formation (Kumar, et. al., 2012). Lewis acid (basic catalysts) catalysed reactions are vital for Lewis acid to form complexes with carbonyl compounds where they play a fundamental role in organic synthesis (Santelli & Pons, 1995) in which Lewis acids acts as electron pair acceptors (Katryniok et al., 2010). In the case of glycerolysis with urea to form glycerol carbonate, Lewis acids plays a fundamental role to activate the carbonyl group of urea (Climent et al., 2010; Sonnati et al., 2013; Kim, D.-W. et al., 2014). On the other hand, the conjugate basic site attached to Lewis acid activates the hydroxyl group of glycerol to assist formation of glycerol carbonate with carbonyl group of urea (Climent et al., 2010; C. R. Kumar et al., 2012; Marakatti & Halgeri, 2015). It was also found that acidic catalyst generally increased formation of isocyanic acid, which was not a favoured route of formation of organic carbonates due to poor yield and selectivity (Q. Li, Zhang, Zhao, Wei, & Sun, 2006).

### 2.7.2 Palm Oil Boiler Ash

Malaysia is the second largest palm oil producer in the world after Indonesia. After the period of 1990's, palm oil has been the most consumed oil in Malaysia after soybean oil. Thus, the production of palm oil has been in increasing pattern since then (Figure 2.21) (Malaysian Palm Oil Board, 2015). In the year 2010, it was reported that the production of palm oil was 17.5 million tons (Foreign Agricultural Service, Production, Supply and Distribution Online, United States Department of Agriculture (USDA), 2010). Besides, several studies reported that about 4 million tons of boiler ash is produced per year from incineration of palm fruits, palm kernel, palm shells, and palm fibre (Lee, K. T. et al., 2004; Zainudin et al., 2005). Therefore, there were rising concern on proper disposal of these ashes that resulted in this research to make use of these ashes as catalysts (Shuit et al., 2009).

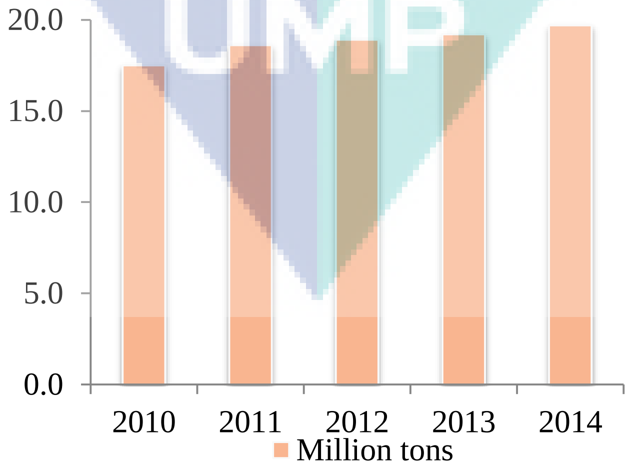


*Figure 2.21*. Production of crude palm oil in Malaysia.

Source: Malaysian Palm Oil Board (MPOB), (2015).

To add on, boiler ash over the years has been vastly used in many area of application. It was found that boiler ash could act as a good absorbent due to its spongy and porous characteristic as reported by Jaturapitakkul, Kiattikomol, Tangchirapat, and Saeting, (2007). Boiler ash composed of mainly silica, potassium, calcium, magnesium and aluminium and other minor elements. Boiler ash being a result of biomass decomposition through incineration had no toxic effect in general (Ooi et al., 2014). Thus, it was employed in a wastewater treatment research where it was capable removing 97% zinc ions from wastewater with capacity of 0.01 mg/g absorbance. Moreover, this research affirmed that boiler ash could act as good absorbent of moisture (Chu & Hashim, 2002). Few research also proposed the use of boiler ash as additional cement-like material where it improved the strength of the cements (Tangchirapat, Tangpakasit, Waew-kum, & Jaturapitakkul, 2003; Sata, Jaturapitakkul, & Kiattikomol, 2004). Furthermore, boiler ash was also utilised to convert waste cooking oil into biodiesel through transesterification (Chin, Hameed, & Ahmad, 2009). Recent study also proposed the use of boiler ash from palm oil mill as suitable catalyst for the synthesis biodiesel (Ho et al., 2012; Ho, Ng, Gan, & Tan, 2014). However, no reports suggested that boiler ash could be used for the synthesis of organic carbonates previously.

### 2.7.3 Boiler Ash and Its Carbon Content Properties

Boiler ash from palm oil mill typically contains variety of metal elements such as potassium, calcium, magnesium, aluminium, sodium, zirconium, zinc, iron and sodium. The basic property of the boiler ash is majorly influenced by these elements existing in metal oxide form. Besides, the presence of carbon in boiler ash also contributed to the basicity, this mainly due to the availability inorganic materials such as silica and metal ions.

Generally, there are four main contributors to carbon basicity that have been identified, namely surface oxygen groups (specifically, pyrone type groups), surface nitrogen (and, possibly, some phosphorus and sulfur) functional groups, basal planes and edges of graphene layers, and some inorganic species. In addition, the concept of site accessibility has been remarked as a necessary condition for a site to contribute effectively to the basicity of carbons (Montes-Moran, Suarez, Angel Menendez, & Fuente, 2012).

Therefore, pure carbon element alone could not possibly pose the basic property of boiler ash. To add on, study by Hammond and co-researchers in 2011 suggested that gold supported on carbon material had poor activity with only 22 % yield of glycerol carbonate which was comparable to the blank reaction. Hence, the activity of carbon is assumed to be limited in catalysing the reaction of glycerolysis with urea. In addition the carbon bonded to hydrogen in ashes are generally hydrophobic in nature which is expected not to interact with hydrogen bonding of glycerol (Ahnert, Arafat, & Pinto, 2003; Goncalves, Molina-Sabio, & Rodriguez-Reinoso, 2010).

On the other hand, the carbon hydrophilicity is generally related to oxygen atoms bonded on surface of carbon and not by carbon itself which tends to react with hydrogens from water and other polar substances. Besides, carbons are usually activated through chemical activation in order to allow hydrophobicity and hydrophilicity nature of the carbon (Müller & Gubbins, 1998). Therefore, this could be a pertinent factor in contribution of the activity of the gold supported on carbon to be low as it does not poses hydrophilic properties as an element by itself.

## 2.8 Reaction Conditions and Parameters for Glycerolysis of Urea to Produce Glycerol Carbonate

In the year 2013 Turney and co-researchers reported that increasing temperature of reaction of glycerol and urea from 100 °C to 150 °C increased yield of glycerol carbonate. However, further increase in temperature to 160 °C shows drastic reduction in yield of product formed. This scenario was supported by Lundström et al., (2011) whereby he proposed that urea decomposes into isocyanic acid at temperature above 150 °C. It is also reported that prolonging duration beyond optimum reaction time the yield of by-products increases considerably. This is due to the decomposition of glycerol carbonate in prolonged reactions (Aresta et al., 2009; Rahim et al., 2012; Kim, D.-W. et al., 2014).

The amount of catalyst loaded may significantly affect conversion of glycerol and selectivity towards glycerol carbonate formation. Study by Narkhede and Patel, (2015) suggests that increasing amount of catalyst from 50 to 150 mg increased the conversion of glycerol but decreased selectivity towards glycerol carbonate while increasing amount of catalyst beyond 100 mg. From the study it is found that glycerol carbonate decomposes into its by-product as catalyst amount is increased to 150 mg. The study reveals that catalyst activity can be majorly influenced by amount of catalyst loaded into the reaction. On the other hand, study by Park et al., (2012) suggest that increasing mol % of catalyst loaded after reaching equilibrium may not alter conversion and effect yield of product formed by increasing amount of active sites beyond sufficient amount.

Typically, the catalytic reaction is operated under reduced pressure to remove formation of ammonia and improve yield of carbonate formation (Climent et al., 2010; Turney et al., 2013). However, conducting reaction under this condition may require use of vacuum and may result in increasing the operational cost. Therefore, the alternative route to remove excess ammonia formed is by flowing inert gas such as nitrogen. Several studies report the use of nitrogen gas by flowing gas into the system continuously (Aresta et al., 2009; Rahim et al., 2012; Kim, D.-W. et al., 2014). Besides, increasing molar ratio of urea to glycerol effects the conversion percentage of glycerol as reported by Rahim et al., (2012); Turney et al., (2013) and Kim, D.-W. et al., (2014). Urea in this scenario acts as a limiting reactant whereby the amount of urea loaded effects the conversion of glycerol significantly and thus influencing the amount of glycerol carbonate formation.

## 2.9 Comparison of Synthesis Mechanistic Pathways

### 2.9.1 Glycerol Carbonate Synthesis using Glycerol and Urea

Over the years synthesis of glycerol carbonate using urea and glycerol as feedstock have interest several researchers due to their interesting chemical properties. However, two alternate synthesis routes with different intermediate and by-product formation have been proposed by researches due to influence of reaction parameters and catalysts. Several researchers proposed synthesis of glycerol carbonate through the formation of 2,3-dihydroxypropyl carbamate (glycerol carbamate) route (Figure 2.22) where by the carbonyl group of urea attaches to the hydroxyl group of glycerol by removing ammonia gas as by-product and forms the intermediate carbamate which further decomposes into glycerol carbonate (Aresta et al., 2009; Hammond et al., 2011; Rahim et al., 2012).

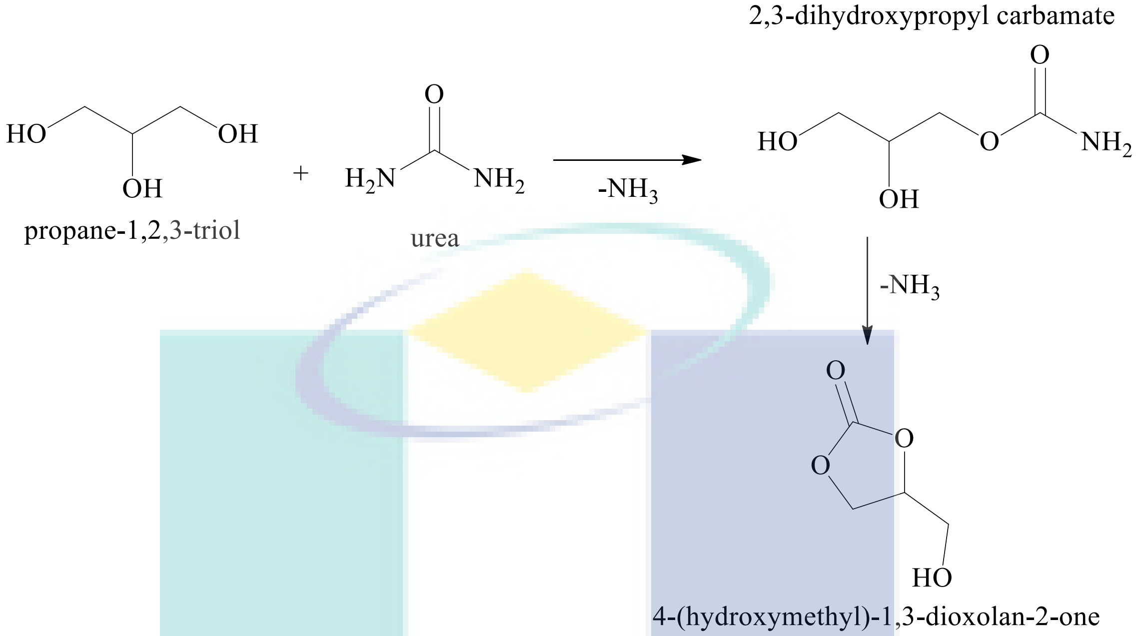


*Figure 2.22.* Glycerol carbonate synthesis route by glycerol carbamate intermediate formation.

Another synthesis route proposed is the isocyanic route (Figure 2.23). Li et al., (2006) described that the reaction involved loss of ammonia from urea to form isocyanic acid in initial stages of reaction. Then this isocyanic acid attacks the hydroxyl group of glycerol forming glycerol carbamate as the intermediate product. Similarly as the earlier reaction synthesis route the carbamate formed decomposes into glycerol carbonate. However, this route suffered from poor yield of carbonate and longer reaction time.

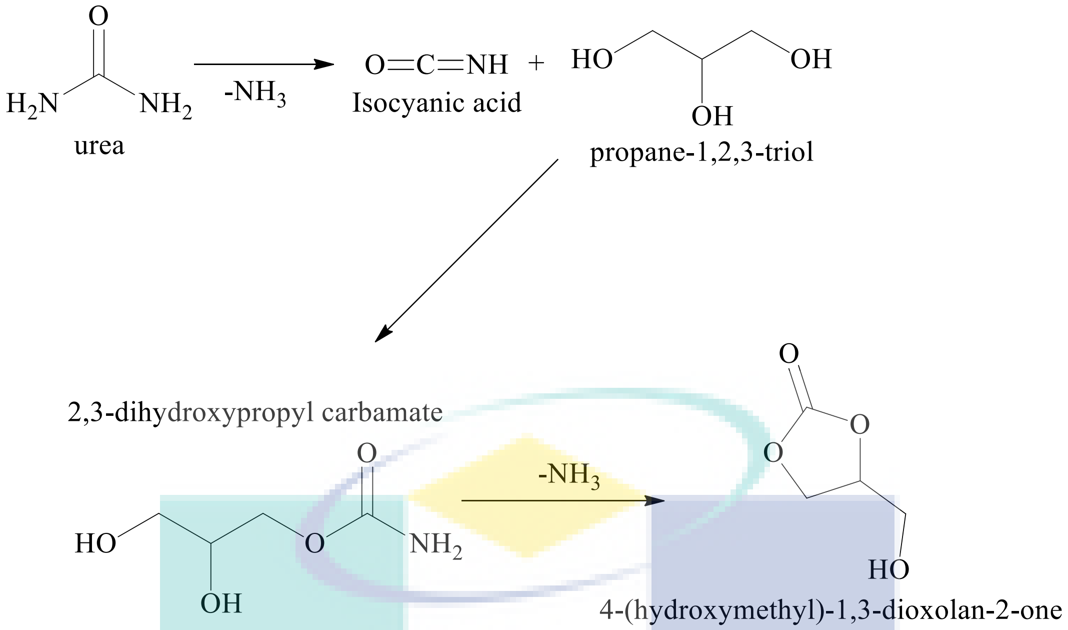


*Figure 2.23.* Glycerol carbonate synthesis route by isocyanic acid formation.

### 2.9.2 Ethylene Carbonate Synthesis using Ethylene Glycol and Urea

Similar to synthesis of glycerol carbonate, the synthesis of ethylene carbonate was reported to follow two different synthesis routes. The first synthesis route involved formation of intermediate carbamate known as 2-hydroxyethyl carbamate (ethylene carbamate) (Figure 2.24) as reported by Bhadauria et al., (2012).

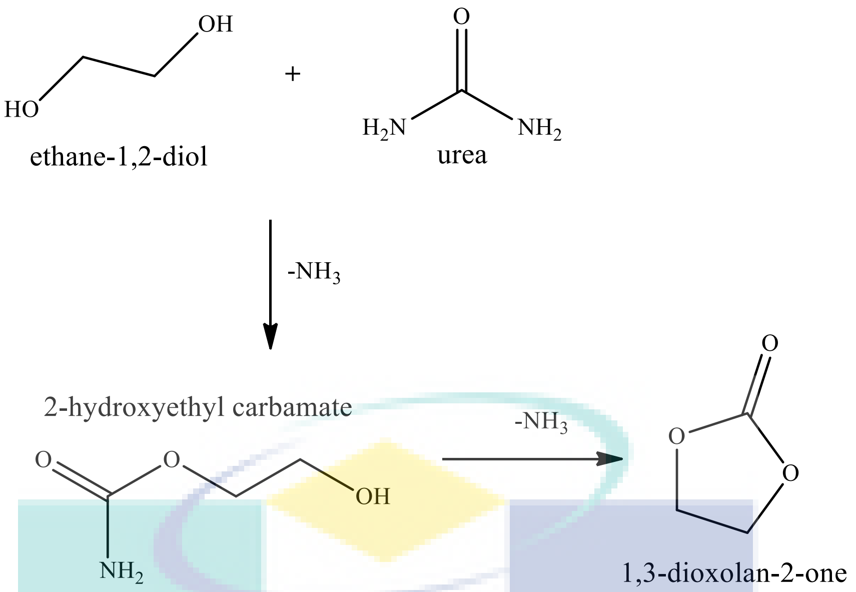


*Figure 2.24.* Ethylene carbonate synthesis route by ethylene carbamate intermediate formation.

The synthesis of ethylene carbonate was also possible through the isocyanic acid formation pathway (Figure 2.25). At elevated temperature similar to synthesis of glycerol carbonate in (section 2.9.1), urea decomposes into isocyanic acid which later reacts with ethylene glycol to form intermediate compound 2-hydroxyethyl carbamate. The carbamate then forms ethylene carbonate (Sharma, Dwivedi, Dixit, & Prasad, 2013). It was also found that acidic catalyst favoured promotion of icocyanic acid (Q. Li et al., 2006).

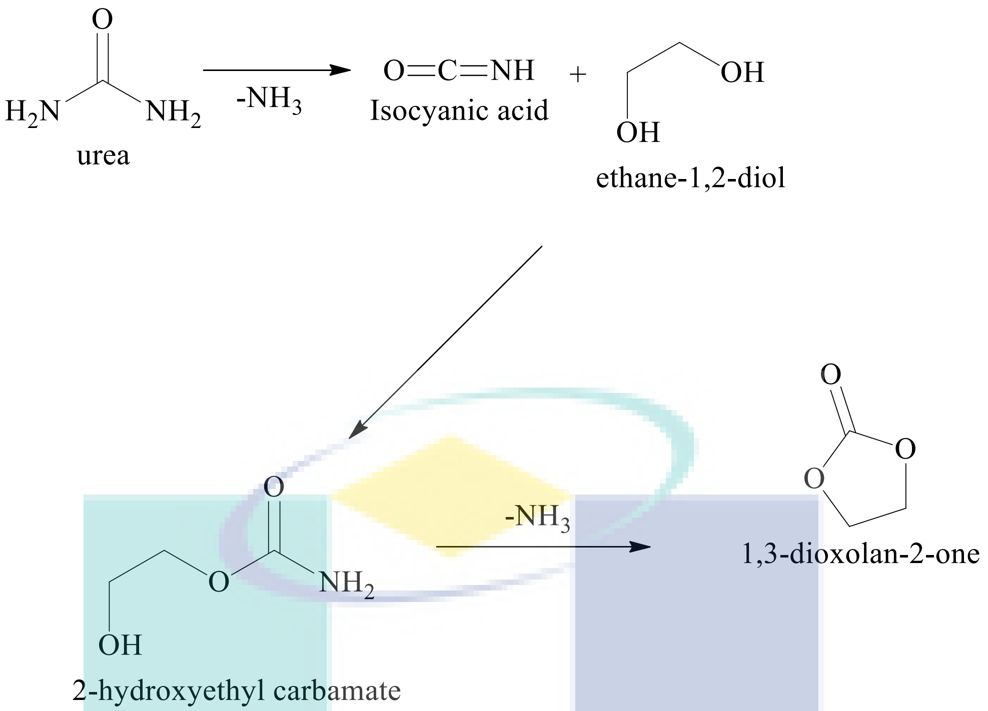


*Figure 2.25*. Ethylene carbonate synthesis route by isocyanic acid formation.

### 2.9.3 Propylene Carbonate Synthesis using Propylene Glycol and Urea

Similar to synthesis of glycerol carbonate and ethylene carbonate, synthesis of propylene carbonate through cycloaddition of urea as well as propylene glycol also can occur through the two different synthesis mechanistic pathway which in involves direct formation of intermediate 2-hydroxypropyl carbamate (Figure 2.26) as reported by Du et al., (2014) and the isocyanic acid (Figure 2.27) pathway .

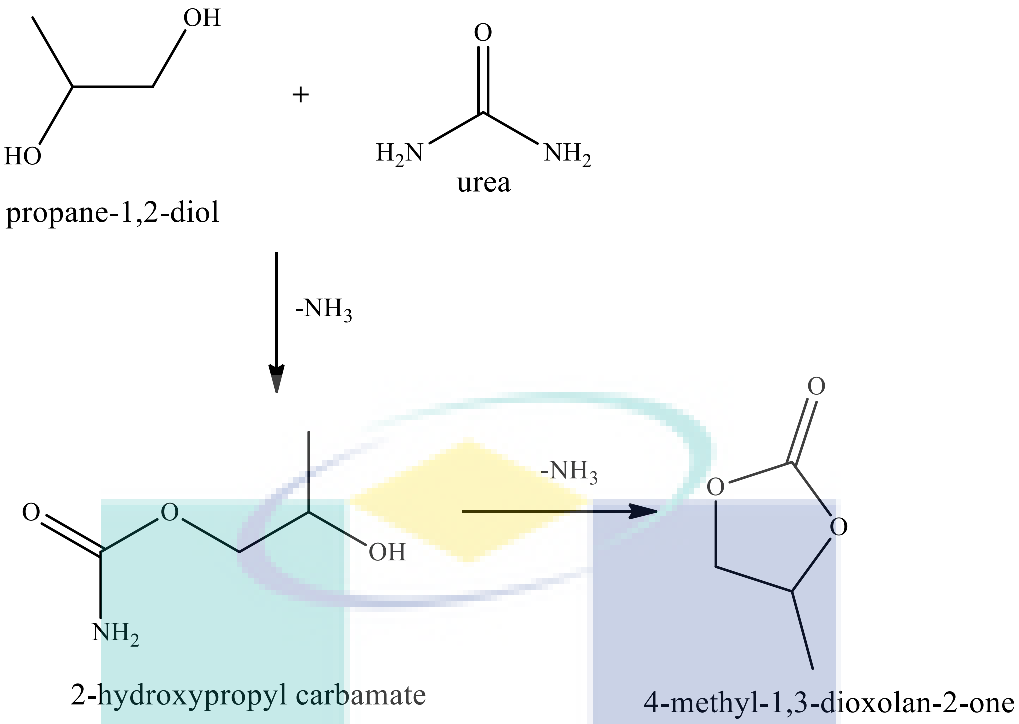


*Figure 2.26.* Propylene carbonate synthesis route by propylene carbamate intermediate formation.

In the study carried out by Wang, D., Zhang, Cheng, Wu, and Xue, (2014), formation of isocyanic acid was confirmed in synthesis of propylene carbonate as in Figure 2.31. The formation of this compound is attributed to the temperature of the reaction which was conducted at 180 °C. This is because urea decomposes at temperature higher than 155 °C into isocyanic acid as reported by Lundström et al., (2011).

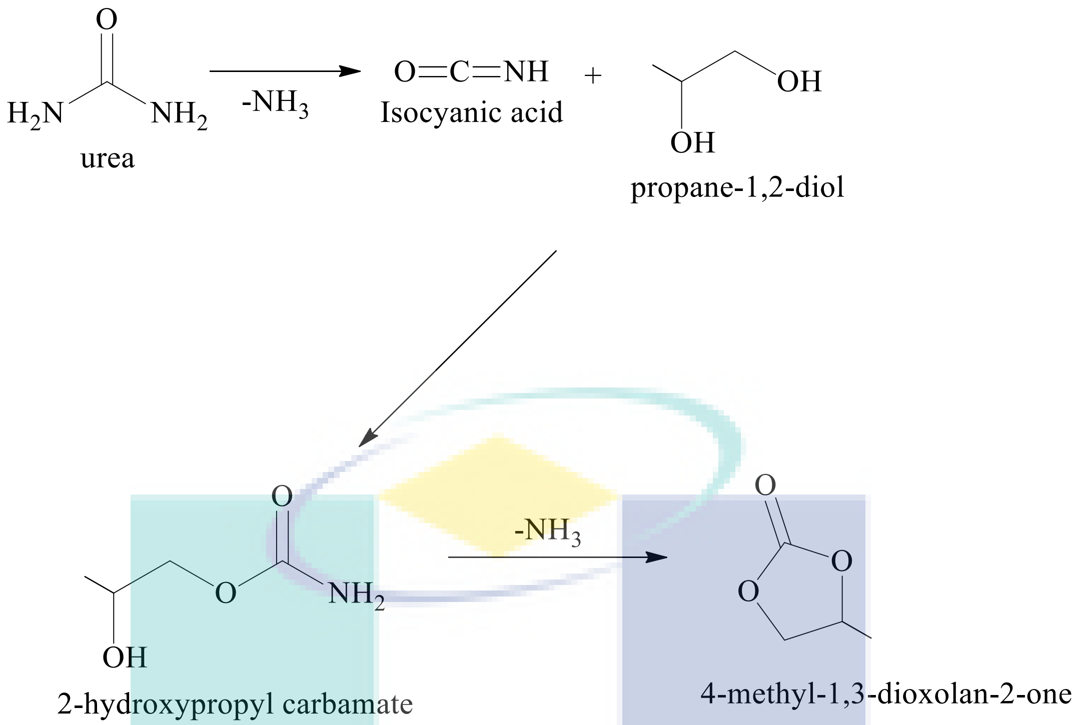


*Figure 2.27.* Propylene carbonate synthesis route by isocyanic acid formation.

## 2.10 Catalytic Comparison through Turnover Frequency (TOF) Value

Turnover frequency (TOF) is described as the amount of mmol of glycerol converted into glycerol carbonate (yield of glycerol carbonate) per gram catalyst per total reaction time (h). A study by Boudart, (1995) claimed that turnover rates as turnover frequency (TOF) in which the term rate referred the number of active catalytic sites available in a catalyst. It was generally classified as number of catalytic cycle per unit time, usually in seconds. In short, there are many advantages of TOF. Firstly, if a complete detail of an experiment is fully described along with their amount of active sites, TOF can be reproduced in different laboratories by repeating the same experiment. Thus the theoretical value of TOF will allow us to compare rates of other catalyst with different material, metal or phases. Besides, even though TOF is only an approximation, it allows researchers to have a rough idea on the catalyst sites while predicting the lifetime of the catalyst up to which cycle. Next, materials with different amount of active sites will have different TOF values in which they can provide experimental results without the effect of heat and mass transfer that can be used to compare catalytic activity of other experiments. Lastly, TOF is useful in judging whether an introduced material has the ability to have better catalytic activity comparing with other catalysts used in similar experiments (Boudart, 1995). In this study, the TOF is used to compare activity of boiler ash and potassium silicate with other catalysts reported by previous researchers.

## 2.11 Summary

From an overall point of view, the major drawback found in previous works related to the current study suggests that there are no available works on direct crude utilisation for the synthesis of glycerol carbonate using glycerolysis reaction with urea. Besides, none of the existing catalyst employed in glycerolysis of urea derived from waste, in which indirectly affect the total operational cost. In addition, most known routes other than glycerolysis reaction with urea poses disadvantages in which they are hazardous, uses synthetically derived catalyst, uses solvent in reactions and poses thermodynamic limitations. Therefore, the use of catalyst derived from boiler ash and direct crude glycerol utilisation through the glycerolysis reaction with urea which is near a complete green chemistry approach study can benefit the industry fundamentally. On the other hand, the feasibility study on the boiler ash to synthesis other organic carbonates such as ethylene carbonate and propylene carbonate which are industrially favoured chemical as reviewed earlier will be an innovation study.

# CHAPTER 3

# METHODOLOGY

## 3.1 Introduction

This chapter is an overall summary of materials and methods used to meet the objectives of the research. This chapter is subdivided into five main parts where the first section lists all materials used. The second section is an elaboration of methods as well as techniques used for catalyst characterisation. The third section discusses the reaction parameters and setup used for catalytic synthesis of organic carbonates. On the other hand, the fourth section is a discussion on analytical techniques used for final product analysis and validation. The final section explains about the methods used for the characterisation of crude glycerol.

## 3.2 Materials

Glycerol, 99.5% was purchased from Sigma Aldrich and urea (AR Grade) was purchased from Friendemann Schmidt Chemical. Waste boiler ash used as catalyst was collected from palm oil mill located in Lepar Hilir, Pahang, Malaysia. The boiler ash used is the mixture of ash obtained from incineration of palm fruits, palm kernel, palm shells and palm fiber. Potassium hydroxide (KOH) ≥85.0%, potassium silicate ($K_2SiO_3$) ≥ 99.9 %, potassium chloride (KCl) ≥ 99.0 %, magnesium oxide (MgO) ≥ 99.0 %, calcium oxide (CaO) ≥ 99.99 %, silicon dioxide ($SiO_2$) of 99.9 % trace metals basis, propylene glycol 99.9 %, ethylene glycol 99.9 %, ethylene carbonate 99.9 % and propylene carbonate 99.9

%, used were purchased from Sigma-Aldrich. Potassium methylate and Sodium methylate used were obtained from Artistic Support Sdn. Bhd. Gases such as nitrogen ($N_2$) and compressed air (78.0 % of nitrogen gas, 21.0 % of oxygen and 1.0 % of other gases such as carbon dioxide, argon and helium) were obtained from Callserv Sdn. Bhd. were also used in this study. Methanol ACS Reagent, ≥ 99.8 % was purchased from Sigma Aldrich.

## 3.3 Catalyst Preparation and Characterisation

### 3.3.1 Catalyst Preparation

Raw boiler ash obtained from palm oil mill in Lepar Hilir, Pahang, Malaysia (Figure 3.1) was dried at 110 ˚C overnight and then powdered using mortar and pestle. Then the ash was sieved using 200µm sized sieve (denoted as BA 110). Later, 2 g of the sieved ash were loaded on the calcination boat and calcined using a Nabertherm horizontal tube furnace under static air environment at temperature (500 ˚C, 700 ˚C, 900 ˚C and 1100 ˚C respectively) for 4 h. The catalysts were later denoted as BA 500, BA 700, BA 900 and BA 1100, respectively. Commercial $K_2SiO_3$, KCl, KOH, MgO, CaO and $SiO_2$ were directly used without any pretreatment.

*Figure 3.1.* Boiler ash from Lepar Hilir 2 Palm Oil Mill Pahang.

### 3.3.2 Catalyst Characterisation

#### 3.3.2.1 Thermogravimetric Analysis (TGA)

As reviewed by Coats and Redfern, (1963), thermogravimetric analysis can be described as a method of thermal treatment subjected to a matter where in which increasing temperature may result in weight loss. These changes relate to the reactions during decomposition, the loss of volatile material and the reactions with the surrounding atmosphere. Thus, it might affect the phase transformation of tested materials. Besides, the TGA studied provides results on highest durable temperature of a specific material tested, additionally with effect of pressure and gas.

In TGA analysis, a crucible containing the sample is heated in a furnace at a controlled rate and weighed continuously. Temperature and mass data are collected and processed by software installed in the computer. This method was used to characterise the physico-chemical property of an element, compound or material. Thermo-gravimetric Analyser Mettler Toledo TGA/DSC-HT/1600 was used to analyse thermal stability and phase transformation of catalyst in the range of temperature between ambient to 1200 ˚C under static air environment at increment of 10 ˚C/min.

#### 3.3.2.2 X-Ray Diffraction (XRD)

X-Ray diffraction is a primary technique used to identify phase of crystalline material and provide unit cell dimension while it can also provide information on elements in amorphous material of partial crystalline system (Connolly, 2007).

X-Ray Diffraction Rigaku Miniflex II was set to analyse the XRD pattern of the catalysts. Diffraction patterns were recorded with Cu Kα radiation (λ = 1.5406 A) operated at 40kV and 30mA over the range of 3 degree to 80 degree at 2 Theta (θ) for crystalline phase determination at scan speed of 0.04 degree/s. The catalysts samples, BA 110, BA 700, BA 900, spent BA 900, $K_2SiO_3$ and spent $K_2SiO_3$ in powder form were loaded individually on a glass sample holder for measurement.

### 3.3.2.3 Energy Dispersive X-Ray Fluorescence (EDXRF)

Energy Dispersive X-Ray Fluorescence (EDXRF) is a very unique analysis that allows detection of chemical composition of all kinds of materials in solid, liquids and filtrates form. The analysis technique is also fast, accurate and non-destructive where it requires simple sample preparation. Elements from Sodium to Uranium can be analysed using EDXRF (Brouwer, 2010). Shimadzu Energy Dispersive X-Ray Fluorescence (EDXRF) 720 was used to analyse metal oxide content in boiler ash (BA 110 and BA 900). The analyses were conducted based on acceptable calibration range at CuKa 8.00-8.05 while the instrument was operated at 50 Kv and 30 µA. Most Industries does not normally deal with individual elements. The elements interested are almost always present in minerals, combined with oxygen. Therefore, XRF calibration software uses the raw intensity of the element being analysed, but since the calibration data is input as % oxides, the instrument converts the elemental intensity to an oxide percentage. The sum of the oxides plus Limiting Oxygen Index (L.O.I) also adds up to close to 100%

### 3.3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectrum is also known as molecular vibrational spectrum. When a sample is exposed to infrared radiation, the molecules in the sample selectively absorb radiation of specific wavelengths which causes change in the dipole moment of sample molecules (Stuart, 2004). Hence, the vibrational energy levels of molecules in the sample transfer from ground state to the excited state. The frequency is then determined by the absorption peak due to the vibrational energy gap. The number of absorption peaks of a sample is related to the number of vibrational freedom of the molecules present in the sample. The change of dipole moment and the possibility of the transition of energy levels are closely related to the intensity of absorption peaks. Therefore, by analysing the infrared spectrum, fingerprint in absorption of peaks from the vibrations of atoms in bonds can be obtained which later on contributed to structural determination information of a compound. In general, no two compounds have similar bonding structure, FTIR can serve as a basis to qualitatively analyse presence of different compound based on their functional group (Lampman, Pavia, Kriz, & Vyvyan, 2010).

The Fourier Transform Infrared spectroscopy (*FTIR)* Perkin Elmer Spectrum 100, USA was used to study the functional group present in the catalyst that could also attribute to depict the phase of metal present in the catalysts BA 110, BA 700, fresh and spent BA 900, fresh and spent $K_2SiO_3$. FTIR transmission data were collected for pressed catalyst disk made with KBr with ratio of (1:10) catalyst to KBr in the scanning range of 4000–400 $cm^{-1}$.

### 3.3.2.5 Field Emission Scanning Electron Microscope – Energy Dispersive X-Ray (FESEM-EDX)

Field Emission Scanning Electron Microscope (FESEM) in general can provide spatial resolution up to 1 nm which is a result of narrower probing beams at low and high electron emission. FESEM coupled with Energy Dispersive X-Ray (EDX) allow elemental analysis of elemental composition and morphological phases present in a sample. The intensity of backscattered electrons generated by electron bombardment can be correlated to the atomic number of the element within the sampling volume. Thus, qualitative elemental information can be revealed (Restivo, Degano, Ribechini, Arantegui, & Colombin, 2014).

Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX), JEOL (JSM-7800f) using Leo Supra 50VP Field Emission with spatial resolution up to 1 nm was used to study the surface morphology and elemental analysis of the catalysts BA 110, BA 900, fresh and spent $K_2SiO_3$.

### 3.3.2.6 Brunauer-Emmett-Teller (BET) Surface Area Measurements

The Brunauer, Emmett and Teller (BET) technique is the most common method for determining the surface area of powders, ashes and porous materials. Nitrogen gas is usually employed as the probe molecule and is exposed to a solid sample under investigation with liquid nitrogen conditions (Zielinski & Kettle, 2013). The BET (Brunauer-Emmett-Teller) method was used to measure the total specific surface areas of the boiler ash catalysts using a Thermo Finnigan Sorptomatic 1990 nitrogen adsorption-desorption-77K analyser. Sample was oven dried at 100 °C for 12 h before analysis. Degassing of sample was conducted at 350 °C for 24 h before analysis. Analysis was conducted on raw boiler ash, BA 110 and BA 900. Micromeritics'ASAP® 2020 Accelerated Surface Area and Porosity Analyser was used to analyse both fresh and spent $K_2SiO_3$. The procedures using BET instrument were initiated with the samples being dried with nitrogen purging. The volume of the gas being adsorbed at the surface of the particles is measured by referring to the boiling point of nitrogen at -196 °C. The number of gas adsorbed corresponds to the particles on total surface area, which includes the pores present on the surface.

#### 3.3.2.7 Hammett Test

Hammett test is known as a preliminary analysis of basic and acidic property of samples using variety of acidic and basic indicators. The Hammett test was carried out on BA 110, BA 500, BA 700, fresh and spent BA 900, BA 1100, fresh and spent $K_2SiO_3$, KCl, KOH, MgO, CaO, $SiO_2$, potassium methylate and sodium methylate where phenolphthalein, 2, 4-dinitroaniline, 4-nitroaniline and methyl red were used as indicators to determine the qualitative acidic as well as basic properties of the catalyst. The method of analysis was performed as reported by Niju, Meera Sheriffa Begum and Anantharaman, (2014) with slight modification. 25 mg of catalyst were weighed and prepared in three batches. 5 mL of methanol was added to the catalyst. Then, 1 mL of the indicator was added to 4 mL of methanol. Final volume of 5 mL indicators were added separately to the catalysts weighed in batches. The mixture was then left to equilibrate for 2 h. The colour changes were observed and noted.

#### 3.3.2.8 Temperature Programmed Desorption – Carbon Dioxide (TPD-$CO_2$)

In temperature programmed desorption (TPD), reactive gas is adsorbed on to the surface of material and desorbed through heating in a flow of inert gas (Klepel & Hunger, 2005). In TPD-$CO_2$, carbon dioxide due to its acidic property acts as a probe by adsorbing on to the material base sites (Tanabe, Misono, Hattori, & Ono, 1989). At different heating levels, adsorbed gaseous are desorbed then analysed using detector, typically thermal conductivity detector (TCD) and mass spectrometer (MS) (Supamathanon, Wittayakun, Prayoonpokarach, Supronowicz, & Roessner, 2012).

The quantitative basicity strength was analysed using Temperature Programmed Desorption, (Thermo FinniganTPD/R/O 1100 Thermo electron) for BA 110, BA 900, fresh and spent $K_2SiO_3$ catalysts. The TPD was equipped with a thermal conductivity detector (TCD). In specific, 50 mg of sample was treated at 200 °C for 1 h by passing helium at a flow rate of 20 mL/min. Then, the sample was saturated with carbon dioxide at a flow rate of 30 mL/min and at temperature ramping of 10 °C/min up to 200 °C for 1 h. Subsequently, the system was flushed with helium (20 mL/min) at 200 °C for 1 h to eliminate physisorbed $CO_2$. Desorption was carried out from ambient temperature to 900 °C at a heating ramp of 5 °C/min.

### 3.3.2.9 Inductively Coupled Plasma – Mass Spectrometer (ICP-MS)

In inductively coupled plasma (ICP), the use of high energy plasma generates positively charged ions. Samples are typically inserted into sample introductory system undergoes nebulization which later the sample emerges as aerosol. As the sample passes through many stages in the ICP chambers, the samples are vaporised, atomised and ionised. These ions are later detected by the mass spectrometer (Ammann, 2007). Inductive Coupled Plasma - Mass Spectrometer (ICP-MS) is an effective technique for multielemental and isotopic material analysis of sample in low quantities with high level of detection limit (Beauchemin, 2006). ICP-MS Agilent 7500c was used to study the environment metal content in the catalyst using in-house method CHEMITEL/WI/CHEM-TM/001 based on (AOAC999.10). The standard sample preparation procedure is as described.

Initially, 0.5 g of solid sample was weighed into the digestion vessel. Then, the vessel was introduced into the HTC safety shield. After that, 6 mL of $HNO_3$ and 2 mL of $H_2O_2$ was added into the vessel and closed as well as tightened. Following that, the microwave program was set and run. When the digestion was complete solution was transferred into 50 mL volumetric flask and diluted to mark with 2 % $HNO_3$. Standard containing environmental metals were prepared at 0, 5, 10, 20 and 50 ppb with 2 % $HNO_3$ for standard calibration. Finally, samples and standards were subjected to analysis with ICP-MS.

## 3.4 Catalyst Testing

Catalysts synthesised in this study were evaluated for different reactions involving glycerol, ethylene glycol and propylene glycol as a polyol feedstock, respectively. Specific procedures for each system were shown in the following sub-section: The final products were analysed using GC-FID based on calibration of standard ethylene glycol, ethylene carbonate, propylene glycol and propylene carbonate. All calibrations of standards were reported in linear format with more than or equal to 0.97 ($r^2 \geq 0.97$). Results of conversion percentage, selectivity percentage and yield percentage were reported based on relative standard deviation, RSD less than 5 % (RSD < 5 %).

### 3.4.1 Glycerol Carbonate Synthesis

The experimental setup is illustrated in Figure 3.2. The reaction was carried out using a three-neck 100 mL round bottom flask attached to a cycle condenser with continuous flow of water. Typically, 13.8 g of glycerol was allowed to heat up to 150 ˚C for under the flow of nitrogen gas for 20 minutes before adding urea and catalyst. The temperature and stirring rate was controlled using IKA@DTS-5 temperature controller. When the temperature reached 150 ˚C, 13.5 g urea and 0.25 g catalyst was added to the reaction and stirred using a magnetic stirrer under 340 rpm of stirring rate. The molar ratio of glycerol to urea used was (1:1.5). Sampling was done from 0 h to 10 h with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. Blank reaction was conducted in absence of catalyst with similar parameter. Each experiment was repeated three times for repeatability study. The temperature of mixture was manually monitored using a thermometer for every 1 h. This method of synthesis was adopted from (Rahim et al., 2012) and modified based on the various parameters of reaction conditions studied.

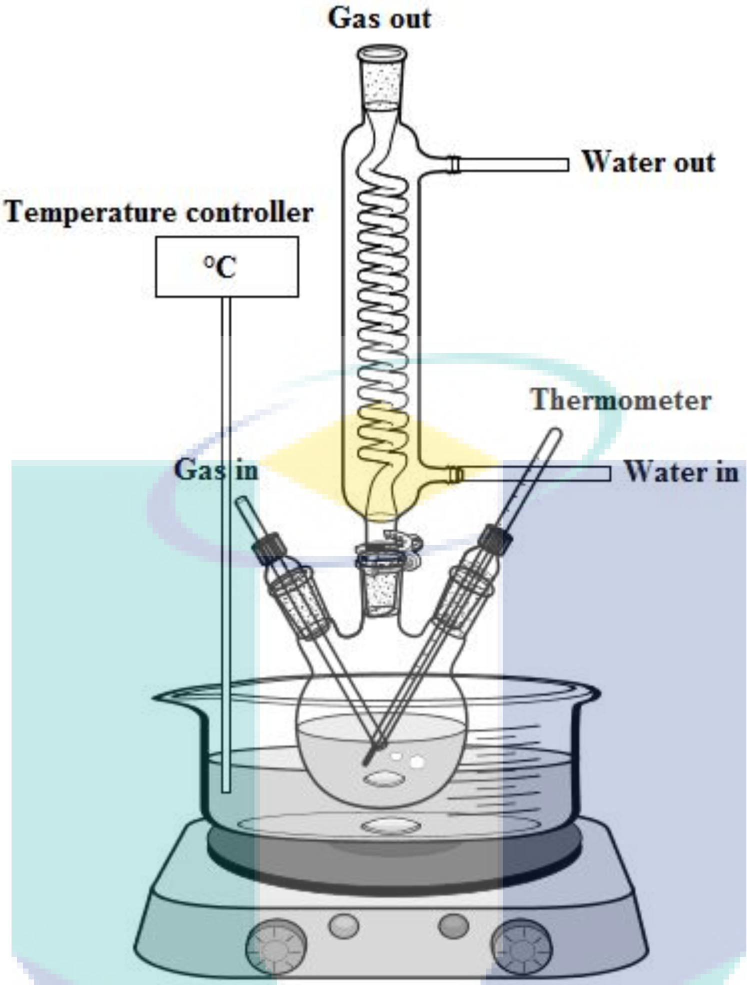


*Figure 3.2.* Reactor setup.

#### 3.4.1.1 Reaction Parameters Study

The reaction parameters studies were carried out following the procedure details in section 3.4.1. For each tested parameter, other parameter was kept constant. The following Table 3.1 summarises the involved parameters.

Table 3.1
**Reaction Conditions of Glycerol Carbonate Synthesis*

| **Reaction Parameter** | **Time (h)** | **Gas** | **Molar ratio (Glycerol: Urea)** | **Mass of Catalyst (g)** | **Stirring rate (rpm)** | **Temperature (°C)** |
|---|---|---|---|---|---|---|
| Temperature | 4 | $N_2$ | 1: 1.5 | 0.25 | 340 | 100-160 |
| Stirring rate | 4 | $N_2$ | 1: 1.5 | 0.25 | 140-640 | 150 |
| Mass of catalyst | 4 | $N_2$ | 1: 1.5 | 0.025-0.35 | 340 | 150 |
| Molar ratio of glycerol to urea | 4 | $N_2$ | 1: (0.25-2.0) | 0.25 | 340 | 150 |
| Gas | 4 | Air | 1: 1.5 | 0.25 | 340 | 150 |
| Time | Up to10 | $N_2$ | 1: 1.5 | 0.25 | 340 | 150 |

* Note that all reactions were carried out in triplicates and results reported are at relative standard deviation (RSD) < 5 %. Sampling was done at interval of 1 h whereby 50 uL of sample was sampled into 1450 uL of deionized water and subjected to quantitative analysis by GC-FID.

#### 3.4.1.2 Catalytic Reaction of Major Metal Content in Boiler Ash

The effect of major metal content in boiler ash which possible controlling the catalytic performance was determined by conducting a series of reaction with different metal phases by following similar synthesis approach with parameters studied for duration of reaction study (Table 3.1). However the duration of reaction was limited to 4 h. The metal phases used in the reaction involved KOH, KCl, $K_2SiO_3$, CaO, MgO and $SiO_2$.

### 3.4.2 Ethylene Carbonate Synthesis

The synthesis of ethylene carbonate was carried out using similar set-up shown in Figure 3.1. In this case, 18.6 g of ethylene glycol was allowed to heat up to 150 ˚C for 10 h under the flow of nitrogen gas for 20 min before adding urea and catalyst. The temperature and stirring rate was controlled using IKA@DTS-5 temperature controller. When the temperature reached 150 ˚C, 12.0 g urea and 0.25 g catalyst was added to the reaction and stirred using magnetic stirrer under 340 rpm of stirring rate. The molar ratio of ethylene glycol to urea used was (1.5:1). Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. Blank reaction was conducted in absence of catalyst with similar parameter. The experiment was repeated three times for repeatability study. The proof of concept study of synthesis of ethylene carbonate was performed using method proposed by Zhao et al., (2008) with minor modification.

### 3.4.3 Propylene Carbonate Synthesis

The synthesis of ethylene carbonate was carried out using similar set-up shown in Figure 3.1. Typically, about 30.4 g of propylene glycol was allowed to heat up to 170 ˚C for 10 h under the flow of nitrogen gas for 20 min before adding urea and catalyst. The temperature and stirring rate was controlled using IKA@DTS-5 temperature controller. When the temperature reached 170 ˚C, 6.0 g urea and 0.25 g catalyst was added to the reaction and stirred using magnetic stirrer under 340 rpm of stirring rate. The molar ratio of propylene glycol to urea used was (4:1). Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. Blank reaction was conducted in absence of catalyst with similar parameter. The experiment was repeated three times for repeatability study. The proof of concept study of synthesis of propylene carbonate was performed using method proposed by Du et al., (2014) with some modification.

## 3.5 Product Analysis and Validation

The routine product analysis of glycerol carbonate, ethylene carbonate and propylene carbonate were carried out using Gas Chromatography Flame-Ionized Detector (GC-FID). In addition, the product validation was done using Gas Chromatography- Mass Spectrometry (GC-MS), Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) and $^{13}$C Nuclear Magnetic Resonance ($^{13}$C NMR).

### 3.5.1 Gas Chromatography - Flame Ionised Detector (GC-FID)

#### 3.5.1.1 Product Analysis using Glycerol as Feedstock

According to (Kealey & Haines, 2002), gas chromatography is a technique for the separation of volatile components of mixtures by differential migration through a column containing a liquid or solid stationary phase. Solutes are transported through the column by a gaseous mobile phase and are detected as they are eluted. The mobile phase is an inert gas, generally nitrogen or helium. The Flame Ionised Detector (FID) is the most widely used universal detector, being extremely sensitive and responding to all organic solutes except formaldehyde, formic acid and fully halogenated compounds. It has the widest linear dynamic range of all GC detectors, making it ideal for quantitative analysis.

Gas Chromatography - Flame Ionised Detector (GC-FID) Agilent Technologies 7890A equipped with Varian Capillary Column, CP-PoraBOND Q (25 m, 0.53 mm, 10 µm) was used to analyse the liquid product of reaction. The temperature ramping was set at 80 ˚C per minute increased up to 300 ˚C. Sampling was done during reaction for analysis from 0 h to 4 h with time interval of 1 h (typical or otherwise mentioned) where 50 µL of sample was added to 1450 µL of deionized water. Standard calibration for glycerol and glycerol carbonate was done using GC-FID before samples from catalytic reaction were analysed. Tetraethylene Glycol (TEG) also was used as external standard. Helium gas was used as the carrier gas with a flow rate of 1.0 mL/min. The temperature of the injector and the detector were 225 °C and 250 °C, respectively. The temperature of the column was programmed to have a 2 min initial hold at 80 °C, then 10 °C/min ramp from 80 °C to 250 °C and 15 °C/min ramp from 250 ˚C to 300 ˚C with 3 min hold time. The split ratio was 1:10 and injection volume was 1 µL.

Standards glycerol and glycerol carbonate were prepared in concentration range of 0.1 M, 0.2 M, 0.3 M and 0.4 M. The highest concentration of glycerol 0.4 M was prepared by dissolving 368.0 mg of glycerol topped with 10 mL deionised water in a 10 mL volumetric flask. Similarly, the 0.4 M standard glycerol carbonate was prepared by dissolving 471.8 mg topped with 10 mL deionised water in a 10 mL volumetric flask. The highest concentrations of these standards were later diluted separately with deionised water to the respective concentrations mentioned earlier respectively. The standards were subjected to GC-FID analysis in which the calibration curve was plotted.

#### 3.5.1.2 Product Analysis using Ethylene Glycol and Propylene Glycol as Feedstock

Gas Chromatography - Flame Ionized Detector (GC-FID) Agilent Technologies 7890A equipped with DB-WAX (60m, 0.25mm, 0.25µm) was used to analyse the product of ethylene carbonate and propylene carbonate. Helium gas was used as the carrier gas with a flow of 1.5 mL/ min. The temperature of the injector and the detector were 225 °C and 250 °C, respectively. The temperature of the column was programmed to have a 2 min initial hold at 80 °C and then 15 °C/min ramp from 80 °C to 250 °C at 5 min hold time. The split ratio was 1:10 and injection volume was 1 µL.

Standards ethylene glycol and ethylene carbonate were prepared in concentration range of 0.1 M, 0.2 M, 0.3 M and 0.4 M. The highest concentration of ethylene glycol 0.4 M was prepared by dissolving 248.1 mg of ethylene glycol topped with 10 mL deionised water in a 10 mL volumetric flask. Similarly, the 0.4 M standard ethylene carbonate was prepared by dissolving 352.3 mg topped with 10 mL deionised water in a 10 mL volumetric flask. The highest concentrations of these standards were later diluted separately with deionised water to the respective concentrations mentioned earlier respectively. The standards were subjected to GC-FID analysis in which the calibration curve was plotted.

Standards propylene glycol and propylene carbonate were prepared in concentration range of 0.1 M, 0.2 M, 0.3 M and 0.4 M. The highest concentration of propylene glycol 0.4 M was prepared by dissolving 304.7 mg of propylene glycol topped with 10 mL deionised water in a 10 mL volumetric flask. Similarly, the 0.4 M standard propylene carbonate was prepared by dissolving 407.8 mg topped with 10 mL deionised water in a 10 mL volumetric flask. The highest concentrations of these standards were later diluted separately with deionised water to the respective concentrations mentioned earlier respectively. The standards were subjected to GC-FID analysis in which the calibration curve was plotted.

The GC-FID analysis parameters for glycerol carbonate, ethylene carbonate and propylene carbonate is summarised in Table 3.2.

Table 3.2
*GC-FID parameters for qualitative analysis of glycerol carbonate, ethylene carbonate and propylene carbonate*

| **Parameters** | **Settings (Gly C)** | **Settings (EC and PC)** |
|---|---|---|
| Chromatograph | Agilent Technologies 7890A GC Systems coupled with FID detector | Agilent Technologies 7890A GC Systems coupled with FID detector |
| Auto-sampler | GC auto sampler | GC auto sampler |
| Column | Varian Capillary Column, CP-PoraBOND Q (25 m, 0.53 mm, 10µm) i.d, film thickness 10 µm) | Polar capillary DB-WAX (60 m, 0.25 mm i.d, film thickness 0.25 µm) |
| Carrier gas | Helium | Helium |
| Gas flow rate | 1.0 mL/min | 1.5 mL/min |
| Injector mode | Split mode (10:1) | Split mode (10:1) |
| Injector temperature | 225 °C | 225 °C |
| Detector temperature | 250 °C | 250 °C |
| Injection volume | 1µL | 1µL |
| Temperature program | 80 °C for 2 min, ramping 1 at 10 °C/min to 250 °C, ramping 2 at 15 °C/min from 250 °C to 300 °C and held for 3 min | 80 °C for 2 min, ramping at 15 °C/min to 250 °C and held for 5 min |
| Runtime | 30.33 min | 18.33 min |
| Lab data system | NIST Library Chem Station software | NIST Library Chem Station software |

### 3.5.2 Gas Chromatography Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometer (GC-MS) is an instrument used to analyse the (m/z ratio) of ions separated from a specific compound analysed. Specific compounds have specific m/z mass fragmentation which can be used to elucidate an unknown compounds structure. Both qualitative and quantitative analysis can be achieved with GC-MS. Gas Chromatography - Mass Spectrometer (GC-MS) Agilent Technologies 7890A equipped with HP-INNOWax (30 m, 0.25 mm i.d, film thickness 0.25 μm) was used to analyse the product and by-product glycerol carbonate synthesis route qualitatively. Helium gas was used as the carrier gas with a flow of 1.0 mL/min. The temperature of the injector and the detector were 225 °C and 250 °C, respectively. The temperature of the column was programmed to have a 2 min initial hold at 80 °C and then 15 °C/min ramp from 80 °C to 180 °C with 2 min hold time. The second ramp was set at 7 °C/min from 180 °C to 250 °C with 17 min hold time. The split ratio was 1:10 and injection volume was 1 µL. The GC-MS parameters are summarised in Table 3.3.

On the other hand, Gas Chromatography - Mass Spectrometer (GC-MS) Agilent Technologies 7890A equipped with DB-WAX (60 m, 0.25 mm i.d, film thickness 0.25 μm) was used to analyse the product and by-product ethylene carbonate and propylene carbonate synthesis route qualitatively. Helium gas was used as the carrier gas with a flow of 1.5 mL/min. The temperature of the injector and the detector were 225 °C and 250 °C, respectively. The temperature of the column was programmed to have a 1 min initial hold at 80 °C and then 10 °C/min ramp from 80 °C to 180 °C 5 min hold time. The split ratio was 1:10 and injection volume was 1 µL. The GC-MS parameters are summarised in Table 3.3.

Table 3.3
*GC-MS parameters for qualitative analysis of glycerol carbonate, ethylene carbonate and propylene carbonate*

| **Parameters** | **Settings (Glycerol carbonate)** | **Settings (Ethylene carbonate and propylene carbonate)** |
|---|---|---|
| Chromatograph | Agilent Technologies 7890A GC Systems coupled with MS detector | Agilent Technologies 7890A GC Systems coupled with MS detector |
| Auto-sampler | GC auto sampler | GC auto sampler |
| Column | HP-INNOWax (30 m, 0.25 mm i.d, film thickness 0.25 µm) | Polar capillary DB-WAX (60 m, 0.25 mm i.d, film thickness 0.25 µm) |
| Carrier gas | Helium | Helium |
| Gas flow rate | 1.0 mL/min | 1.5 mL/min |
| Injector mode | Split mode (10:1) | Split mode (10:1) |
| Injector temperature | 225 °C | 225 °C |
| Detector temperature | 250 °C | 250 °C |
| Injection volume | 1µL | 1µL |
| Temperature program | 80 °C for 1 min, 1st ramping at 10 °C/min to 180 °C while held for 2 min, 2nd ramping at 7 °C/min to 250 °C while held for 17 min | 80 °C for 2 min, ramping at 15 °C/min to 250 °C and held for 5 min |
| Runtime | 40.0 min | 18.33 min |
| MS Source | 250 °C | 250 °C |
| MS Quadrupole | 150 °C | 150 °C |
| Lab data system | NIST Library Chem Station software | NIST Library Chem Station software |

### 3.5.3 Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR)

Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR*)* Perkin Elmer, USA was used to study the functional group present in the time online analysis of product from 0 min to 10 h, which could attribute to the product and by-product present in the reaction mixture as a validation. A single drop of reaction mixture and standards (i.e. glycerol as well as glycerol carbonate) respectively was placed on the liquid holder and the transmission data were collected in the range of 4000–700 $cm^{-1}$.

### 3.5.4 $^{13}C$ Nuclear magnetic resonance ($^{13}C$ NMR)

Nuclear magnetic resonance (NMR) (1D $^{13}C$-125MHz Bruker (USA)), was used in this study to identify products and by-products formed in synthesis of glycerol carbonate, ethylene carbonate and propylene carbonate. NMR is a technique used to obtain structural information on organic compounds. NMR is active when the nucleus has a zero spin angular momentum, $^{13}C$ has I=1/2. The principle of the NMR works when a sample is placed and subjected to radiofrequency (RF) radiation nuclei in the sample will absorb the energy. The energy absorbed depends on three things which are the nucleus of the sample (eg. $^{1}H$ or $^{13}C$), chemical environment of the sample and spatial location of the magnet. $^{1}H$ and $^{13}C$ are the most dominant elements in organic compounds, thus they give higher peak absorptions (James, 1998). Typically 0.15 mL of sample was diluted with 0.7 mL (Deuterated methanol-$d_4$, $CD_3OD$). Data acquisition, conversion and analysis were controlled under Bruker TopSpin version 1.3.

## 3.6 Catalyst Reusability Study and Analysis

The reusability study was carried out for boiler ash (BA 900) and potassium silicate ($K_2SiO_3$) catalyst. Detail procedures as in the following sub-sections.

### 3.6.1 Procedure for Catalyst Reusability Study

The reaction was carried out as mentioned in section 3.4.1 but scaled up to two times. When the temperature reached 150 ˚C, 27.0 g urea and 0.5 g catalyst ($K_2SiO_3$ or BA 900) was added to the reaction. Sampling was done at 4 h. 50 µL of sample was transferred in 1450 µL of deionized water. The reaction mixture was immediately placed into a 100 mL centrifuge tube and centrifuged for 1 h at 8000 rpm. The catalyst that deposits as residue at the bottom of the centrifuge tube was carefully transferred into a clean 100 mL centrifuge tube and washed with deionized water. The water was removed from the centrifuge tube after 30 minutes of centrifugation. This step was repeated for 4 more times. The final catalyst was filtered and dried over night at 110 ˚C. The synthesis of glycerol carbonate using remaining dried catalyst was repeated by scaling down amount of feedstock loaded for the second cycle. The same procedure was repeated until the third cycle. The experiment was repeated three times for repeatability study.

### 3.6.2 Metal Leaching Study

Inductive Coupled Plasma - Mass Spectrometer (ICP-MS) Agilent 7500c was used to study the possible potassium and other elements leaching in reaction mixture using in-house method CHEMITEL/WI/CHEM-TM/001 based on AOAC999.10. Sample was centrifuged in hot conditions immediately after sampling. Analysis was conducted for both samples obtained from reaction using BA 900 and $K_2SiO_3$. The standard sample preparation procedure is as described in the following paragraph.

Initially, 0.5 mL of liquid sample was weighed into the digestion vessel. The vessel was then carefully introduced into the HTC safety shield. Later, 6 mL of $HNO_3$ and 2 mL of $H_2O_2$ was added into the vessel and closed as well as tightened. Following that, the microwave program was set and run. When the digestion was complete solution was transferred into 50 mL volumetric flask and diluted to mark with 2 % $HNO_3$. Standard containing potassium metal was prepared at 0, 5, 10, 20 and 50 ppb with 2 % $HNO_3$ for standard calibration. Finally, samples and standards were subjected to analysis with ICP-MS.

The amount metal elements of catalyst lost or leached from the initial catalyst loaded was also confirmed through FESEM-EDX where by the fresh and spent catalyst $K_2SiO_3$ were analysed based on analysis described in section 3.3.2.4.

### 3.7 Characterisation of Crude Glycerol

The crude glycerol obtained from Artistic Support Sdn. Bhd. was from two different sources. The first source of crude glycerol was obtained from biodiesel production process using sodium methylate as catalyst while the second source was obtained from biodiesel production catalysed by potassium methylate (Figure 3.3). The glycerol source containing sodium methylate was a solid wax-like sample in pale yellow colour. On the other hand, the glycerol containing potassium methylate was a viscous substance in mild brown colour.

*Figure 3.3.* Glycerol sodium methylate and glycerol potassium methylate.

The analysis involving crude glycerol characterisation was carried in Biodiesel production facility, Artistic Support Sdn. Bhd located in North Port, Klang, Selangor, Malaysia. The results obtained are depicted in the certificate of analysis. Following are the typical in-house method used for the analysis of crude glycerol in the industry:

### 3.7.1 Glycerol Content Analysis

To analyse the glycerol content in the crude glycerol, 0.35 – 0.50 g of sample was weighed into a beaker and dissolve with approximately 50 mL distilled water. Then, few drops of phenol red indicator were added and neutralised with either a sulphuric acid solution (0.01N) or a sodium hydroxide solution (0.01N). A faint colour was expected to be observed. Concurrently, a blank was prepared in the same manner with only using distilled water and the pH was adjusted to (6.5 ± 0.1). Later, 50 mL of sodium meta-periodate solution was pipetted into each beaker and swirled gently (0.014 moles of $IO_4^-$ ). The beaker was covered with a watch glass and was allowed to stand for 30 min in a dark place. After 30 min, 10 mL of ethylene glycol solution was added and allowed the mixture to stand for another 20 min in a dark place. The solution was diluted to 300 mL with distilled water and titrated with a standardised sodium hydroxide solution (0.1 N) using a pH meter to determine the end point. The end point of blank was pH (6.5 ± 0.1) and for the sample was pH (8.1 ± 0.1). The glycerol content was calculated using equation, Eq. (3.1).

$$\text{Glycerol Content (\%)} = \frac{(\text{S} - \text{B})\text{x } 92.09 \text{ x N}}{\text{SW}} \qquad (3.1)$$

Where:

S = Volume of sodium hydroxide solution used for sample.
B = Volume of sodium hydroxide solution used for blank. (volume B will be > 4.5mL)
N = Normality of standardised sodium hydroxide solution.
SW = Weight of sample used in (g)
Molecular weight of glycerol = 92.09 g/mol

### 3.7.2 Oil Content Analysis

The oil content in the crude glycerol was determined by weighing 25 g ± 0.1 g of sample accurately in a beaker and then transferred into a 100 mL separation flask whereby 25 mL of hexane was added. Then 5 mL of ethanol was added and shaken well. The mixture was let to stand until 2 layers were complete separated. The bottom layer (glycerol) was drained out into one beaker and the top layer (hexane) was pre-weighed into a beaker/round-bottom flask. The glycerol layer was transferred into the separation flask. The steps from adding ethanol were repeated for the bottom layer (glycerol) for two times. The hexane extracts were combined later. The hexane was then evaporated using a water bath in the fume hood and then dried in the oven (at 90 °C). The dried hexane extract was weighed. Finally, the amount of oil was calculated using Eq. (3.2).

$$\text{Hexane Extractable, X} = \frac{100 \text{ x } W1}{W2} \tag{3.2}$$

Where:-

W1 = Weight of hexane extractable, (g).
W2 = Weight of sample used, (g).

### 3.7.3 Soap Content Analysis

The soap content in crude glycerol was analysed based on Table 3.4, the appropriate amount of the sample was weighed into a 250 mL conical flask. Based on the sample amount, 100 mL of the appropriate solvent was added (refer to Tables 3.4. Water was used for glycerol. Then, 0.5 mL of bromophenol blue indicator was added to the solution and gently swirled until the sample fully dissolves. The solution was then standardised by titrating with HCl until a permanent yellow colour end point appears. The amount of soap was calculated using (Eq. 3.3).

Soap content as sodium oleate or potassium oleate,

$$\text{wt \%} = \frac{V \text{ x } N \text{ x } 30.44}{SW} \tag{3.3}$$

Where:

N = Normality of the Standardised Hydrochloric (HCI).

V = Volume of Standardised Hydrochloric (HCI) used to neutralised the sample.
SW = Weight of sample used in grams (g).
Molecular weight of Sodium Oleate = 304.44 g/mol
Molecular weight of Sodium Palmitate = 278.41 g/mol
Molecular weight of Oleic Acid = 282.46 g/mol

Table 3.4
*Titration conditions for methyl esters and glycerol from the biodiesel plant of Artistic Support Sdn. Bhd.*

| **Product** | **Normality of Titrant** | **Sample Weight (g)** | **Solvent** |
|---|---|---|---|
| Glycerol from V302 and Tank Farm | 0.5N | 10.0 – 15.0 | 100 % Distilled Water |

*Note: V302 is Vessel 302.

### 3.7.4 Catalyst Content Analysis

The catalyst content in crude glycerol was analysed by weighing 250 mL sample into a conical flask by referring to Table 3.5. Then, 100 mL of the appropriate solvent were added into the conical flask as in Table 3.5. Later, 2 mL of phenolphthalein indicator was added into the flask and swirled gently until the sample was fully dissolved. The sample was titrated with standardised HCI prepared by pipetting 89mL of concentrated hydrochloric acid (35-37 %) into a 1 L volumetric flask containing 500 mL distilled water until the pink or red colour just disappears. The catalyst concentration was calculated based on Eq. (3.4).

$$\text{Catalyst Concentration, } (\%) = \frac{\text{V x N x CV}}{\text{SW}} \tag{3.4}$$

Where:-

N = Normality of the Standardised Hydrochloric Acid (HCI).
V = Volume of Standardised Hydrochloric Acid (HCI) used to determine the concentration of catalyst (mL).

SW = Weight of sample used in gram (g).

C = Constant Value

Constant Value for NaOH = 4.00

Constant Value for NaOMe = 5.40

Table 3.5

*Recommended sample sizes and solvents*

| **Product** | **Normality of Titrant** | **Sample Weight (g)** | **Solvent** |
|---|---|---|---|
| Solution from T851, T103A and T103B | 1.0 N | 3.0 – 5.0 | 100 % Warm Distilled Water |

*Note: T851 is tank 851, T103A is tank T103A and T103B is tank 103B.

### 3.7.5 Moisture Content Analysis

The moisture content in both crudes of glycerol was determined using the determination of moisture content method (AOAC, 1999). An empty dish and lid was dried at 105 °C for 3 h in an oven. The dish and lid was later placed in a desiccator to cool down and weighed. 3 g of sample was weighed into the dish and spread evenly. The lid was used to partially cover the dish. Sample was dried at 105 °C for 3 h in the oven and then removed and placed in the desiccator to cool down with partially covered lid. The sample and dish with the lid was weighed again. The moisture content was calculated based on the following formula (Eq. 3.5).

$$Moisture, (\%) = \frac{W1-W2}{W1} \times 100 \qquad (3.5)$$

W1= Weight (g) of sample before drying

W2= Weight (g) of sample after drying

### 3.7.6 Methanol Content Analysis

The methanol content in crude glycerol was determined using Gas Chromatography-Flame Ionised Detector (GC-FID), Agilent 7890A and headspace sampler technique following the method standard method (EN14110) “Determination of Methanol Content” with modification. Standard methanol in glycerol of 0.1, 0.2, 0.5 and 1.0 wt % was prepared and calibrated to $r^2>0.97$. 1 mL of standard and sample was allowed to contact with the QHSS-40 headspace sampler in a concealed bottle for 30 min and was subjected for testing. The column used was Agilent, CP9083 (0.32 mm × 30 m × 0.33µm). The GC-FID specification following EN14110 was set at 80 °C (0.5 min isothermal) and ramped at 20 °C/min for 2 minutes. The split ratio was set at 50:1. Detector temperature was set at 275 °C and injector at 250 °C. Sample loop was 1 mL and injection volume was 1 µL. Carrier gas of helium with flow of 2.0 mL/min was used. The amount of methanol present in the crude was determined by substituting peak area of sample in calibration curve of methanol.

### 3.7.7 Ash content Analysis

Ash content in crude glycerol was determined by incinerating crude glycerol at 750 °C using for 3 h using standard method (ISO 2098-1972). 1 g of sample was weighed and placed in the furnace and heated to 750 °C for 4 h. The remaining sample was weighed after cooled. The formula for calculation of ash content is based on (Eq. 3.6).

$$Ash\ content, (\%) = \frac{W1-W2}{W1} \times 100 \qquad (3.6)$$

W1= Weight (g) of sample before incineration
W2= Weight (g) of sample after incineration

### 3.7.8 Matter of Organic Non Glycerol (MONG) Content Analysis

The matter of organic non glycerol was calculated using the following formulae Eq. 3.7.

$$MONG, \% = [100 - (\%\ \text{glycerol content}\ + \%\ \text{moisture content}\ + \%\ \text{ash content})] \qquad (3.7)$$

## 3.8 Catalytic Testing of Crude Glycerol and Analysis

The experiment was conducted similar to the set-up and procedure stated in section 3.4.1. Typically, 150 mmol of crude glycerol was allowed to heat up to 150 ˚C for under the flow of nitrogen gas for 20 minutes. The molar ratio of crude glycerol to urea used was (1:1.5). Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. Blank reaction was conducted in absence of catalyst with similar parameter. The experiment was repeated three times for repeatability study.

The liquid product from the reaction was subjected to similar analysis stated in section 3.5.1.1.

## 3.9 Simulated Crude Glycerol Study

Simulated crude glycerol study is required in order to assess the possible effect of major impurities available in crude glycerol which affecting the overall catalytic activity. Detail experimental procedures as following sub sections.

### 3.9.1 Catalytic Testing of Pure Glycerol Simulated with 10 wt % Water

The reaction was conducted as method mentioned in section 3.4.1.Typically, 150 mmol of pure glycerol simulated with maximum 10 wt % of water in accordance to the obtained certificate of analysis. The molar ratio of glycerol to urea used was (1:1.5). Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. The experiment was repeated three times for repeatability study.

#### 3.9.1.1 Moisture Analysis of Pure Glycerol Simulated with 10 wt % Water

The moisture analysis of glycerol mimicked with 10 wt % deionised water was carried using 870 KF Tritino Plus. The sample was analysed based on the method of Mehtrohm Moisture Analyser. When the drift value is below 20 and without fluctuation, the 870 KF Titrino Plus is ready for sample injection. The weighing spoon was tarred to zero, and then 2 mL of sample was introduced by sample addition. The instrument measures the sample weight and sample weight was keyed in. The sample solution was then titrated until the end point was reach and result was shown on the screen in %. The analysis was repeated three times using the same procedure for repeatable results.

### 3.9.2 Catalytic Testing of Pure Glycerol Simulated with 5 wt % Methanol

The reaction was carried out based on method mentioned in section 3.4.1. Typically, 150 mmol of crude glycerol mimed with maximum 5 wt % of methanol in accordance to the certificate of analysis. Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. The experiment was repeated three times for repeatability study.

### 3.9.3 Catalytic Testing of Pure Glycerol Simulated with Mixture of Moisture and Methanol

The reaction was carried out by mixing pure glycerol with mixture of moisture and methanol based on the certificate of analysis (COA) obtained from Artistic Support Sdn. Bhd. Two different sets of solutions were prepared. The first set of solution contained 150 mmol of glycerol simulated with 10 wt % of deionised water and 5 wt % of methanol. The second set of solution contained 150 mmol of glycerol simulated with 3.15 wt % of deionised water and 0.8 wt % of methanol. The reaction was carried based on method mentioned in section 3.4.1. Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. The experiment was repeated three times for repeatability study.

### 3.9.4 Catalytic Testing of Pure Glycerol Simulated with 1.6 wt % Sodium Methylate

The reaction was carried based on method mentioned in section 3.4.1. Typically, 150 mmol of crude glycerol was mixed with maximum 1.6 wt % of Sodium Methylate in accordance to the certificate of analysis. Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. The experiment was repeated three times for repeatability study.

### 3.9.5 Catalytic Testing of Pure Glycerol Simulated with 1.6 wt % Potassium Methylate

The reaction was carried based on method mentioned in section 3.4.1. Typically, 150 mmol of crude glycerol mixed with maximum 1.6 wt % of Potassium Methylate in accordance to the certificate of analysis. Sampling was done from 0 h to 10 h (typical or otherwise mentioned) with the time interval of 1 h. 50 µL of sample was transferred in 1450 µL of deionized water. The experiment was repeated three times for repeatability study.

## 3.10 EQUATIONS AND FORMULAS

In terms of quantitative analysis, the conversion, selectivity and yield percentage can be calculated by plotting the standard calibration curve of both polyols and organic carbonates before conducting the product analysis. The calculation based on calibration curve was then validated by using alternative calculation method based on TEG as external standard. Turnover Frequency (TOF) also calculated to quantify the specific activity of catalytic sites for a special reaction under defined reaction conditions. After all the necessary information obtained from the calibration curve, the conversion, selectivity and yield and TOF can be calculated by using the following formulae listed in eq. (3.8), (3.9), (3.10) and (3.11):

$$\text{Conversion \%} = \frac{\text{Total no.of mol} - \text{No.of mol of substrate (polyol)}}{\text{Total no.of mol}} \times 100 \quad (3.8)$$

$$\text{Selectivity \%} = \frac{\text{No.of mol of product (Organic carbonate)}}{\text{Total no.of mol} - \text{No.of mol substrate (polyol)}} \times 100 \quad (3.9)$$

$$\text{Yield \%} = \frac{\text{Conversion \%} \times \text{Selectivity \%}}{100} \quad (3.10)$$

$$\text{Turnover Frequency, (TOF)} = \frac{\frac{\text{Mols of Polyol used} \times \text{yield \% of Organic carbonate}}{(\text{Mass of catalyst} \times 100)}}{\text{Duration of reaction (h)}} \quad (3.11)$$

## 3.11 Research Methodology Flow Chart

The following flowchart (Figure 3.4) briefly summarised the research methodology involved for the whole study reported in this thesis. The green boxes reflect the main objectives of the research while the blue box arrives to the significant findings of the research. On the other hand, the black boxes resemble the techniques and methods used to arrive to the conclusion of the study. The yellow box demonstrates the feasibility of the catalyst to synthesise cyclic organic carbonates.

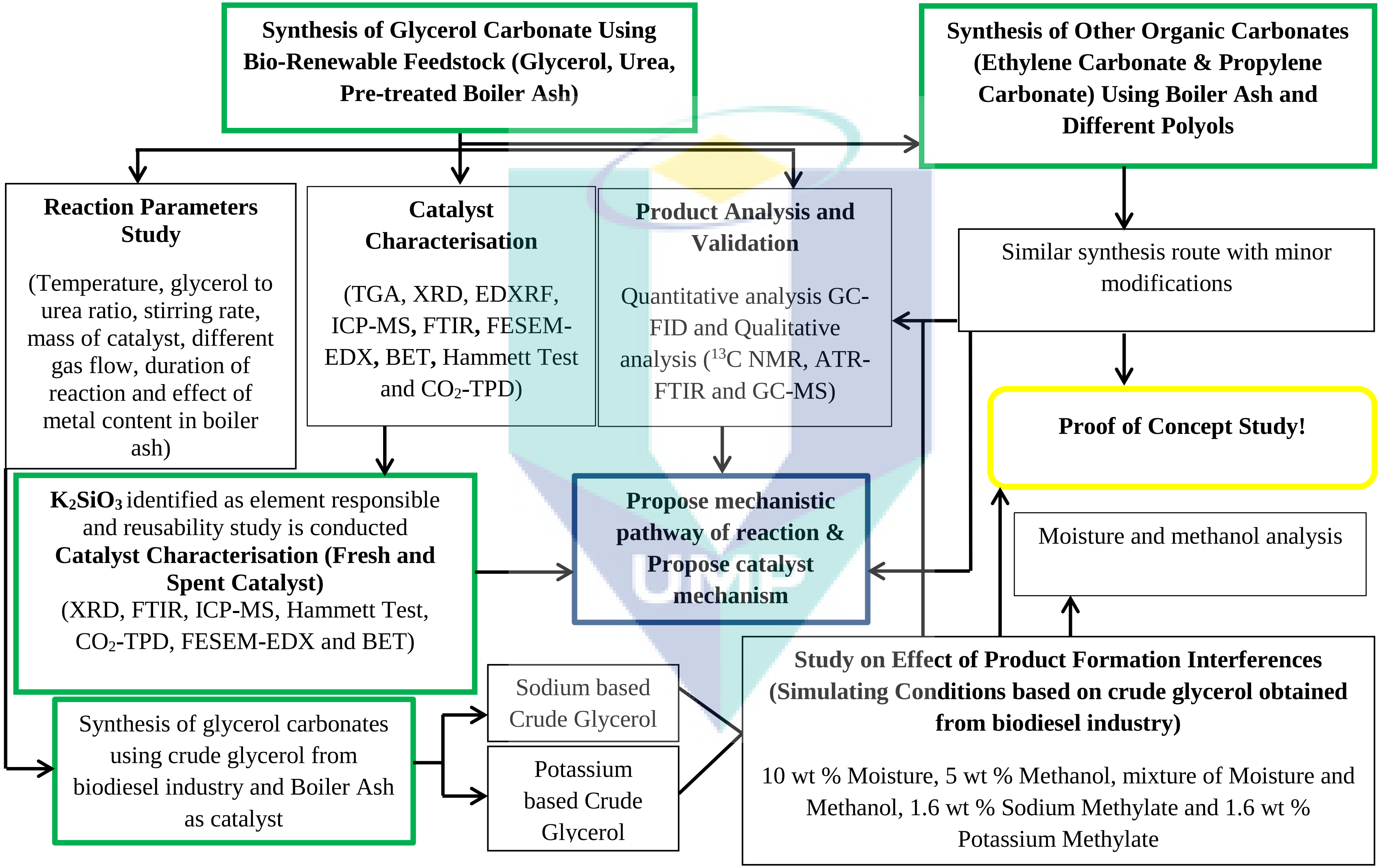


Figure 3.4: Flow Chart of Research Methodology.

## 3.12 Summary

This chapter in short discusses the materials, methods, instrumentations and equations used to meet the objectives of this study which are proposed in chapter 1. The chapter begins with introducing materials used in this research followed by catalyst preparation and characterisation. This section discusses techniques and instruments used to analyse the catalyst. Next is the catalyst testing and product validation which involves use of reactor setup and chromatography techniques as well as other instrumentation techniques for analysis of products formed. The chapter expands into discussing methods used for reusability study and analysis. Then, the method and techniques used for industrial characterisation of crude glycerol in industry is elaborated in this section. The section also covers method and techniques used for catalytic testing of crude glycerol as well as simulated study followed by analysis of the product. Apart from that, equations and formulas used to quantify product formation and TOF is also described in this chapter. Finally, a summary of the research methodology is illustrated in the research methodology flow chart.

# CHAPTER 4

# SYNTHESIS OF GLYCEROL CARBONATE USING CATALYST DERIVED FROM BOILER ASH

## 4.1 Introduction

This chapter is an elaboration of results and discussion to meet the first objective of this research which is to synthesise glycerol carbonate using bio-renewable feedstock and catalyst derived from waste boiler ash. In this chapter, the effect of calcination temperature on tuning the physico-chemical property of boiler ash are presented and discussed with correlation to their catalytic performance towards glycerol carbonate synthesis. The catalyst active sites also were identified via various means of analysis involving FTIR, XRD, EDXRF, FESEM-EDX, ICP-MS, Hammett Test and $CO_2$-TPD. The suitable reaction conditions for synthesis of glycerol carbonate was also studied. Besides, both potassium silicate and boiler ash catalyst were subjected to catalyst reusability testing. The characteristics of fresh and spent catalyst were analysed through several means of characterisation technique. The information gains from both catalytic studies as well as characteristic of catalysts were used to propose the possible reaction mechanism involved in those reactions.

## 4.2 Catalyst Characterisation

This section of the chapter discusses the application of various catalyst characterisation techniques used to study the properties and activities of boiler ash as well as potassium silicate. The catalyst characterisation techniques used includes thermogravimetric technique (TGA), Fourier Transform Infrared (FTIR), X-Ray Diffraction Analysis (XRD), Energy Dispersive X-Ray Fluorescence (EDXRF) Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (FESEM-EDX), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), *Brunauer–Emmett–Teller* (*BET*) surface area analysis, acidity and basicity analysis using Hammett test and Temperature Programmed Desorption – Carbon Dioxide ($CO_2$-TPD).

### 4.2.1 Thermogravitmetric (TGA) Analysis

The analysis involving thermogravimetric study on raw boiler ash was conducted to understand the stability and phase transformation of boiler ash at various temperatures under static air environment. This analysis was essential to depict which calcination temperature require to tune the characteristic of boiler ash, subsequently produced an active and selective catalyst to give maximum yield of glycerol carbonate as target product in the following catalytic testing study. Based on Figure 4.1 (a), the TGA thermogram displays significant weight loss in boiler ash where the weight decreased from 100% to 60% from temperature 0 ˚C to 1100 ˚C. There is about 40% loss in weight percentage which is due to presence of different components in the boiler ash such as moisture and other organic matter, that can be lost through heating (Shuit et al., 2009; Ho et al., 2012). Besides, halogenated metal compound containing chlorine could have resulted in evaporation under high thermal treatment. For example, sylvite (KCl) could have been transformed into potassium silicate ($K_2SiO_3$) under high thermal treatment at 700 °C and above. Under high thermal heat treatment at 900 °C and above huge amount of the carbon is also lost. These phenomena can be also compared and observed from the XRD diffractogram (see section 4.2.3). Moreover the DTG thermogram in Figure 4.1 (b) illustrates the possibility of the boiler ash catalyst to exist in various phases at different calcination temperature.

As mentioned earlier, at temperature 100 ˚C to 200 ˚C there is variation in peaks drop that could indicate moisture lost through heating. The transformation of peak from temperature 400 ˚C to 1100 ˚C which indicated loss of elements such as organic matters and phase transformation of the catalyst. This analysis was done to identify changes in phase transformation at various level of temperature. Therefore, based on the DTG curve the boiler ash was dried at 110 ˚C and calcined at 500 ˚C, 700 ˚C, 900 ˚C and 1100 ˚C in order to obtain suitable catalyst.

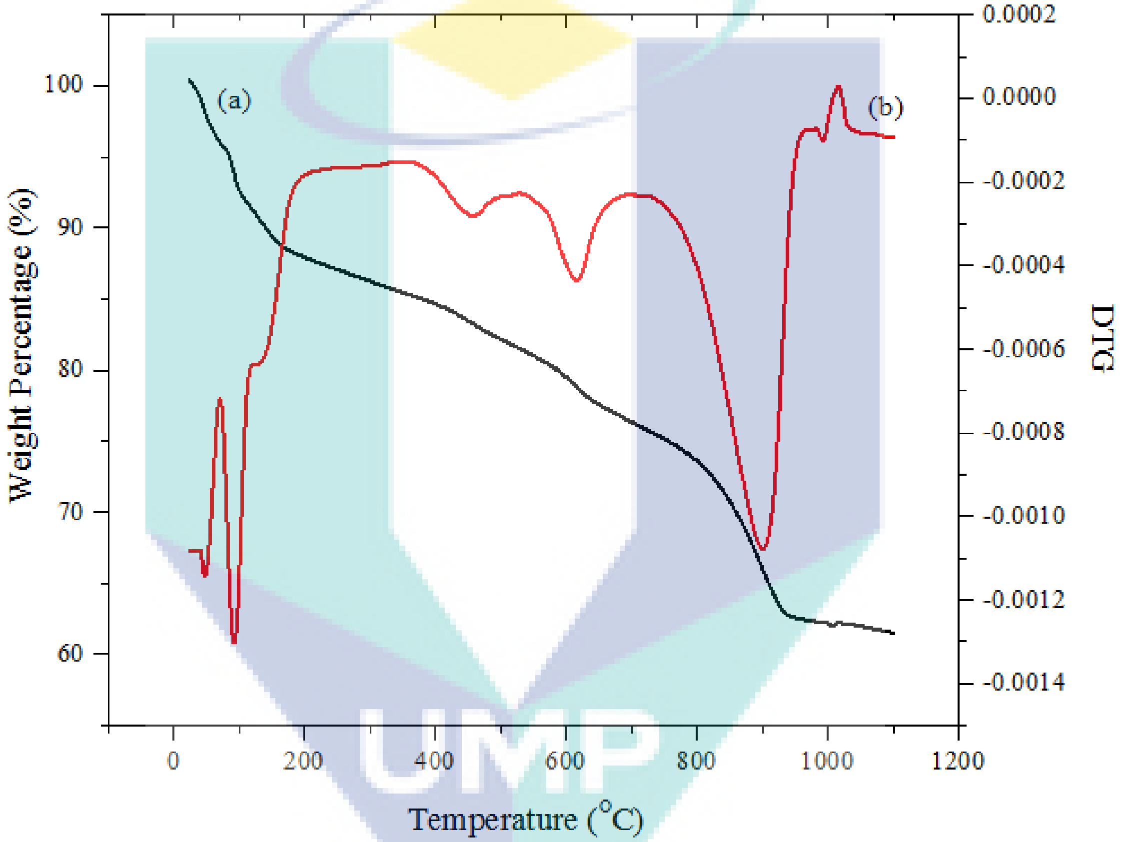


*Figure 4.1*. Thermogravimetric analysis (TGA) of boiler ash, (a) is weight percentage (%) loss and (b) derivative thermal gravimetric (DTG).

### 4.2.2 Fourier Transform Infrared (FTIR) Analysis of Catalysts

The analysis using FTIR was conducted on BA 110, BA 700 and BA 900 catalysts in order to study the presence of functional groups in the two different phases and their influence on the catalytic behaviour of boiler ash. Results from FTIR analysis (Figure 4.2) on the boiler ash (BA) suggests that major peak for BA 700 and BA 900 catalyst was observed at 3325.47 cm$^{-1}$ which is attributed to the presence of –OH functional group.

Similarly the –OH band was observed in BA 110 at 3245.63 cm$^{-1}$. The presence of –OH group was confirmed with peaks observed in both catalyst at 680-620 cm$^{-1}$ where it assigns –OH out of plane bending. The presence of the band indicates water adsorbed on the surface of the catalyst from the atmosphere (Yin, Kadir, Lim, Syed-Ariffin, & Zamzuri, 2008). As observed with FESEM-EDX analysis (section 4.2.6), boiler ash is found to have spongy and porous characteristic which contributed to moisture absorption capability. The band at range of (1300-1400) cm$^{-1}$ attributes the deformation of –OH (Chin et al., 2009). Other than that, the presence of band at range (1010 -1020) cm$^{-1}$ was attributed to alternating –SiO and –AlO bands in BA 700 and BA 900 (Boey et al., 2011). It is visible from the FTIR spectrum that metal ions present in the boiler ash BA 700 as well as BA 900 have gone transformation to form metal oxides, metal hydroxides and other forms of metals such as MgO, $Al_2O_3$, CaO, KOH and $K_2SiO_3$, where there is sharp peak indicating presence of oxide at (1010-2010) cm$^{-1}$ (Boey et al., 2011) and broad range of –OH functional group at 3325.47 cm$^{-1}$, respectively. It is also evident that both BA 700 and BA 900 exhibits similar FTIR pattern which may attribute to findings in this study that the catalytic behaviour is relatively similar. The FTIR study on these catalysts also corresponded to the XRD results in section (4.2.3) whereby sharp peak of –SiO band in BA 700 and BA 900 indicated higher amount of silicate from formation of potassium silicate as dominant element. It was noted that the property of boiler ash was not exactly similar of those reported earlier by Boey et al., (2011) due to different calcination technique used where the boiler ash was heated in an open system using tubular furnace in the current research. BA 500 was not further subjected to FTIR analysis due to the catalysts having no distinct difference in the catalytic activity compared to BA 110 as reported in section 4.3. Catalyst having the highest and the lowest yield were selected to be characterised by the FTIR analysis in order to understand the effect of the specific calcination temperature towards catalyst activity.

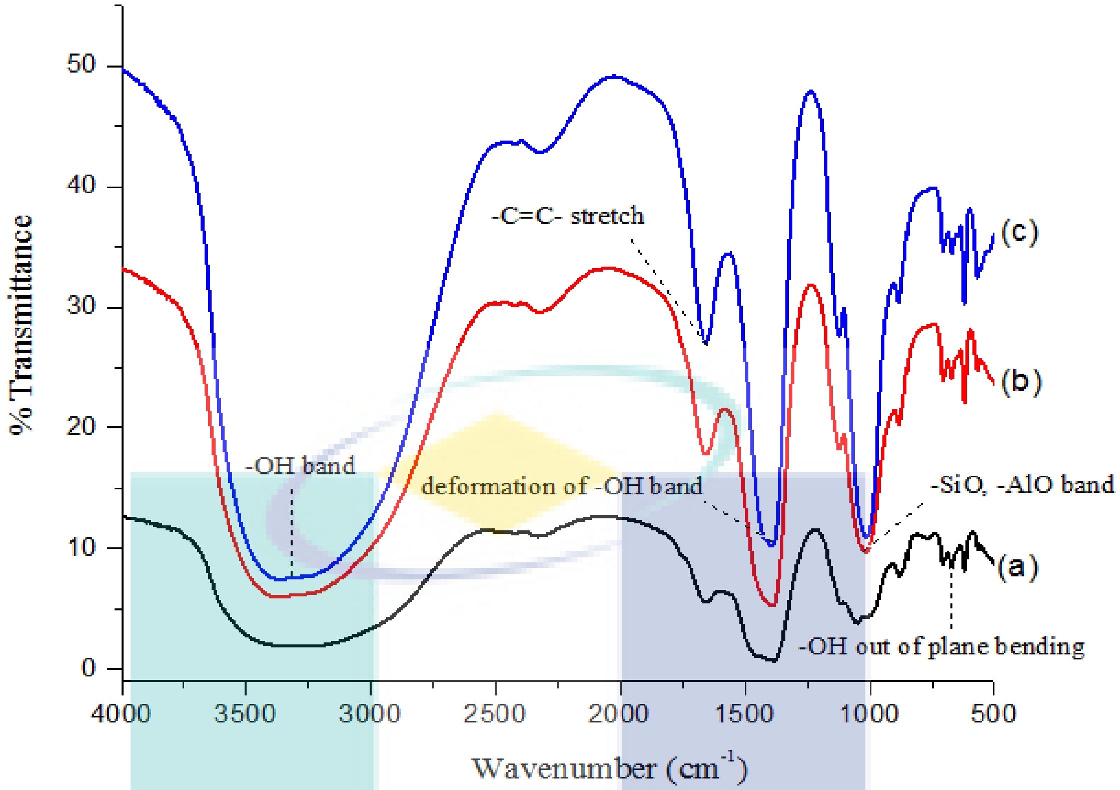


*Figure 4.2.* FTIR spectrum of a) BA 110 and b) BA 700 and c) BA 900.

### 4.2.3 X-Ray Diffraction (XRD) Analysis

It can be seen from Figure 4.3 that BA 110 showed the characteristics peak of sylvite (KCl) at $2\theta = 28.60^\circ$, $40.69^\circ$, $66.71^\circ$ and $73.85^\circ$, respectively. The presence of calcite ($CaCO_3$) could be examined at diffraction peak of $2\theta = 30.61^\circ$ whereas potassium silicate ($K_2SiO_3$) was detected at $2\theta = 30.93^\circ$. For BA 700, similar phase composition as BA 110 containing KCl, $CaCO_3$ and $K_2SiO_3$ were observed to be present. However, for BA 900, in addition to $CaCO_3$ and $K_2SiO_3$, calcium oxide (CaO) was identified to be present at $2\theta = 26.46^\circ$ and $32.83^\circ$ respectively. The occurrence of CaO in BA 900 is expected since $CaCO_3$ is known to decompose into CaO when calcination treatment is higher than 800 °C.

The change in the XRD pattern could be mainly influenced by calcination temperature where at different calcination temperatures, phase transformation occurred as evident from TGA data in Figure 4.1 and FTIR analysis in Figure 4.2. In general, potassium from sylvite form in BA 110 transformed into potassium silicate with higher thermal heat treatment as observed in BA 700 and BA 900. Even though, KCl was not detected in XRD diffractogram of BA 900, it was found that KCl is still present in BA 900 as referred to the elemental analysis at minor levels using FESEM-EDX (section 4.2.6). This could be due to the non-homogeneously distributed sample analysed. However, only minor amount of chlorine was detected through the FESEM-EDX analyses which indicate most of the KCl have transformed into $K_2SiO_3$. Moreover, the presence of potassium as the predominant element is detected in all three catalysts. Therefore, this factor might contribute to only minor difference in catalytic results for all three catalysts. However, BA 900 and BA 700 exhibits better catalytic results than BA 110 due to the dominance presence of potassium silicate phase at higher calcination temperature. In addition, the calcium carbonate peak observed at $2\theta = 56.79^\circ$ in BA 900 could be a result of non-homogeneity of the boiler ash due to different batches of dried boiler ash at 110 °C being calcined at selected temperatures.

It is important to note that the present reported study on boiler ash characteristic is not relatively similar of those reported earlier (Boey et al., 2011). In previous study Boey and co-workers in 2011 reported that calcining boiler ash at 900 °C will result in presence of potassium sylvite which is not similar to the current study. The difference in the particular characteristic could have been due to difference in calcination method, where in previous study calcination in closed system in which elements are not lost was employed and in the current study the calcination process was carried out under static air in an open tube furnace. Even though, magnesium was not detected in the major peaks visible from the XRD diffractogram, it is believed that magnesium metals are present in minor amount in boiler ash which is supported by the elemental analysis using EDX and ICP-MS (section 4.2.6). Since magnesium and calcium are generally present in lower amount in oil palm boiler ash as reported in elemental analysis study by Boey and co-researchers in 2011 using X-ray Fluorescence (XRF), it plainly supports that the detection level of these specific elements to be very minimal in this characterisation technique by XRD. These elements were particularly looked through because magnesium and calcium supported catalyst have shown promising yield of glycerol carbonate in previous studies (Hammond et al., 2011). Besides, these metals are reported to be in the form of oxides in palm oil boiler ash by Boey and co-researches in 2011. Thus, it is likely evident that metal present in boiler ash exist in solid metal oxides phase.

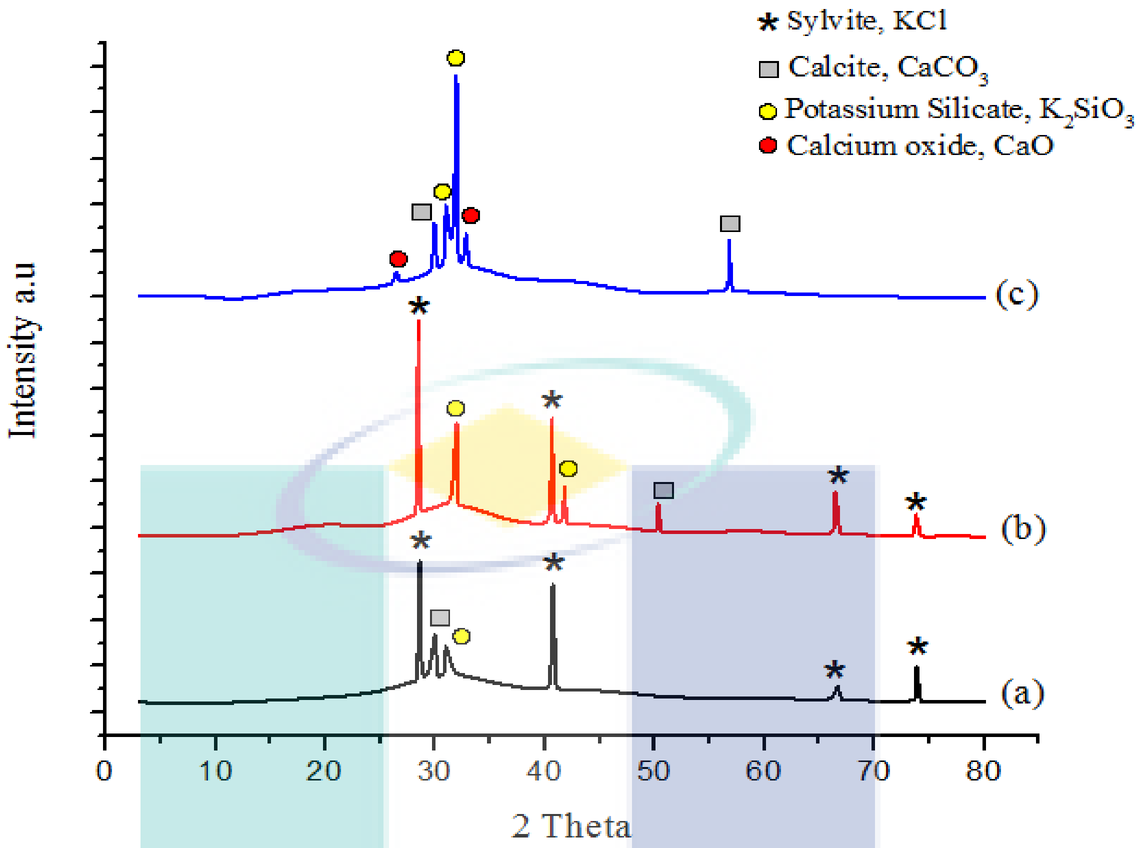


*Figure 4.3.* XRD Diffractogram of (a) BA 110, (b) BA 700 and (c) BA 900 catalysts.

### 4.2.4 Energy Dispersive X-Ray Fluorescence (EDXRF) Analysis

The presence of $K_2SiO_3$ predominantly in calcined boiler ash (BA 900) was verified using EDXRF analysis (Table 4.1). It was also found that at higher heat treatment under static air environment, KCl that exist in dried boiler ash is later transformed into $K_2SiO_3$ where the loss of chlorine ion can be expected (Table 4.2). The presence of other elements such as MgO, CaO, $Al_2O_3$, $Fe_2O_3$, $P_2O_5$, $ZrO_2$ are at minor level that do not significantly affect the catalytic activity of boiler ash. Additionally, the presence of $SiO_2$ also does not affect the catalytic activity of boiler ash and gives the yield of glycerol carbonate amount to be comparable to uncatalysed reaction. Indeed, it was found that potassium ion along with its conjugated basic site (i.e. KCl, KOH and $K_2SiO_3$) acted as the most effective metal element of interest. Apart from that, the XRF analysis conducted is in agreement with the ICP-MS and FESEM-EDX analysis in which the dominant metal element detected in all three analyses was potassium.

Table 4.1
*X-Ray Fluorescence of BA 900 (metal oxides)*

| Composition | Mass percentage |
|---|---|
| $SiO_2$ | 58.69 |
| $K_2O$ | 12.70 |
| $CaO$ | 15.90 |
| $MgO_2$ | 4.27 |
| $Al_2O_3$ | 3.42 |
| $Fe_2O_3$ | 3.35 |
| $P_2O_5$ | 1.29 |
| $ZrO_2$ | 0.38 |
| $K_2O + SiO_2$ | 71.39 |

Note: chlorine was not detected and carbon was detected at 3.33 %.

Table 4.2
*X-Ray Fluorescence of BA 110 (metal oxides)*

| Composition | Mass percentage |
|---|---|
| $SiO_2$ | 54.62 |
| $K_2O$ | 19.13 |
| $CaO$ | 12.47 |
| $MgO_2$ | 3.98 |
| $Al_2O_3$ | 3.94 |
| $Fe_2O_3$ | 2.78 |
| $P_2O_5$ | 2.12 |
| $ZrO_2$ | 0.96 |
| K + Cl | 41.40 |

Note: chlorine and carbon were detected at 22.27 % and 12.78 % respectively from elemental analysis

### 4.2.5 BET Surface Area ($S_{BET}$) Analysis

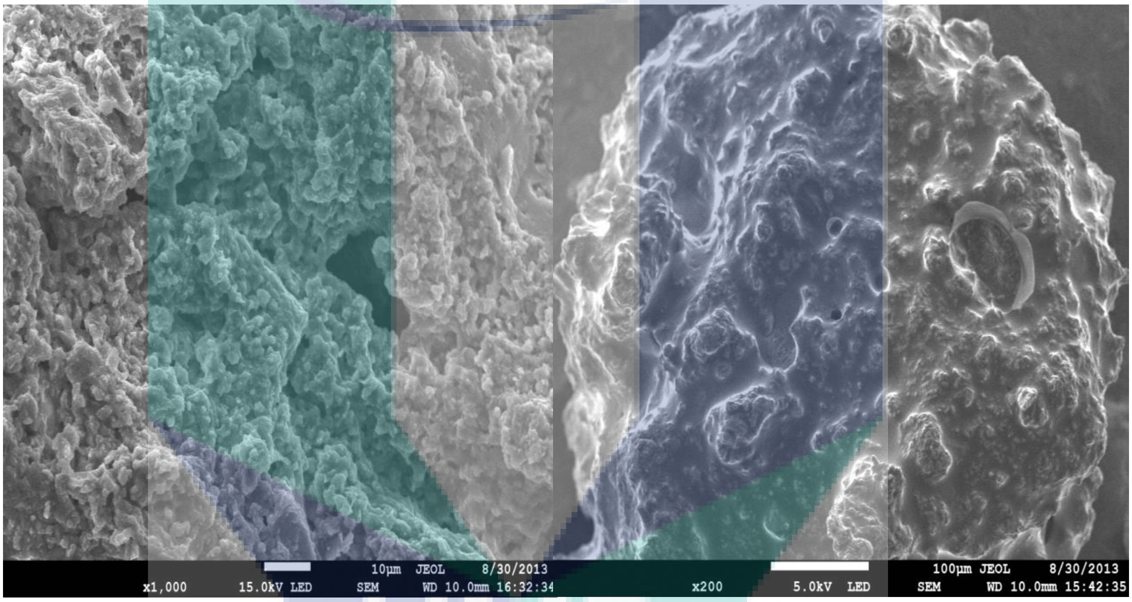
From the BET analysis, it was found that raw boiler ash had surface area of 29.77 $m^2$/ g, BA 110 had surface area of about 8.05 $m^2$/ g and BA 900 had surface area about 2.00 $m^2$/ g. The surface area of the raw and dried boiler ash at 110 °C was relatively larger than the boiler ash calcined at 900 °C. This is because at higher temperature agglomeration of particles occur causing particles to bind closely to each other and exist as cluster where this dramatically causes surface area to decrease. In contrast, boiler ash calcined in closed system reported by Boey et al., (2011) at 900 °C had a larger particle size of 25.8 $m^2$/ g. Theoretically, the catalyst with bigger surface area will produced superior catalytic activity, but in this particular catalytic reaction, surface area clearly did not influence the catalytic results ever since no distinct difference in the catalytic data of current study (Table 4.7) was observed. The isotherm graph of both BA 110 and BA 900 suggest that the catalyst follows type III isotherm which is characterised by heats of adsorption less than the adsorbate heat of liquefaction, adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface (Appendix A). Type III isotherm also indicates that the catalyst are mesoporous in nature.

### 4.2.6 Morphology and Elemental Analysis of Boiler Ash using Field Emission Scanning Electron Microscopy – Energy Dispersive X-Ray (FESEM-EDX)

From Table 4.3, it is apparent that potassium is the most dominant chemical element present in boiler ash which supports the catalytic activity of the boiler ash to be influenced by potassium. Besides, the minimal amount of Mg (3.39 %) further explained unobservable diffraction peaks for possible magnesium oxide and carbonate in XRD diffractogram. These elemental results also correlated to previous results reported by Yin et al., (2008). Figure 4.4 on the other hand, depicts the nature of boiler ash to be spongy and porous where it could act as a good absorbent of moisture (Chu & Hashim, 2002; Boey, Ganesan, Maniam, Khairuddean, & Lim, 2012). Ash containing potassium is also reported to be a good moisture absorbent by Ali and Strand, (2013). This characteristic is important because waste glycerol contains moisture and catalyst which can absorb moisture will allow formation of glycerol carbonate.

Table 4.3
*Elemental analysis of BA 900 using FESEM-EDX*

| **Element** | **Weight %** |
|---|---|
| C | 9.97 |
| O | 53.24 |
| Mg | 3.39 |
| Al | 0.70 |
| Si | 6.01 |
| S | 1.42 |
| Cl | 1.10 |
| K | 18.53 |
| Zr | 5.65 |
| Total | 100.00 |



(a) (b)

***Figure 4.4.*** FESEM of (a) BA 110 and (b) BA 900.

### 4.2.7 Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) Analysis

As a validation to the elemental composition in boiler ash conducted using EDX, the analysis using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) was carried out. Total concentration of metals exist in BA 900 is summarised in Table 4.4. It is obvious that potassium is the most dominant metal present in boiler ash which significantly corresponds to the FESEM-EDX data.

Table 4.4

*Metal content in BA 900 (ICP-MS)**

| **Metals** | **Percentage (%)** |
|---|---|
| Potassium (K) | 86.8 |
| Calcium (Ca) | 9.8 |
| Magnesium (Mg) | 2.0 |
| Aluminium (Al) | 1.1 |
| Others (Fe, Ag, Cu, and Na) | 0.4 |

Note: * analysis carried out for environmental metals only.

### 4.2.8 Acidity and Basicity Analysis

#### 4.2.8.1 Hammett Test

It is important to analyse the basicity and acidity level of boiler ash because basic catalyst are favoured for the glycerolysis reaction with urea (Climent et al., 2010; Jagadeeswaraiah et al., 2014). Therefore, pre-analysis of basicity and acidity of boiler ash was confirmed through the Hammett test. Based on Table 4.8 4.5, it can be summarised that the Hammett test showed that all catalyst BA 110, BA 500, BA 700, BA 900, BA 1100, KOH, KCl, fresh $K_2SiO_3$, MgO and CaO changed the colour of phenolphthalein (H_=8.2) from colourless to pink. However, for all three indicator 2, 4 – Dinitroaniline (H_=15), 4 – Nitroaniline (H_=18.4) and methyl red (H_=4.8) remained unchanged. Therefore, it can be concluded that the basicity of the catalyst BA 900 lie in the range of 8.2 < H_< 15 and the catalyst is not acidic in nature. On the other hand, $SiO_2$ showed no changes indicating it is a neutral material similar to the rice husk silica containing silicon dioxide tested (Hindryawati, Maniam, Karim, & Chong, 2014) . In concise, all calcined catalysts tested are basic in nature based on the Hammett test carried out. The low basicity of the catalyst is essentially influenced by $OH^-$ groups, medium basicity by metal $O^-$ groups and strong basicity by $O^{-2}$ groups (Deng, Fang, Liu, & Yu, 2011).

Table 4.5

*Hammett Test analysis of tested catalyst*

| **Catalyst** | **Methyl Red (H_=4.8)** | **Phenolphthalein (H_=8.2)** | **2, 4 – Dinitroaniline (H_=15)** | **4 – Nitroaniline (H_=18.4)** |
|---|---|---|---|---|
| BA 110 | No changes | Colourless to pink solution | No changes | No changes |
| BA 500 | No changes | Colourless to pink solution | No changes | No changes |
| BA 700 | No changes | Colourless to pink solution | No changes | No changes |
| BA 900 | No changes | Colourless to pink solution | No changes | No changes |
| BA 1100 | No changes | Colourless to pink solution | No changes | No changes |
| KOH | No changes | Colourless to pink solution | No changes | No changes |
| KCl | No changes | Colourless to pink solution | No changes | No changes |
| $K_2SiO_3$ | No changes | Colourless to pink solution | No changes | No changes |
| MgO | No changes | Colourless to pink solution | No changes | No changes |
| CaO | No changes | Colourless to pink solution | No changes | No changes |
| $SiO_2$ | No changes | No changes | No changes | No changes |

#### 4.2.8.2 Carbon Dioxide - Temperature Programmed Desorption ($CO_2$-TPD)

After evaluating preliminary results from the Hammett test, it was found that boiler ash was a basic material. From there, further basicity analysis was conducted using Temperature Programmed Desorption analysis with $CO_2$ as chemical probe ($CO_2$-TPD). From Figure 4.5 and Table 4.6, BA 110 is classified as a basic material with total gas $CO_2$ desorbed about 7066.9 µmol/ g. A total of four distinct peaks were observed at different temperatures with different amount of $CO_2$ gas desorbed ranging from weak basic property to high basic property. This is regard to the influence of homogeneously distributed weak alkaline metals and strong alkaline metals in BA 110. BA 700 on the other hand showed basic property with total amount of $CO_2$ gas desorbed about 780.3 µmol/ g while BA 900 showed 1249.3 µmol/ g of $CO_2$ gas desorbed. A total of three peaks were observed with different amount of gas desorbed. According to $CO_2$-TPD technique, it can be roughly classified that peaks absorbed at temperature (< 200 °C) contains weak basic sites, at temperature (200 °C – 400 °C) contains medium basic sites and at temperature (> 400 °C) contains strong basic sites respectively (Wang, L. et al., 2011).

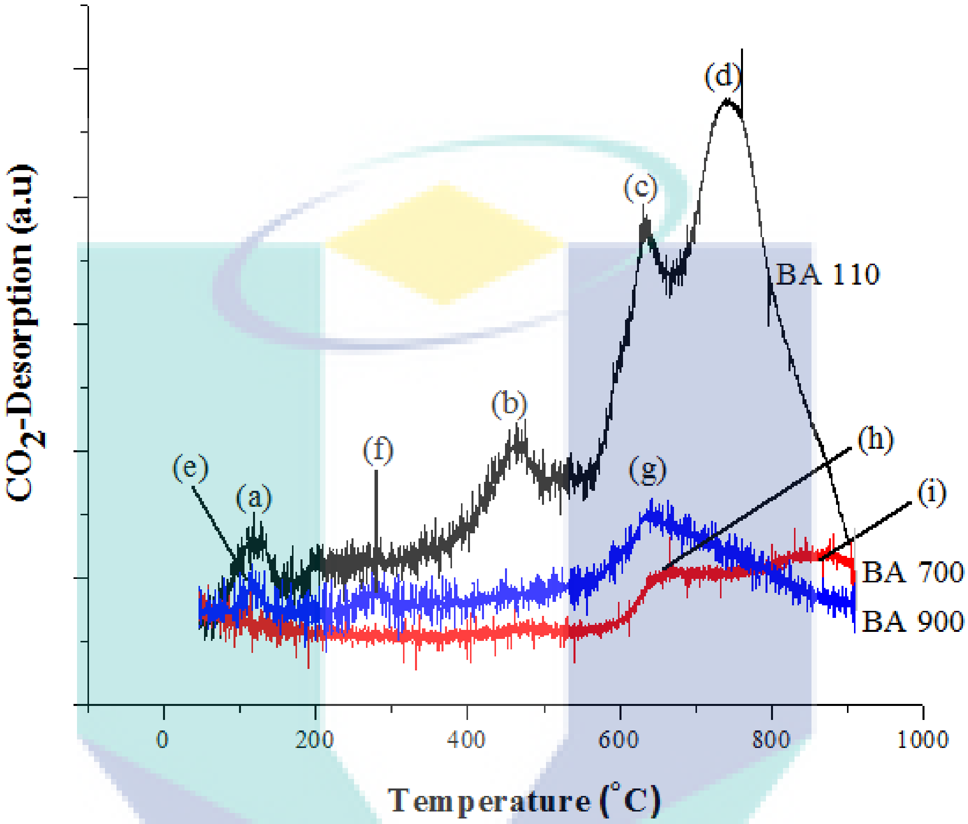


*Figure 4.5.* $CO_2$-TPD of BA 110, BA 700 and BA 900.Note: (a) is weak peak of BA 110, (b), (c) and (d) is strong peak of BA110. (e) is weak peak of BA 900, (f) is medium peak of BA 900 and (g) is strong peak of BA 900, (h) and (i) is strong peak of BA 700.

Table 4.6

*Basic sites distribution calculated on the basis of $CO_2$-TPD profile*

| **Catalyst** | **Basic sites ( μmol/ g)** | | | | **Contribution of strong basic site (%)** |
|---|---|---|---|---|---|
| | **Weak** | **Medium** | **Strong** | **Total** | |
| BA 110 | 265.1 | - | 6801.7 | 7066.9 | 96 |
| BA 700 | - | - | 780.3 | 780.3 | 100 |
| BA 900 | 44.9 | 54.8 | 1149.6 | 1249.3 | 92 |

For the case of BA 110, strong basic sites corresponds to the peak desorbed at temperature 446 °C (b), 635 °C (c) and 744 °C (d) respectively. On the other hand for BA 900 strong basic site is present at peak 647 °C (g) while BA 700 exhibited strong basic sites at peak 667 °C (h) and 834 °C (i). Even though, all three BA 110, BA 700 and BA 900 contain strong basic sites, the Hammett test indicated these three catalysts to show mild basic property. Thus, this could be an influence of mixture of weak and strong metal oxides that results in mild basic property of boiler ash in the Hammett test as previously depicted in Table 4.5 (section 4.2.8.1). Even though, BA 110 exhibits almost 6 times higher basic property from the $CO_2$-TPD analysis, BA 700 and BA 900 still depicted higher yield of glycerol carbonate compared to BA 110. This because higher amount of carbon attached to inorganic materials in BA 110 result in higher basic sites as previously described by Montes-Moran and co-researchers in 2012. In contrast, BA 900 and BA 700 had lower values of active sites due to the loss of carbon through incineration. However, the activity of carbon was not essentially influenced by the amount of basic sites but by the different sources of basic metal oxides. Thus, it is expected that the potassium metal ion which acts as a weak Lewis acid had played the major role in the catalytic activity. This is because it is found that Lewis acid sites activates the carbonyl group of urea while the conjugated basic site activates hydroxyl group on glycerol to form glycerol carbonate (Climent et al., 2010). It is also understood that the preform of potassium does not show a major effect on the catalytic data obtained. In addition to that, presence of $K_2SiO_3$ is more dominant in BA 700 and BA 900 compared to BA 110 which is evident from the XRD as well as FESEM-EDX data. Therefore, the availability of $O^{-2}$ species could assist in superior catalytic activity of BA 700 and BA 900 to form glycerol carbonate.

In previous study by Ochoa-Gómez et al., (2009) using glycerol and dimethyl carbonate as a carbonyl source it was found that basic catalyst were favoured compared to acidic catalyst. This is because based on the study it was found that activity of acid catalyst was limited to longer duration of reaction whereby the reaction was kinetically controlled. The use of acid catalyst also suggested lower yields compared to the use of base catalyst. On the other hand, study by Marakatti and Halgeri, (2015) using solid acid catalyst in reaction of glycerolysis with urea suggested that better activity with Zn-HY zeolite. However, the claim suggested that $Zn^{2+}$ played the main role as a Lewis acid which indicates that the activity of catalyst used was influenced by the basicity of catalyst whereby increase in more $Zn^{2+}$ in HY zeolite increased conversion, selectivity and yield of glycerol carbonate. Therefore, the current study is well suited to be conducted with basic catalyst boiler ash as.

## 4.3 Effect of Calcination Temperature of Boiler Ash towards Glycerol Carbonate Synthesis

The pretreatment carried out on solid catalyst either involved chemical or physical techniques is one of the typical practices in catalyst development, with the target in minds to tune the physico-chemical characteristic of the catalytic material. Thus, a simple and fast calcination technique was used to pre-treat the waste boiler ash and its effect towards glycerol conversion, glycerol carbonate selectivity and glycerol carbonate yield is summarised in Table 4.7. From the reaction conducted, it is evident that boiler ash is capable of selectively converting glycerol into glycerol carbonate. However, calcination of catalyst at various temperatures did not significantly alter the conversion of glycerol. All catalyst used reported had almost relatively comparable glycerol conversion which was ≥ 90 % at 4 h reaction time. BA 900 showed the highest selectivity and yield of about 90.1 ± 1.0 % and 84.3 ± 1.1% respectively which was significantly higher than reaction conducted without catalyst. It is worth to note that glycerol carbonate yield obtained from blank reaction is comparable with previously reported literature (Hammond et al., 2011; Rahim et al., 2012).

Table 4.7
*Effect of boiler ash calcination temperature on glycerol conversion, glycerol carbonate selectivity and yield*

| **Catalyst** | **Heat treatment (°C)** | **Gly. conv. %** | **Selectivity %** | | | | **Gly C Yield %** | **TOF (mmol/g.cat. $h^{-1}$)** |
|---|---|---|---|---|---|---|---|---|
| | | | **Gly C** | **Comp. (3)** | **Comp. (5)** | **Comp. (6)** | | |
| Blank | - | 78.7 | 32.8 | 24.0 | 43.1 | - | 25.8 | - |
| BA 110 | 110 | 91.1 | 83.5 | 1.9 | 11.1 | 3.5 | 76.2 | 114.3 |
| BA 500 | 500 | 91.1 | 82.7 | 4.3 | 10.0 | 2.9 | 75.3 | 113.0 |
| BA 700 | 700 | 94.1 | 88.6 | 3.5 | 4.8 | 2.9 | 83.4 | 125.1 |
| BA 900 | 900 | 93.6 | 90.1 | 4.1 | 3.9 | 1.9 | 84.3 | 126.5 |
| BA 1100 | 1100 | 89.8 | 85.6 | 5.5 | 6.4 | 2.4 | 77.0 | 115.5 |

Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Time, 4 h; Standard stirring rate, 340 rpm. TOF: calculated based on the mmol of glycerol multiply by yield percentage of glycerol carbonate per gram catalyst per total reaction time (h). Relative Standard Deviation (RSD): < 5%. Note: Gly. is Glycerol; Gly C is Glycerol carbonate; Comp. (3) is 2, 3-dihydroxypropyl carbamate; Comp. (5) is 4-(hydroxymethyl) oxazolin-2-one; Comp. (6) is (2-oxo-1,3-dioxolan-4-yl)methyl carbamate.

The yield of glycerol carbonate obtained follows the order of BA 900 > BA 700 > BA 1100 > BA 110 > BA 500. This could have resulted from the influence of basic metal oxides present in the catalyst as confirmed through Hammett test, which all tested catalysts showed almost similar basicity strength even after different heat pretreatment was carried out. Besides, the data was further validate through justification that potassium is the most major metal in the catalyst which was identified through X-ray diffraction (XRD) and inductively couple plasma-mass spectrometer (ICP-MS) analyses which have been the target metal that has actively played the role in the catalytic activity of boiler ash. Detailed discussions on the actual role of both acidity-basicity strength as well as the potassium as proposed active site are discussed in section 4.2.8. The activity of BA 900 and BA 700 were comparable due to presence of potassium silicate being dominant as discussed earlier in XRD and EDXRF analysis. The calcination treatment allows agglomeration of the element potassium and silicate present in raw boiler ash to form potassium silicate at these specific temperatures.

The catalytic data obtained for BA 900 as catalyst was comparably higher compared to recently published study where 75% yield of glycerol carbonate was obtained using metal monoglycerolates as catalyst under same temperature conditions (Turney et al., 2013). Besides, the turnover frequency, TOF (mmol/g.cat.$h^{-1}$) of boiler ash was relatively higher than most of the previously reported study which uses tin-tungsten mixed oxide, metal monoglycerolates, gold, gallium, and zinc supported on oxides and zeolite ZSM-5, Ionic liquids immobilized onto a structurally modified Merrifield peptide resin, calcined Zn hydrotalcite as well as $Co_3O_4$/ZnO nanodispersion as catalysts (Table 4.8). It is essential to note that TOF value is independent indicator for the catalytic performance comparison under different reaction conditions and parameters. Thus, it can be said that BA 900 showed promising catalytic rate subsequently promises good yield and selectivity of glycerol carbonate as target product. However, γ-zirconium phosphate had higher TOF value compared to BA 900 but comparatively had lower yield than BA 900 and used higher pressure for synthesis reaction. Hence, BA 900 could serve as a better catalyst for reaction under atmospheric pressure with lower cost operational value. In addition, γ-zirconium phosphate is also synthetically derived. In concise, the current finding suggests that this study could critically ensure an alternative method for proper disposal of waste boiler ash.

Table 4.8

*Turnover Frequency (TOF) (mmol/g.cat.h$^{-1}$) of other selected catalysts reported in literature*

| **Catalyst** | **Glycerol/urea ratio (mol:mol)** | **Temp. (˚C)** | **Pressure (MPa)** | **Reac. Time (h)** | **Gly C Yield (%)** | **TOF (mmol/g.cat. h$^{-1}$)** | **References** |
|---|---|---|---|---|---|---|---|
| Tin-Tungsten mixed oxide | 2:1 | 140 | - | 4 | 49.0 | 13.5 | (Jagadeeswaraiah et al., 2014) |
| Metal Monoglycerolates | 1:1.5 | 150 | $4.0 \times 10^{-3}$ | 7 | 75.0 | 23.1 | (Turney et al., 2013) |
| Gold, gallium, and zinc supported on oxides and zeolite ZSM-5 | 1:1.5 | 150 | 0.1 | 4 | 55.0 | 82.5 | (Hammond et al., 2011) |
| Ionic liquids immobilized onto a structurally modified Merrifield peptide resin | 1:1 | 140 | $1.4 \times 10^{-2}$ | 6 | 46.0 | 16.7 | ( Kim, D.-W. et al., 2011)<br>. |
| Calcined Zn hydrotalcite | 1:1 | 145 | $3.9 \times 10^{-3}$ | 5 | 72 | 31.1 | (Climent et al., 2010) |
| $Co_3O_4$/ZnO nanodispersion | 1:1 | 145 | 0.1 | 4 | 69 | 31.1 | (Rubio-Marcos et al., 2010) |
| γ-Zirconium phosphate | 1:1 | 145 | $2.0 \times 10^{-5}$ | 3 | 80 | 485.7 | (Aresta et al., 2009) |

TOF: calculated based on the mmol of initial polyols multiply by yield percentage of carbonate per gram catalyst per total reaction time (h)

## 4.4 Reaction Conditions of Glycerol Carbonate Synthesis

In any catalytic reaction involving new catalyst material, an optimisation on the reaction conditions is required. Thus, the effect of variation on reaction parameters were further discusses in this section. In specific, the section is subdivided into various tested parameters studied which include details discussion on the effect of reaction duration, effect of temperature, glycerol to urea molar ratio, catalyst mass, stirring rate, and effect of different gas flowed. The study of parameters as mentioned was carried out using one factor at a time (OFAT) analysis method. Since detailed catalytic testing data discussed in section 4.3 point out that BA 900 represents the best catalyst for the synthesis of glycerol carbonate at standard reaction condition, the catalyst was used herein.

### 4.4.1 Effect of Reaction Duration

It is important to identify the optimum reaction time in any chemical reaction. In industrial process, duration of reaction may eventually influence overall operational cost. Figure 4.6 illustrates the time online study for boiler ash in the reaction with glycerol and urea from 0 h to 10 h reaction time. From the Figure, it is evident that glycerol conversion using BA 900 shows a consistent increase in conversion from 0 h to 6 h. At 6 h, 8 h and 10 h, the conversion hits a maximum level and remains unchanged which is about 97% conversion. It was found that the maximum yield of glycerol carbonate is at 4 h reaction time reaching 84.3 ± 1.1% of yield of glycerol carbonate from the triplicate study of BA 900. On the contrary, selectivity percentage and yield percentage of glycerol carbonate decreased gradually from 5 h to 10 h. Low selectivity and yield at prolonged reaction time was due to the transformation of glycerol carbonate into carbamate of glycerol carbonate. This is due to the availability of primary hydroxyl group (-OH) in glycerol carbonate molecule which has higher possibility to react with urea to form (2-oxo-1,3,-dioxolan-4-yl)methyl carbamate (denoted herein as compound 6) (Hammond et al., 2011). The availability of urea at prolonged reaction time was confirmed by the time online analysis using ATR-FTIR and $^{13}$C NMR (section 4.6.1). Therefore, the time online analysis (TOL) depicts that 4 h reaction time is the most suitable time of reaction with BA 900 to assist production of maximum yield.

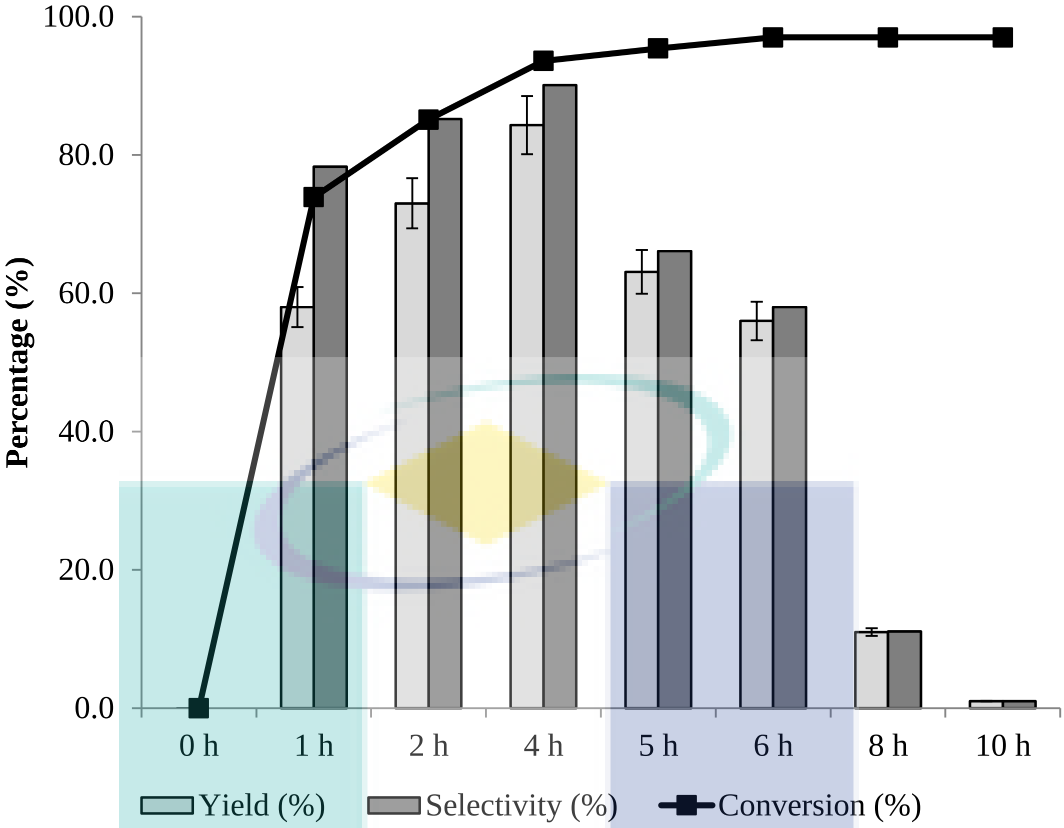


*Figure 4.6.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of BA 900. Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

On the other hand, Figure 4.7 illustrates the selectivity percentage of glycerol carbonate, glycerol carbamate (denoted herein as compound 3), 4-(hydroxymethyl) oxazolidin-2-one (denoted herein as compound 5) and (2-oxo-1,3,-dioxolan-4-yl)methyl carbamate (compound 6). It is evident that by prolonging the reaction time, decomposition of glycerol carbonate into compound (6) increases and at the same time formation of compound (5) originated from carbamate intermediate also increased. The Figure 4.7 also depicts that the glycerol carbamate, formed was decomposed into glycerol carbonate in an accelerated manner. It is important to note that in previous studies, compound (3) was observed to be present in large amount in the initial stages of reaction and then gradually converted into glycerol carbonate at prolonged reaction time (Climent et al., 2010; Rahim et al., 2012; Jagadeeswaraiah et al., 2014). However, in the current study selectivity of intermediate carbamate (compound 3) did not correspond to the selectivity of glycerol carbonate.

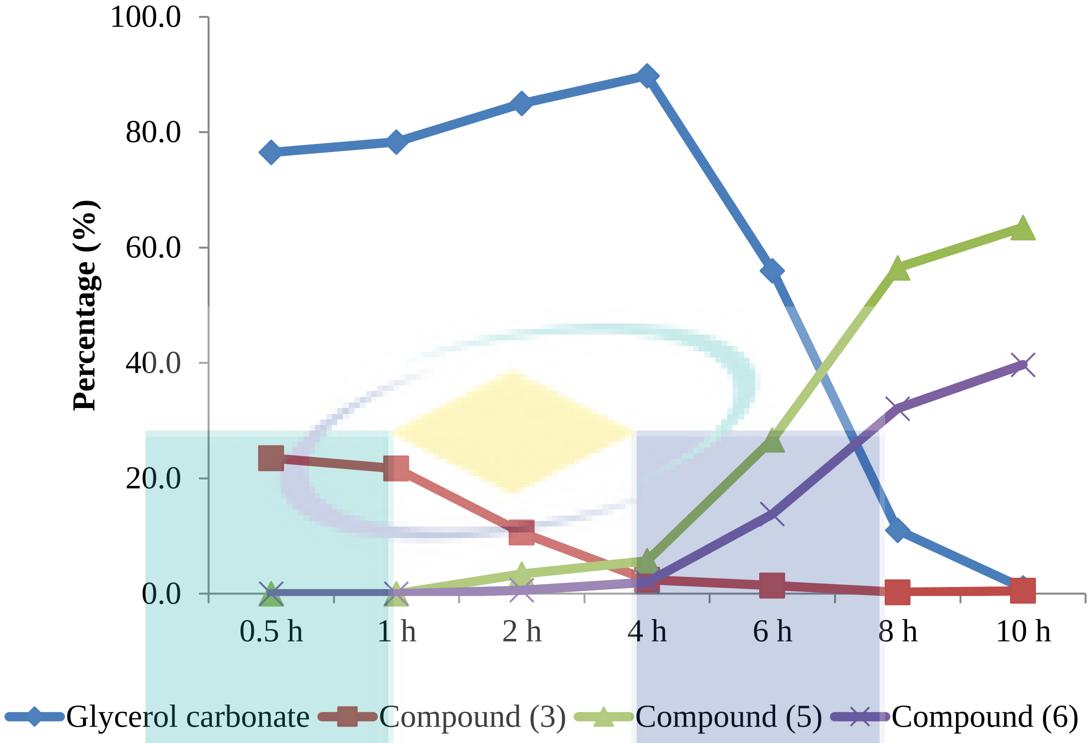


*Figure 4.7*. Time online analyses (TOL) of selectivity of compounds in glycerol carbonate synthesis with BA 900 catalyst. Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

To corroborate and confirm the aforementioned discussion on products distribution observed during reaction time study, ATR-FTIR analysis (Figure 4.3) was carried out on glycerol standard, glycerol carbonate standard, product of reaction at 4 h and 10 h. From Figure 4.8, it is evident that glycerol is detectable through ATR-FTIR where transmittance of peak at range (1500-1200) $cm^{-1}$ indicates glycerol moiety as in pattern (a) and (c). These peaks are assigned to overlapping of C-H in planes and O-H bending in the glycerol molecule. The O-H bending is further supported by the –OH stretching at peak range of (3500 - 3000) $cm^{-1}$ (Hazimah et al., 2003). On the other hand, glycerol carbonate is evident to be present in pattern (b) and (c). The occurrence of O-H vibration from 2-hydroxyethyl chain at peaks 3432 $cm^{-1}$ and 3343.57 $cm^{-1}$ indicates presence of –OH functional group. Besides, peak observation from range (2950-2850) $cm^{-1}$ further specifies presence of glycerol carbonate. The two peaks observed are due to $-CH_2$ and -CH vibration of the O-methylene and O-methylindyne groups of cyclic carbonate. Moreover, the peak present at range (1790-1760) $cm^{-1}$ signifies C=O functional group which is a result of C=O stretching of the 5 membered cyclic carbonate.

Peaks at range (1200-1000) $cm^{-1}$ also support the presence of glycerol carbonate where these peaks indicate C-C and C-O stretching of 2-hydroxyethyl chain (Calvino-Casilda et al., 2011). In pattern (c) the two peaks ranging from (1610-1670) $cm^{-1}$ indicate presence of urea as previously reported (Hammond et al., 2011). The urea peak is still visible in pattern (d) for the product of reaction catalysed by BA 900 at 10 h reaction time signifying urea is not completely used up in the prolonged reaction as urea is employed excessively. However, the decrease of glycerol moiety peaks were noticed in pattern (d) indicating loss of glycerol where it suggest almost 97% conversion of glycerol in prolonged reaction time. Besides, the C=O stretch was also shifted in pattern (d) to the right from 1790 $cm^{-1}$ into 1730 $cm^{-1}$ due to decrease in selectivity of formation of glycerol carbonate and increase in formation of 4-(hydroxymethyl) oxazolidin-2-one (compound 5) at prolonged reaction time at 10 h. The shifted peak was observed to occur due to the (C=O) being adjacent to N-H group in compound (5). As for glycerol carbonate, the C=O is partly adjacent in between two –O groups which indicates the peak in spectrum (b) and (c) to be in-line and sharper compared to spectrum (d). Thus, C=O group is still expected to persist at 10 h due to the increase formation in compound (5).

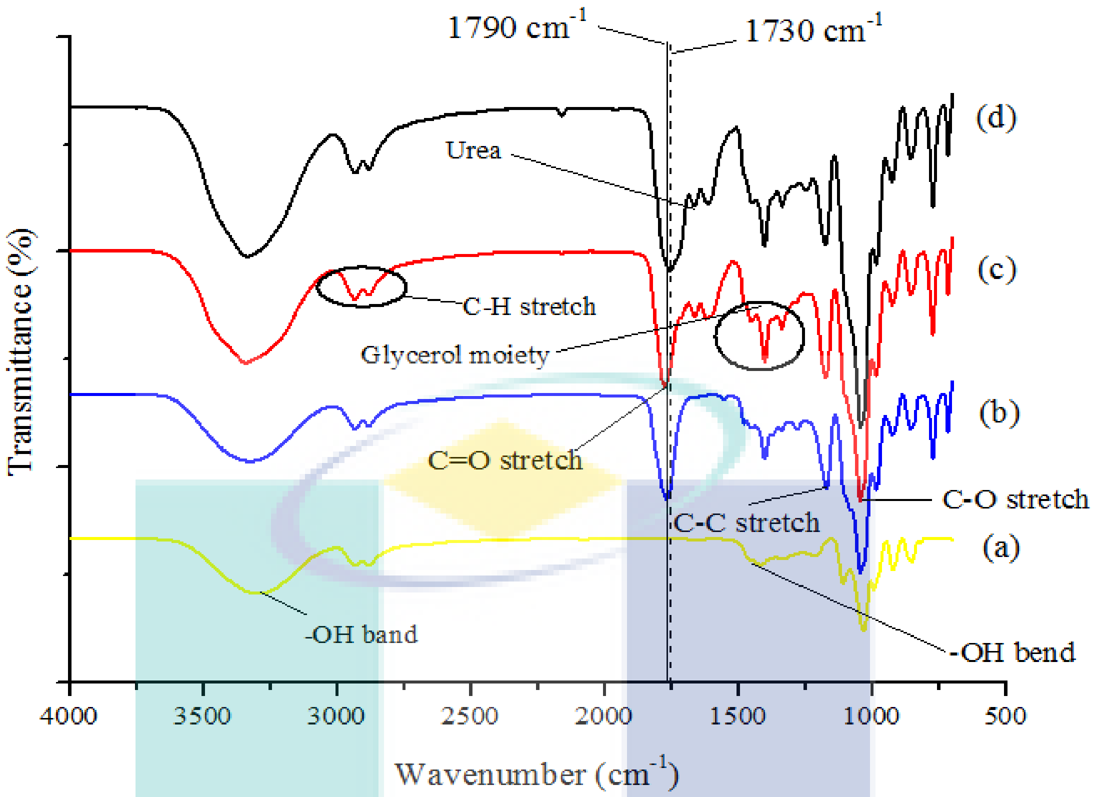


*Figure 4.8.* ATR-FTIR spectrum of a) Standard glycerol, b) Standard glycerol carbonate, c) Product of reaction catalysed using BA 900 at 4 h reaction time and d) Product of reaction catalysed by BA 900 at 10 h reaction time.

### 4.4.2 Effect of Reaction Temperature

In order to identify the most optimum temperature for the synthesis of glycerol carbonate using BA 900, a set of reaction at temperature in range of 100 °C to 160 °C was tested. BA 900 was chosen based on the catalytic activity reported in section (4.3). From Figure 4.9, it is clear that reaction at 150 °C shows the maximum yield and selectivity towards glycerol carbonate formation. Besides, an increasing pattern of glycerol carbonate yield and selectivity was observed when temperature was gradually increased from 100 °C to 150 °C. However, yield and selectivity declined as temperature of reaction was increased to 160 °C. These phenomena persist to occur as at higher temperature the decomposition of glycerol carbamate favoured formation of 4-(hydroxymethyl)-1,3-dioxolan-2-one (compound 5) while glycerol carbonate (compound 4) decomposed into (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (compound 6). Therefore, lost in selectivity towards glycerol carbonate formation concurrently affected the yield. Besides, previous study by Lundström and co-workers in 2011 discusses that urea at temperature 150 °C and above decomposes into isocyanic acid (HNCO) (Lundström et al., 2011). Thus, this phenomenon could possibly alter the formation of desired product glycerol carbonate. The reaction between glycerol and urea is relatively temperature sensitive and it is necessary to control reaction below 155 °C (Zhang & He, 2014a). The conversion of glycerol on the other hand, increased with increasing temperature. Similar pattern in increment of glycerol conversion with accordance to increase in temperature were also reported previously by Wang, D. and Zhang, (2015) as well as Narkhede and Patel, (2015). Hence, it is concluded that 150 °C is the most optimum temperature for the reaction to be conducted.

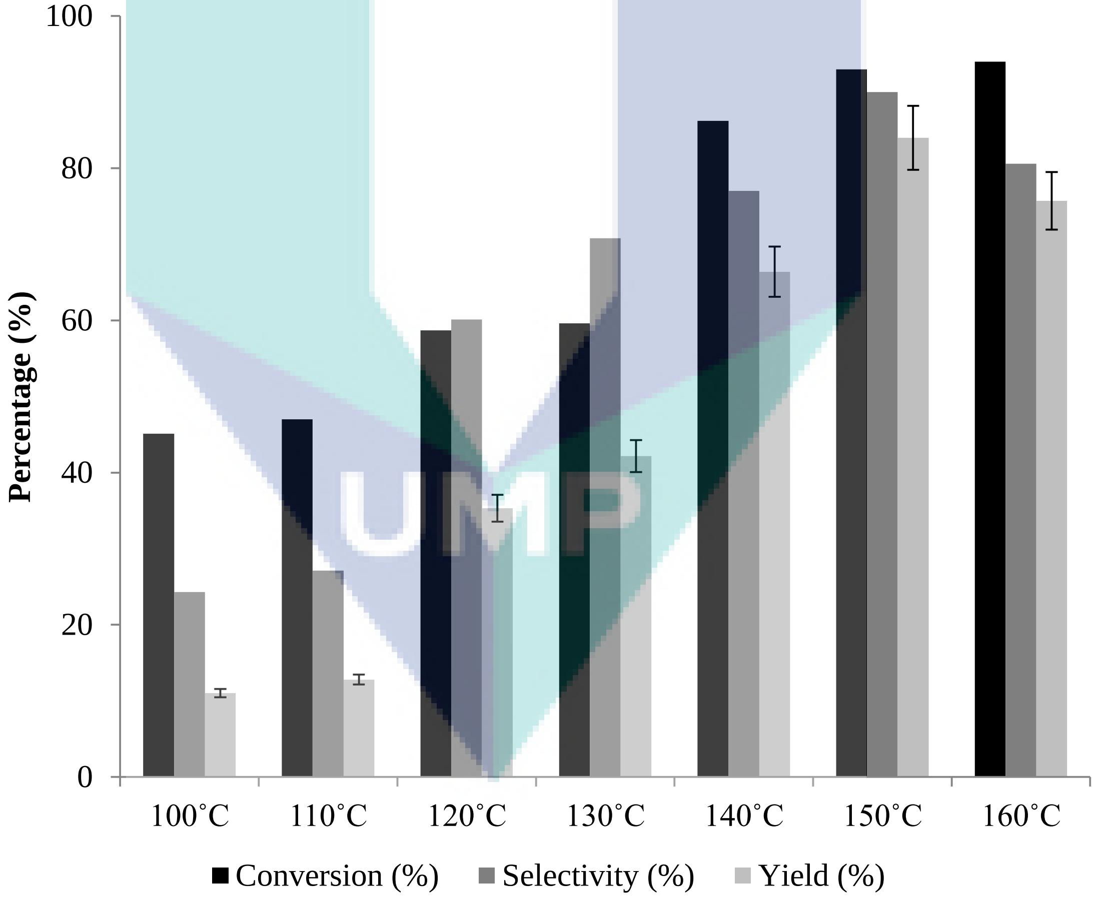


*Figure 4.9.* Effect of temperature towards glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of BA 900 at 100 ˚C, 110 ˚C, 120 ˚C, 130 ˚C, 140 ˚C, 150 ˚C and 160 ˚C. Reaction conditions: Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); catalyst mass 0.25 g; Time: 4 h; standard stirring rate: 340 rpm.

### 4.4.3 Effect of Glycerol to Urea Molar Ratio

It is well known in catalytic reaction that the ratio of reactants loaded might alter the conversion of feedstock and yield of products. Figure 4.10 elucidates the effect of glycerol, to urea molar ratio towards glycerol carbonate formation. From the graph, it is evident that at 1:1.5 molar ratio of glycerol to urea, maximum yield and selectivity towards glycerol carbonate was observed. Increasing the molar ratio of glycerol to urea increases the glycerol carbonate formation. Urea in excess did not favour 100 % conversion or 100 % yield. In theory, the stoichiometry equation suggests that 1 mol of urea is required to react with 1 mol of glycerol to form 1 mol of glycerol carbonate and 2 mol of ammonia. However, previous study by Turney and co-researchers in 2013 supports that conversion of glycerol is directly proportional to the increasing molar ratio of urea to glycerol. In addition, the molar ratio of 1:1.5 was found to be the most suitable molar ratio for the reaction to be carried as also reported by Turney et al., (2013). Therefore, indicates that selectivity of the reaction is not only influenced by the molar ratio of increasing urea alone but also due to other reaction parameters. On the other hand, increasing molar ratio of glycerol to urea from 1:1.5 to 1:2 does not show any significant changes in the catalytic results. This result suggests that the most suitable molar ratio is 1:1.5. However, the effect of molar ratio studies suggests that higher amount of urea is required to achieve optimum yield of Gly C. This phenomena suggests that higher amount of carbonate source from excess urea accelerates the transcarbonation reaction at an optimum rate by allowing mass transfer, hence facilitate the interaction of the reactant molecules for the formation of the intermediate carbamate at a more convenient route.

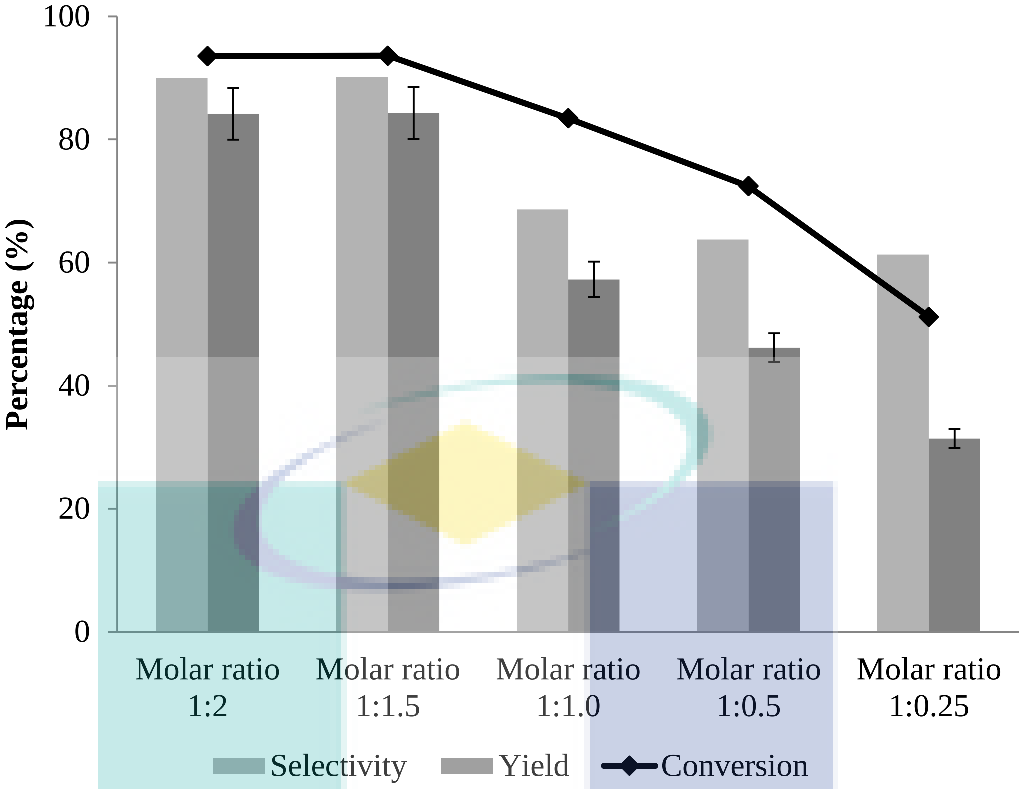


*Figure 4.10.* Effect of molar ratio of glycerol to urea towards glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) at 1:2, 1:1.5, 1:1, 1:0.5 and 1:0.25. Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Stirring rate, 340 rpm; catalyst mass 0.25 g; Time: 4 h.

### 4.4.4 Effect of Catalyst Mass

In an industrial commercialisation aspect, the amount of catalyst loaded is a crucial factor. In case, of using synthetically derived catalyst this might increase operational cost. Besides, it is important to identify the prime amount of catalyst suitable for a reaction as lower amount may result in poorer selectivity and conversion of product while higher amount may cause catalyst deactivation. Figure 4.11 illustrates the effect of catalyst mass loading towards glycerol carbonate formation. From the Figure, it is evident that 0.25 g of catalyst is the most suitable amount of catalyst to be loaded for the reaction since it shows the maximum yield and selectivity towards glycerol carbonate. The trend of the mass effect of catalyst increased with increasing catalyst amount from 0.025 g to 0.25 g. This scenario is expected to occur due to increasing Lewis acidity from increase in potassium ion. It has been reported that by increasing Lewis acidity, formation of selective glycerol carbonate is favoured (Marakatti & Halgeri, 2015). Besides, there are also a number of research studies that affirms the need of Lewis acidity and conjugate basic sites for glycerol carbonylation (Malyaadri et al., 2011; Jagadeeswaraiah et al., 2014; C. R. Kumar et al., 2012). Thus, the significant increase towards selectivity of glycerol carbonate is simply influenced by increasing amount of potassium ion. However, increasing amount of catalyst from 0.25 g to 0.35 g significantly lowered yield and selectivity of toward glycerol carbonate transformation. This observation might be due to several interrelated factors. The presence of excess ion and active sites may trigger deposition of reactant molecules to be clogged into pores of silicate of the catalyst and cause catalyst deactivation. Hence, limit of mass transfer can be observed from there in. High catalyst loading could possibly generate excess amount potassium ions inside the reaction solution. Therefore, influence the decomposition of glycerol carbonate into compound (6) and rapid transformation of glycerol carbamate into compound (5) can be observed (Figure 4.12). Thus, reduce the overall yield of glycerol carbonate. Additionally, the formation of potassium carbonate can occur from those surplus active potassium ions (Esteban, Domínguez, Ladero, & Garcia-Ochoa, 2015). Thus, the carbonate ion needed for the formation of the desired product may reduce being used up by the potassium ion and significantly affect the yield of glycerol carbonate. Besides, deactivation by coking can be expected by increasing amount of potassium ion which later develops into carbonaceous ion that clogs pores of the active silicate which subsequently limits the mass transfer of desired product formation (Klaewkla, Arend, & Hoelderich, 2011).

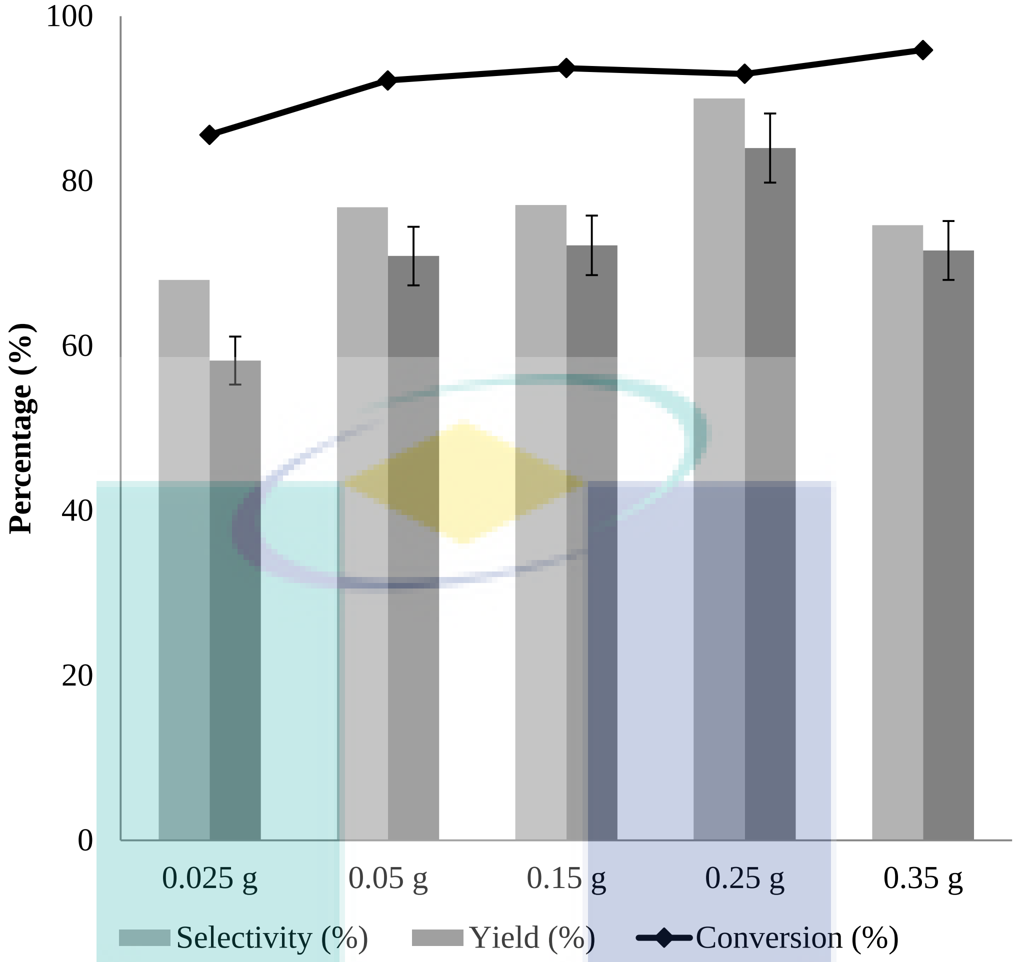


*Figure 4.11.* Effect of catalyst mass towards glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of BA 900 at 0.025 g, 0.05 g, 0.15 g, 0.25 g and 0.35 g. Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Time: 4 h; standard stirring rate: 340 rpm.

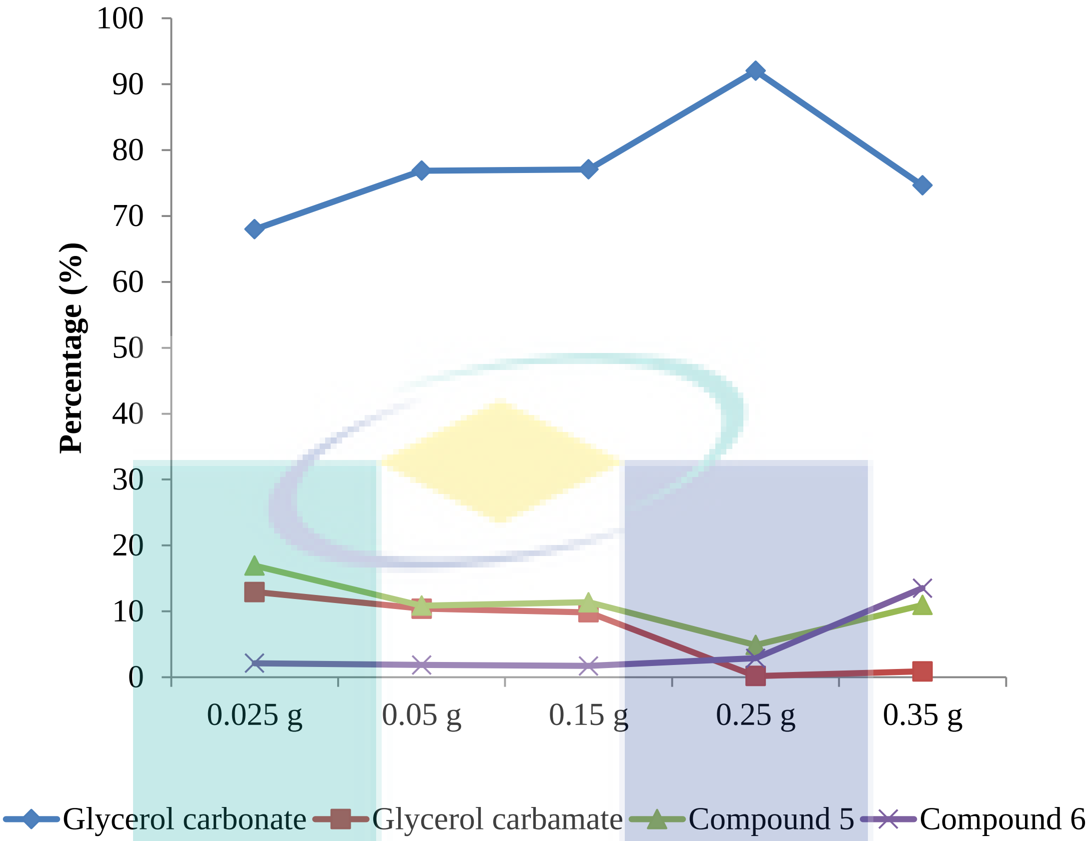


*Figure 4.12*. Effect of catalyst mass towards selectivity (%) of Glycerol carbonate, compound (3), compound (5) and compound (6) using waste glycerol with BA 900 at 0.05 g, 0.15g, 0.25 g and 0.35 g. Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Time: 4 h; standard stirring rate: 340 rpm.

### 4.4.5 Effect of Stirring Rate

In two-phase catalytic systems, where the solid catalyst is in contact with liquid reactant, proper agitation is required. It is expected that by increasing stirring rate, kinetics of reaction will increase and subsequently increase the level of conversion as well as selectivity. However, higher stirring rate may also effect decomposition of desired product into by-product above optimum stirring speed. Figure 4.13 elucidates the effect of stirring rate towards glycerol carbonate formation. From the graph it is evident that at 340 rpm maximum yield and selectivity towards glycerol carbonate were observed. However, increasing stirring rate from 340 rpm to 440 rpm and 640 rpm respectively showed a gradual decrease in desired product formation. This because increasing stirring speed of the reaction causes glycerol carbonate (4) to easily transform into compound (6) and intermediate (3) into compound (5) at a faster rate. The formation of compound (5) and Gly C occurs concurrently. Increase in the stirring speed is expected to affect the contact time of catalyst active sites with reactants to be shorter which results in poor selectivity towards Gly C formation. This scenario causes increased formation of compound (5). On the other hand, the increase in stirring speed also increases kinetics of reaction as mentioned earlier. This phenomena result in mass transfer between the excess urea, Gly C and catalyst to increase, thus facilitating the decomposition of Gly C at a faster rate into compound (6).

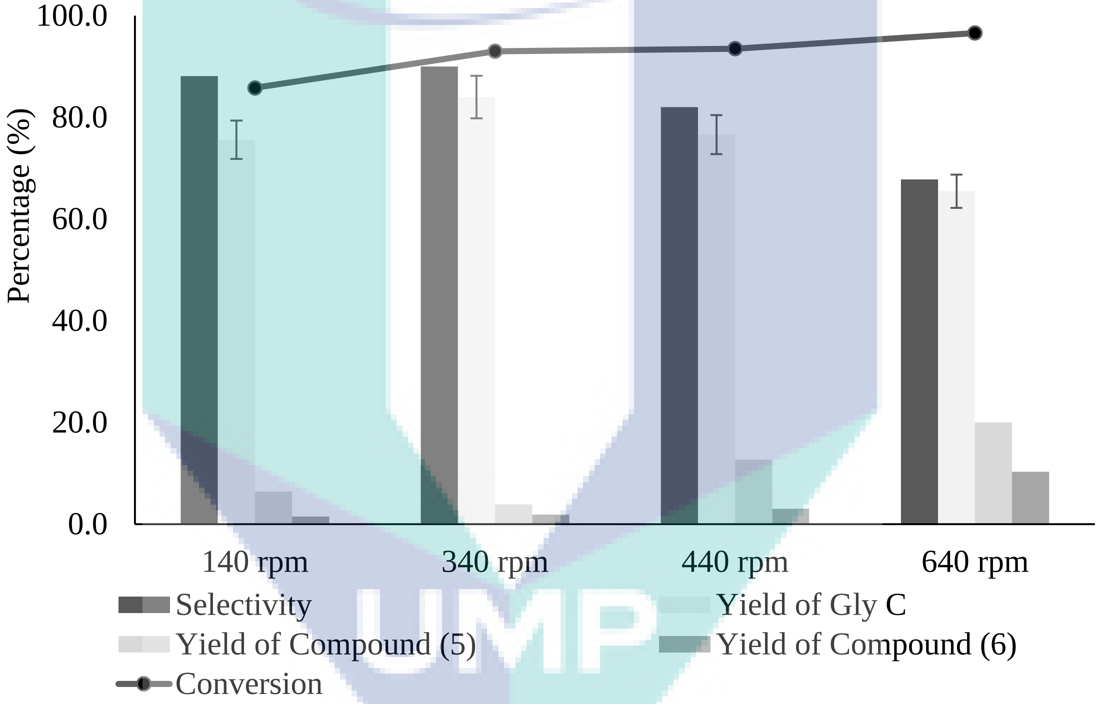


*Figure 4.13.* Effect of stirring rate towards glycerol conversion (%), glycerol carbonate selectivity (%), glycerol carbonate yield (%), compound (5) yield (%) and compound (6) yield (%) at 140 rpm, 340 rpm, 440 rpm and 640 rpm. Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); catalyst mass 0.25 g; Time: 4 h.

### 4.4.6 Effect of Different Type of Flowing gas

In any catalytic process, any possible factors which might contribute in affecting the yield of target compound shall be identified. Since the nitrogen gas was essentially used for the purpose of ammonia removal from the reaction medium, possible utilisation of any cheaper and easily available gas might add on extra value for the developed catalytic system. Thus, compress air was used instead of inert gas, i.e. nitrogen, $N_2$.

Based on Figure 4.14, the results obtained were significantly comparable with the time online analysis conducted with nitrogen gas indicates that the presence of oxygen and other reactive gas inside the air did not involve in catalytic reaction. For note, compress air contains 78 % of nitrogen gas, 21 % of oxygen and 1 % of other gases such as carbon dioxide, argon and helium. The possible glycerol oxidation reaction to occurred is less likely since no oxidised compound was observed. The oxidation of glycerol is limited by factors such as increasing concentration of glycerol decreases solubilisation of oxygen and typically the oxidation reactions are operated at very high pressure to allow gaseous contact with glycerol (Ducoulombier et al., 2009; Katryniok et al., 2011). Besides, high reaction temperatures also decreases the mass transfer coefficient of oxygen, thus limit the solubility of gases in glycerol (Rischbieter & Schumpe, 1996). Similar case was expected for possible direct carbonylation with $CO_2$. Therefore, it can be concluded that different flow of gas only helps to remove the ammonia formed and does not affect the conversion, selectivity and yield. In addition, the time online study (TOL) of BA 900 conducted with compress air similarly corresponded to the TOL of BA 900 conducted with nitrogen gas (section 4.4.1). Kim, D. & Park, (2014) reported that, reaction conducted in increasing vacuum rate increased the formation of glycerol carbonate.

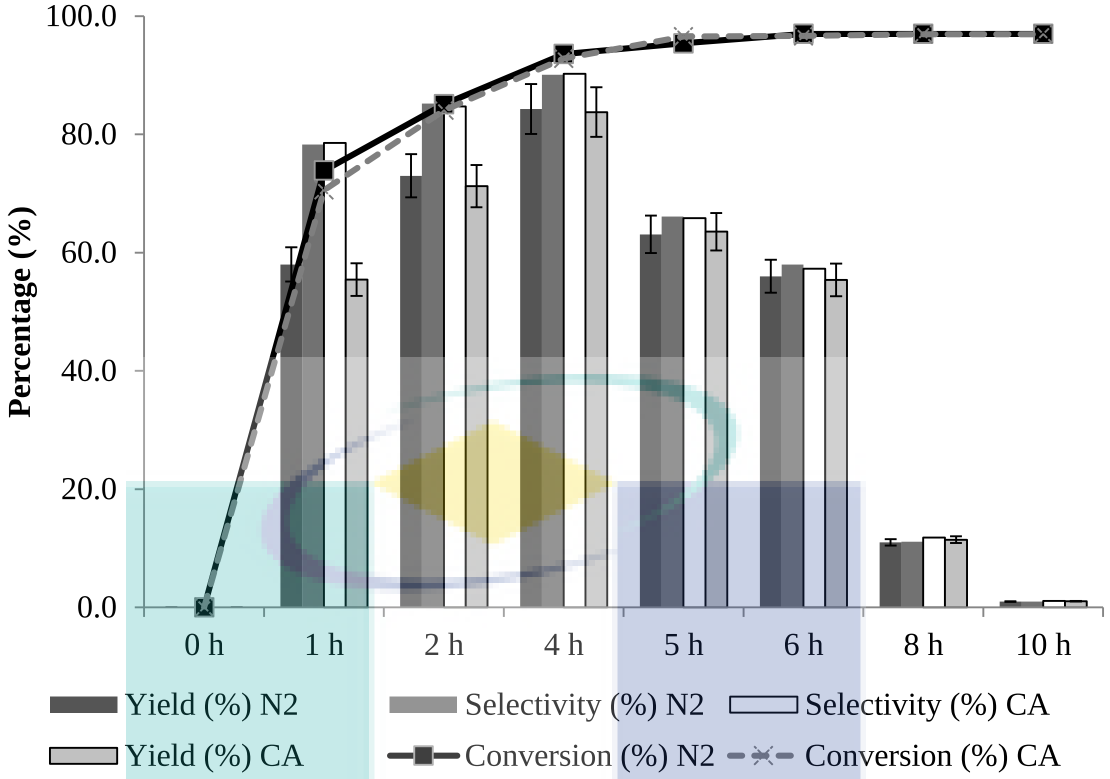


*Figure 4.14.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of nitrogen gas labelled ($N_2$) and compress air labelled (CA) respectively. Reaction conditions: Temperature, 150 ˚C; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

## 4.5 Effect of Metal on Catalytic Activity

In order to clearly identify the metal or element which has played the role in controlling the catalytic activity, a series of reaction comprising various metals from most dominant metal content in boiler ash were carried out. The metals for analysis were chosen based on the elemental analysis carried out using ICP-MS (section 4.2.7) and XRD analysis (section 4.2.3). Reactions involving sylvite (KCl), potassium silicate ($K_2SiO_3$), potassium hydroxide (KOH), calcium oxide (CaO), magnesium oxide (MgO) and silicon oxide ($SiO_2$) were carried out and are illustrated in Figure 4.15. It is evident that the potassium regardless in the form of hydroxide (KOH), sylvite (KCl) or silicate ($K_2SiO_3$) has the highest catalytic effect towards glycerol carbonate yield and selectivity compared to other metal oxides such as MgO and CaO. Besides, the catalytic reaction of $SiO_2$ also yielded lower glycerol carbonate. This phenomenon is expected since $SiO_2$ is a covalently bonded non-polar molecule which does not affect the catalytic behaviour of the reaction. As characterised using XRD analysis, potassium was confirmed to exist predominantly as KCl and potassium silicate ($K_2SiO_3$) in boiler ash. However for this reaction, KOH was also used for the reason that potassium does not only leach while dissolving into reaction solution as potassium ion and activate the transformation of glycerol into the target product but also absorbs moisture from the environment. Thus, it is supposed that the preform of potassium metal does not play a significant role in the reaction but the catalytic reaction is subjected to the presence of potassium ion.

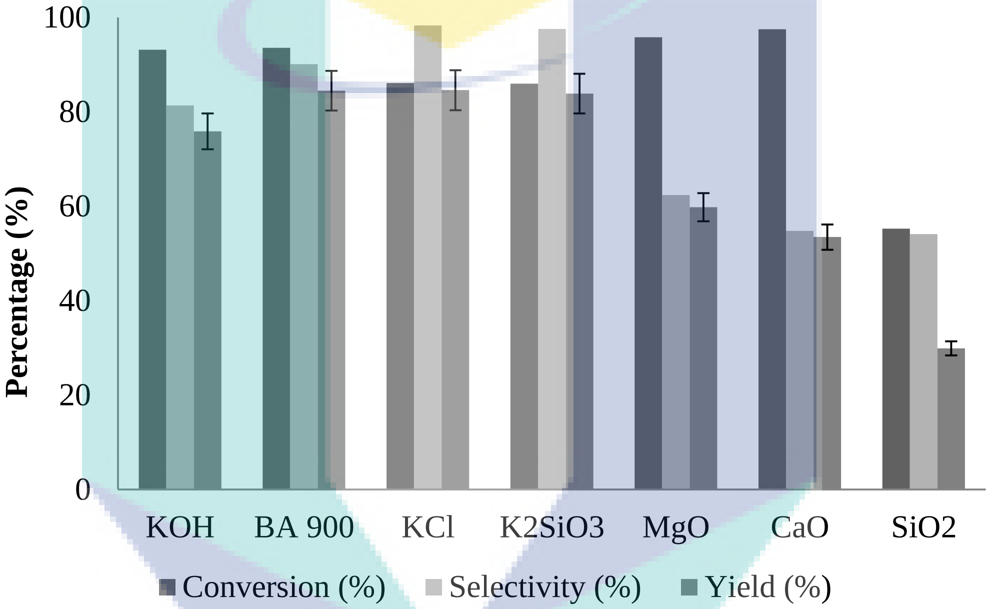


*Figure 4.15.* Effect of metals towards glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%). Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Time, 4 h; Standard stirring rate, 340 rpm.

On top of that, the role of potassium silicate in controlling the catalytic performance of boiler ash was further proved by its almost identical yield of glycerol carbonate with similar reaction catalysed by boiler ash (Table 4.9). Therefore, it can be inferred that potassium ion is the responsible metal that acts as a weak Lewis acid to catalyse the reaction.

Table 4.9

*Comparison of conversion, selectivity, yield and TOF of $K_2SiO_3$ and BA900*

| **Catalyst** | **Conversion (%)** | **Selectivity (%)** | **Yield (%)** | **TOF[a] mmol/ g.cat.$h^{-1}$** |
|---|---|---|---|---|
| $K_2SiO_3$ | 86.2 ± 0.3 | 97.1 ± 0.3 | 83.7 ± 0.5 | 125.6 |
| BA 900 | 93.6 ± 0.4 | 90.1 ± 1.0 | 84.3 ± 1.1 | 126.5 |

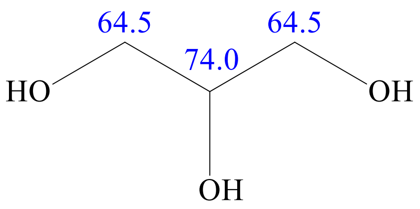
[a] TOF: calculated based on the mmol of glycerol multiply by yield percentage of glycerol carbonate per gram catalyst per total reaction time (h).

In addition, study on other minor metal elements presence in boiler ash such as aluminium (Al) and iron (Fe) was not carried out as it was previously reported with poor yield and selectivity of glycerol carbonate in form of mixture of Al/Ca (metal oxide) and Fe/Mg hydrotalcites. The yield obtained was only 10 % and 39 % respectively. An increase in aluminium and iron content decreases the basic site density which decreases active sites to catalyse the reaction (Climent et al., 2010). Besides, other metal such as zirconium in form of $ZrO_2$ was also reported to produce lower yield of glycerol carbonate (31%) (Lelovský & Kaszonyi, 2009). Zr was detected to be present in boiler ash in low levels through FESEM-EDX analysis (see section 4.2.6). Furthermore, the catalytic reaction in the presence of carbon in synthesis of glycerol carbonate were expected to be less significant due to the basicity nature of carbon, in which predominantly being influenced by the inorganic metal ions as discussed by (Montes-Moran et al., 2012) and not essentially by carbon itself. Moreover, Hammond et al., (2011) reported that gold supported on carbon had poor catalytic activity in glycerolysis reaction with urea yielding about only 22 % of glycerol carbonate. Besides, carbon is also found to be present at a lower amount in BA 900 at 3.33 % based on the EDXRF analysis (see section 4.2.4). However, a slightly higher amount of carbon was present in the FESEM-EDX (Table 4.3) analysis due to non-homogeneously distributed sample but the analysis reveal that potassium metal is present predominantly in boiler ash.

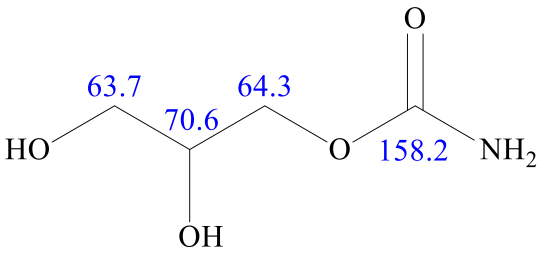
## 4.6 Glycerol Carbonate Synthesis Pathway

### 4.6.1 Mechanistic Study of Glycerol Carbonate Synthesis Using Boiler Ash

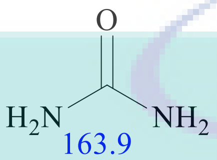
From Figure 4.16, the $^{13}C$ NMR labelling of all compounds involved in the synthesis of glycerol carbonate can be summarised accordingly. Glycerol $^{13}C$ NMR ($CD_3OD$, 125MHz) δ ppm 64.5(-$CH_2$-OH), 74.0 (>CH-OH); glycerol carbonate $^{13}C$ NMR ($CD_3OD$, 125MHz) δ ppm 157.9 (C=O, carboxy), 78.9 (>CH-OH), 67.5 (-$CH_2$-OH), 62.3 (-$CH_2$-O-); 2,3-dihydroxypropyl carbamate $^{13}C$ NMR ($CD_3OD$, 125MHz) δ ppm 158.2 (C=O, amides), 70.6 (>CH-OH), 64.3 (-$CH_2$-OH), 63.7 (-$CH_2$-OH); 4-(hydroxymethyl)oxazolidin-2-one $^{13}C$ NMR ($CD_3OD$, 125MHz) δ ppm 161.2 (C=O, amides), 78.8 (>CH-N<), 63.5 (-$CH_2$-O-), 42.9 (-$CH_2$-OH); (2-oxo-1,3-dioxolan-4-yl)methyl carbamate $^{13}C$ NMR ($CD_3OD$, 125MHz) δ ppm 162.5 (C=O, amides), 157.9 (C=O, carboxy), 68.5 (-$CH_2$-O-), 64.2 (-$CH_2$-O-), 55.2 (>CH-C, C tertiary); urea $^{13}C$ NMR ($CD_3OD$, 125MHz) δ ppm 163.9 (C=O, amides). This peak directly corresponds to the C=O group that is attached to amide group in urea. The pattern of the decomposition of urea is also clear as the C=O peak of urea gradually reduces from 30 min to 10 h until only a minimal amount of urea is left. The result also corresponds to spectrum (d) in Figure 4.12 for analysis of product using ATR-FTIR at 10 h reaction time where presence of urea is still detected at minimal amount. However, the present study reports the quantity of (3) did not show direct correlation to glycerol carbonate formation as (3) was not clearly observed at 0.5 h of reaction time. Nonetheless, presence of intermediate (3) may have attributed to the formation of glycerol carbonate but in an acceleration manner as the intermediate (3) formed quickly transformed into glycerol carbonate. These results also correlated to the previous analysis of TOL using GC-FID (Figure 4.6 of section 4.4.1) which resulted in the highest glycerol carbonate yield at 4 h reaction time and the yield decreased with prolonged reaction time as the selectivity towards glycerol carbonate decreased due to formation of (5) and (6). From the study, it is believe that the synthesis route of glycerol carbonate still follow the mechanistic pathway reported by Rahim and co-researchers in 2012 as well as Kim, D.-W. and co-researchers in 2014 but the selective transformation of glycerol carbamate intermediate decomposed in an accelerated manner to form glycerol carbonate (Rahim et al., 2012; Kim, D.-W. et al., 2014).



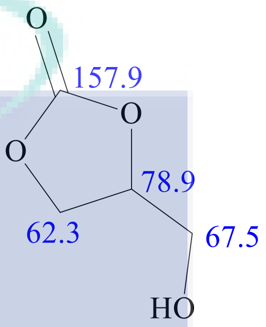
Glycerol
(Compound 1)



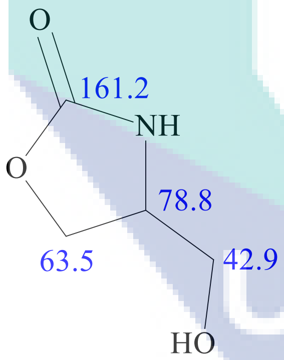
2,3-dihydroxypropyl carbamate
(Compound 3)



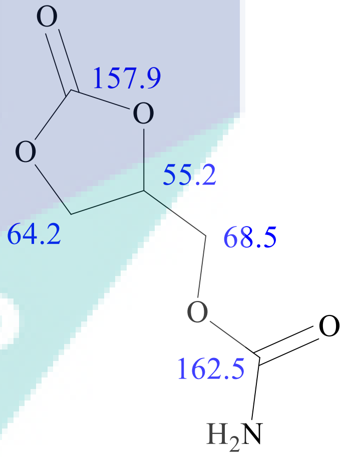
urea
(Compound 2)



4-(hydroxymethyl)-1,3-dioxolan-2-one
(Compound 4)



4-(hydroxymethyl)oxazolidin-2-one
(Compound 5)



(2-oxo-1,3-dioxolan-4-yl)methyl carbamate
(Compound 6)

*Figure 4.16.* Compounds in synthesis of glycerol carbonate using boiler ash and their corresponding $^{13}$C NMR labelling of δ ppm.

Figure 4.17 illustrates the $^{13}$C NMR analysis for time online analysis (TOL) of BA 900. From the $^{13}$C NMR pattern, it is evident that glycerol carbonate (4) was selectively formed through carbonylation of intermediate 2, 3-dihydroxypropyl carbamate (3) similar to previously reported study (Climent et al., 2010). At 4 h of reaction time, 4-(hydroxymethyl) oxazolin-2-one (5) and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (6) was seen to be present. As the reaction time was prolonged up to 10 h, gradual increase in the peak pattern of (5) and (6) was observed which clearly indicated that selectivity towards glycerol carbonate formation decreased from 4 h onwards due to formation of (5) and (6). This is due to the further reaction of glycerol carbonate with excess of urea forms (6) and the intermediate 2, 3-dihydroxypropyl carbamate (3) forms compound (5) through a parallel reaction ( Kim, D.-W. et al., 2014).

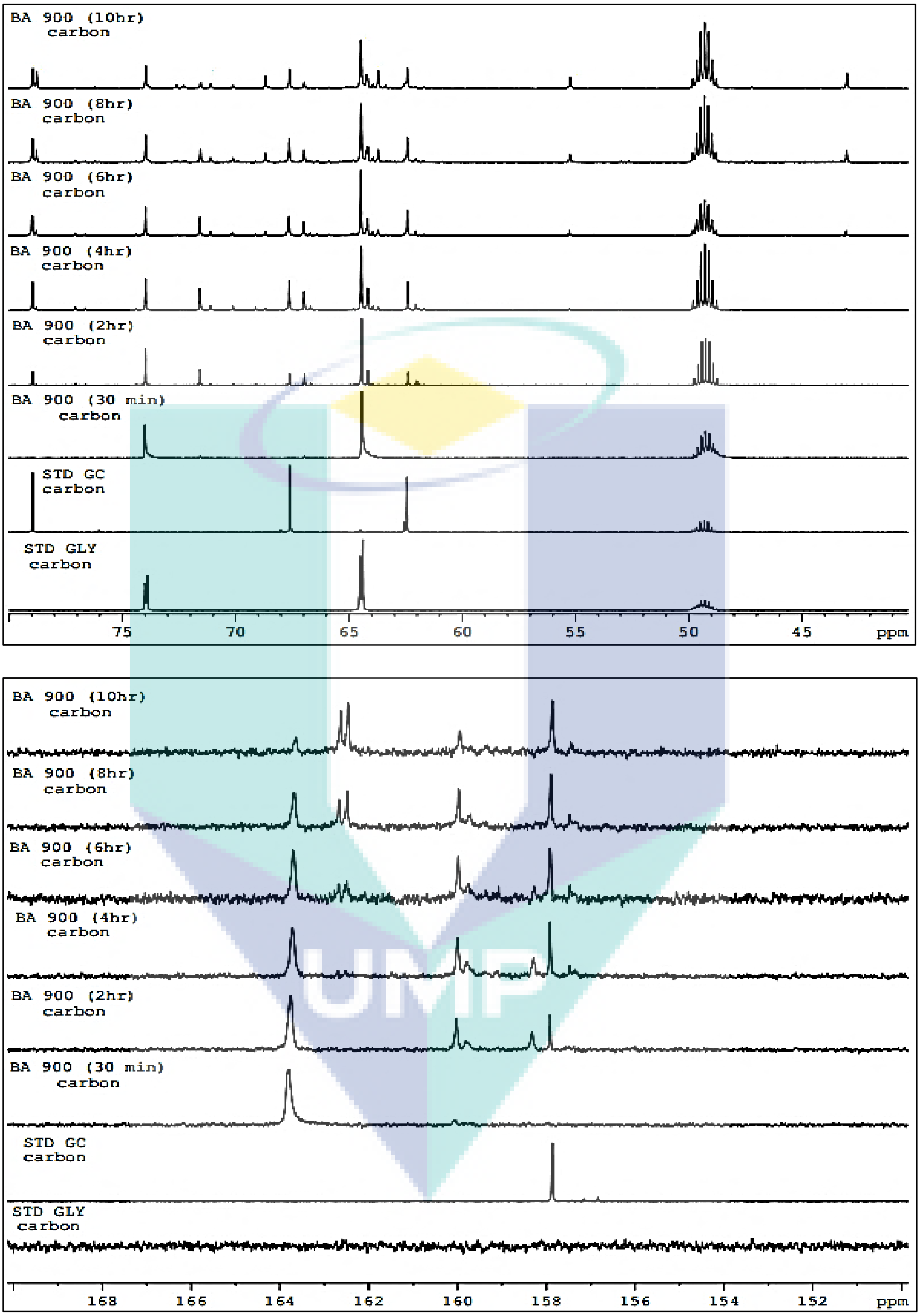


*Figure 4.17.* $^{13}$C NMR overlay of standard glycerol (STD GLY), standard glycerol carbonate (STD Gly C) and TOL of BA 900.

To validate the $^{13}$C NMR results on time online analysis of BA 900, analysis using ATR-FTIR was carried out for the reaction from 0.5 h to 10 h (Figure 4.18). From the spectrum it is observed that glycerol (1) peak gradually shifted from 1450 cm$^{-1}$ closer to 1400 cm$^{-1}$ as the time for reaction was prolonged. Peak of urea (2) also showed similar behaviour of where the two peaks (1665 and 1620) cm$^{-1}$ was observed to gradually shift. This phenomenon is expected to persist as most glycerol quickly converted into glycerol carbonate and other products. Intermediate (3) was detected at 2 h and 4 h reaction time in range of (1710-1715) cm$^{-1}$. However, from 6 h to 10 h the peak shifted to 1730 cm$^{-1}$ (urethane group) indicating the conversion of carbamate (3) into product (5) ( Kim, D.-W. et al., 2014). Presence of peak at 1790 cm$^{-1}$ indicated C=O stretch of glycerol carbonate (4) at 2 h onwards. However, glycerol carbamate peak (3) was not clearly observed at 0.5 h to 4 h due to reaction mechanism occurring in an accelerated manner to directly decompose intermediate (3) into (4). This result was also in agreement with the previously discussed $^{13}$C NMR. Besides, no peaks were observed in range of 2250 cm$^{-1}$ indicating the presence of N-C-O stretching of isocyanic acid which was also similar to several studies previously reported (Aresta et al., 2009; Kim, D.-W. et al., 2014). Further validation and confirmation of product and by-product from the reaction was evident from the GC-MS analysis (refer appendix B6).

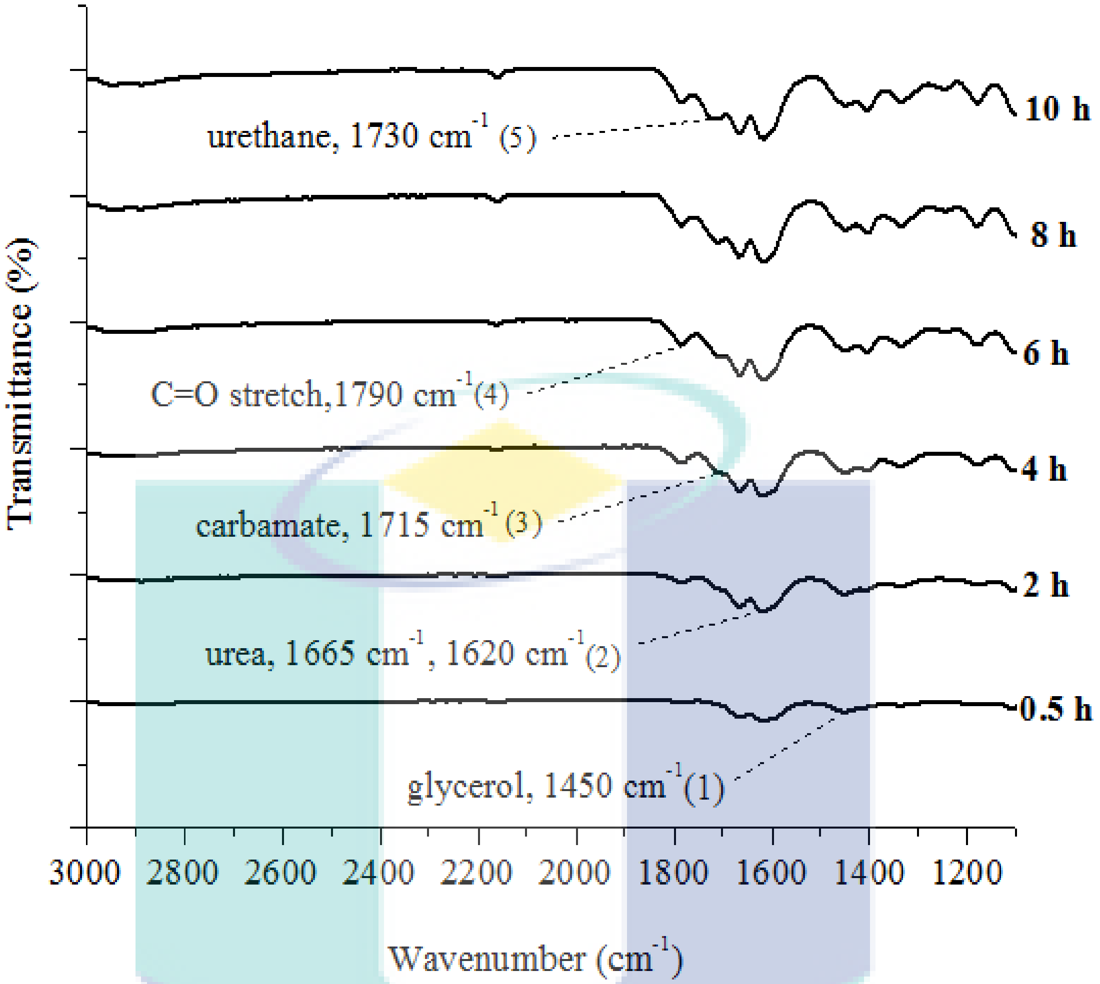
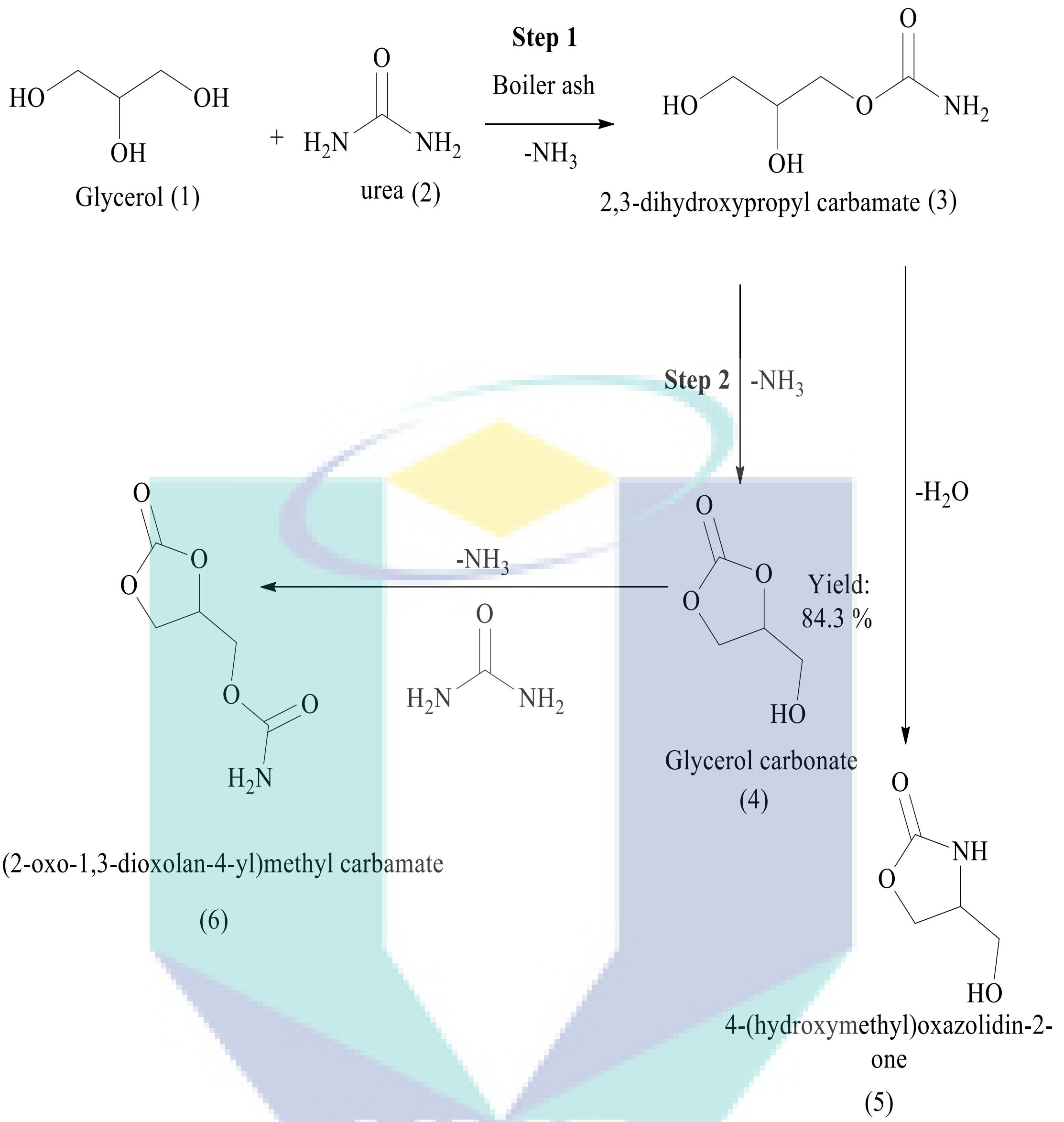


*Figure 4.18.* ATR-FTIR spectrum for time online analysis of BA 900 reaction from 0.5 h to 10 h. Key: (1) Glycerol; (2) Urea; (3) 2, 3-dihydroxypropyl carbamate; (4) Glycerol carbonate; (5) 4-(hydroxymethyl) oxazolin-2-one.

Therefore the mechanistic pathway for the synthesis of glycerol carbonate using BA 900 is suggested as in scheme 1.

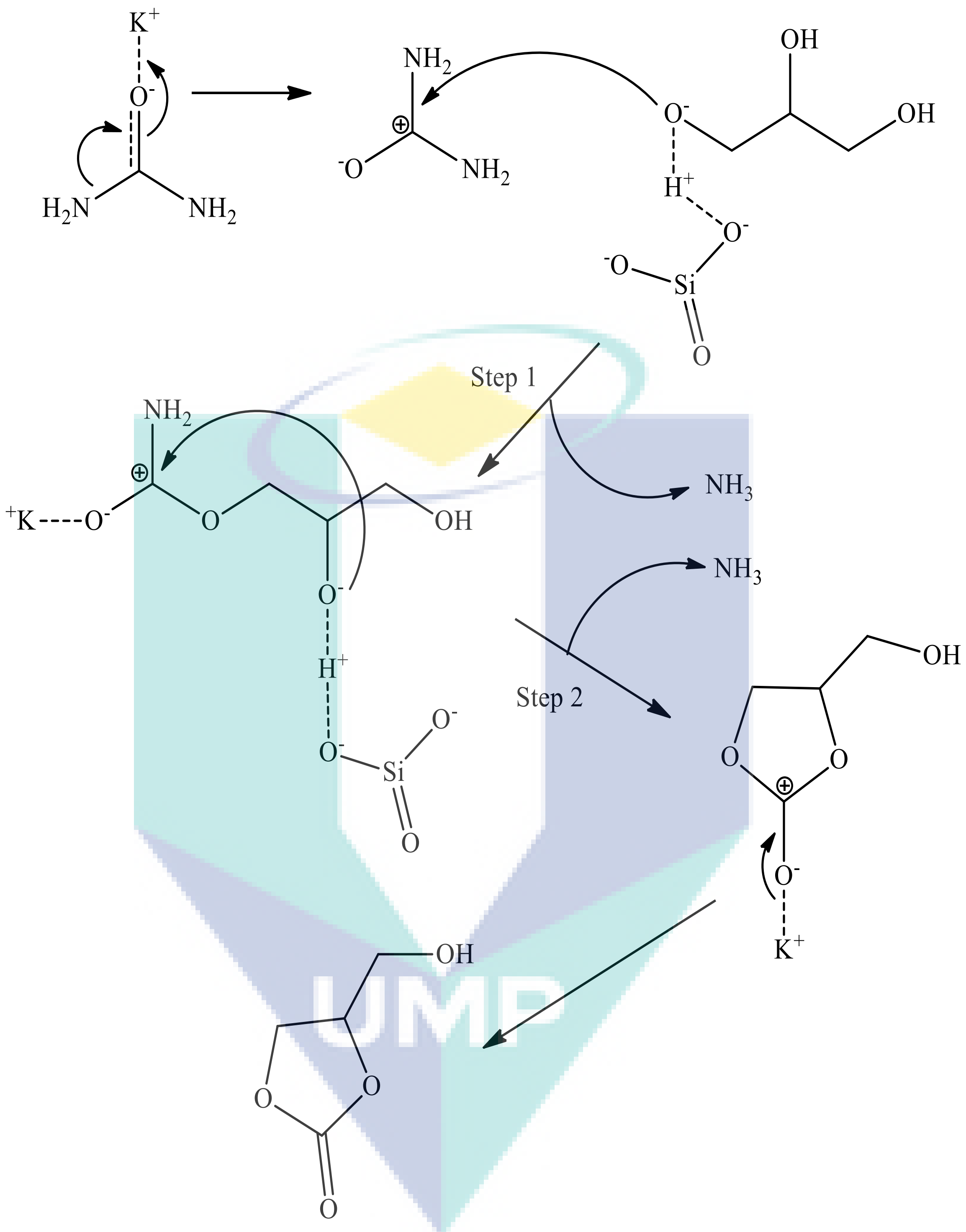


Scheme 1. Mechanistic pathways for synthesis of glycerol carbonate using glycerol, urea and boiler ash (BA 900) as catalyst. Key: (1) Glycerol; (2) Urea; (3) 2, 3-dihydroxypropyl carbamate, (4) Glycerol carbonate; (5) 4-(hydroxymethyl) oxazolin-2-one; (6) (2-oxo-1,3-dioxolan-4-yl) methyl carbamate.

### 4.6.2 Catalyst Mechanism Route of Potassium Silicate

From the information obtained in section 4.44.5, potassium silicate ($K_2SiO_3$) contained in boiler ash has been the major element that has influenced the catalytic behaviour of boiler ash in synthesising glycerol carbonate from glycerol and urea. As mentioned earlier, it can be deduced that the $K^+$ acts as a weak Lewis acid by activating the carbonyl group of urea. On the other hand, $SiO_3^{2-}$

acts an effective conjugate basic site to activate the hydroxyl group of glycerol (Corma, Iborra, & Velty, 2007; Climent et al., 2010). The activation of the carbonyl group of urea grounds the carbonyl group to become positively charged acting as an electrophile. In contrast, the activated hydroxyl group of glycerol acts as a nucleophile (Rahim et al., 2012; Ochoa-Gómez et al., 2012). In step 1, the nucleophilic attack of hydroxyl group towards the electrophilic carbonyl of urea forms the carbamate intermediate while releasing ammonia gas. It is believed that the second step is the most the anticipated reaction phase where the selectivity towards desired product formations is evidently observed due to the influence of the catalyst. The cyclisation is complete by the loss of more ammonia gas, followed by ring formation and rearrangement of the carbonyl double bond to form glycerol carbonate. The catalytic mechanism of potassium silicate contained in boiler ash towards synthesis of glycerol carbonate is briefly illustrated in scheme 2.



Scheme 2. Catalytic mechanisms of glycerol carbonate synthesis using $K_2SiO_3$.

## 4.7 Reusability Study of Potassium Silicate and Boiler Ash

Reusability is one of the crucial parameters for industrial catalyst. Thus, both boiler ash and $K_2SiO_3$ were subjected to reusability test carried out under standard reaction conditions. As can be seen from Figure 4.19 and 4.20, the conversion, selectivity and yield was significantly unchanged and showed optimal performance in all three cycles.

The reusable capability of $K_2SiO_3$ catalyst is expected since the fresh and spent catalyst exhibits almost similar physical pattern of FTIR (Figure 4.21, section 4.7.8) and XRD (Figure 4.22, section 4.7.8) which indicated the characteristic of catalyst remains unchanged. However, only 56.3 wt % of catalyst was recovered after the third cycle. Therefore, loss of catalyst during reaction is expected due to minor metal leaching which was confirmed through Inductively Couple Plasma-Mass Spectroscopy (ICP-MS) with 2.4 % K and 18.21 % of Si leach-out which also corroborates with EDX analysis Figure 4.23, 4.24, 4.25, 4.26, Table 4.10. The turnover frequency of $K_2SiO_3$ is 125.6 mmol/ g.cat.$h^{-1}$ which do not ideally deviate from the TOF value of BA 900 Table 4.1.

Similar to $K_2SiO_3$, BA 900 was also used for three consecutive cycles (Figure 4.20) and only 31.7 wt % of catalyst was recovered after the third cycle. About 84.3, 82.1 and 81.4 yield % of glycerol carbonate was obtained for cycle 1, 2 and 3 respectively. It is also notable that the FTIR spectrum (Figure 4.27) of spent BA 900 and spent $K_2SiO_3$ showed almost similar patterns. Besides, there is also no significant difference between the FTIR spectrum (Figure 4.27) of fresh BA 900 and spent BA 900. Moreover Hammett test from Table 4.3 and Table 4.10 also indicate the basic property of all fresh and spent BA 900 as well as $K_2SiO_3$ to be comparable. Therefore, the activity of reusable boiler ash is expected to be comparable as the reusable $K_2SiO_3$. Both boiler ash and potassium silicate are relatively pseudo-homogeneous in nature due to the partial recoverability. The catalyst activity is predominantly influenced by the activity of potassium and silicate ions.

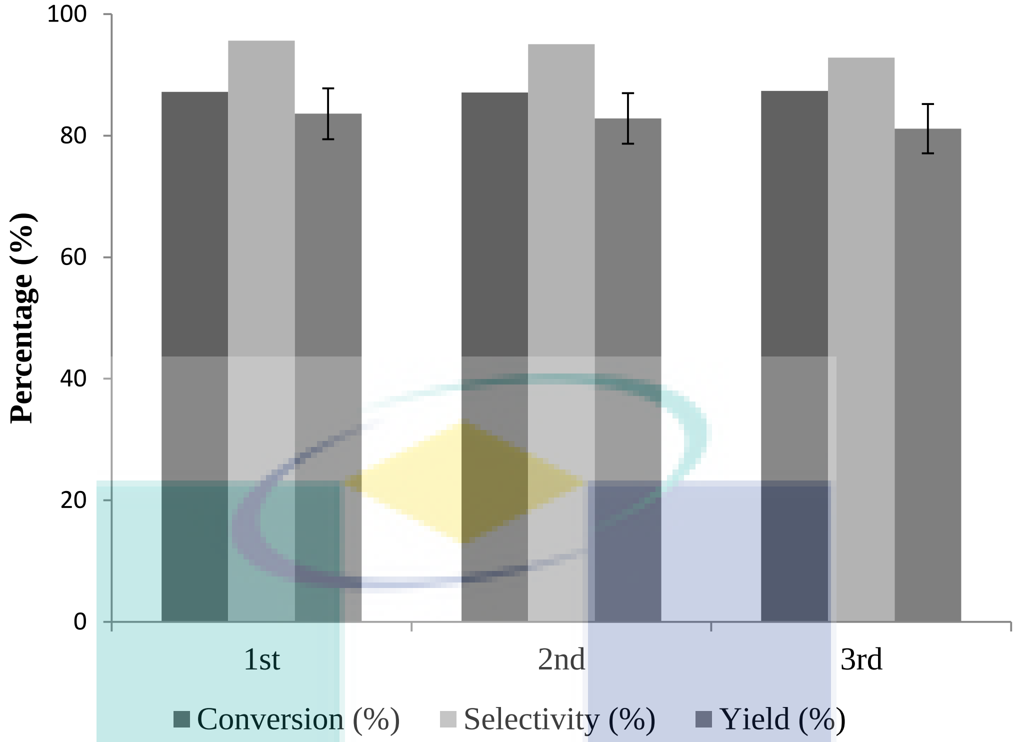


*Figure 4.19.* Reusability study of glycerol carbonate using $K_2SiO_3$.

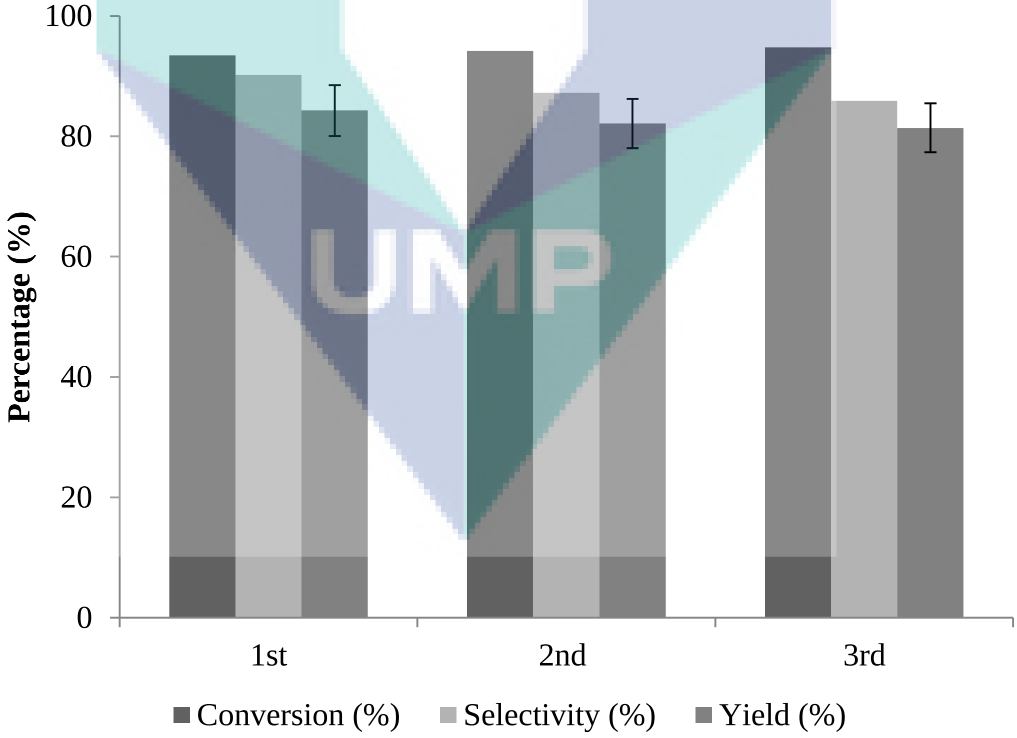


*Figure 4.20.* Reusability study of glycerol carbonate using BA 900.

## 4.8 Characterisation of Spent Catalyst

Based on the reusability study of potassium silicate in section 4.7, it was found that the spent catalyst show similar catalytic activity as fresh catalyst counterpart. Following that, the spent catalyst ($K_2SiO_3$) was subjected to similar characterisation technique using FTIR, XRD, ICP-MS, FESEM-EDX, Hammett Test, $CO_2$-TPD and BET.

Figure 4.21 illustrates the FTIR spectra of fresh and spent $K_2SiO_3$. From the Figure, it was found that potassium silicate showed almost similar pattern in presence of functional group even after the third cycle. There was presence of a sharper peak at 791 $cm^{-1}$. This sharper intensity of the peak observed is due to the dominant stretching of -SiO which increases in the spent catalyst (Ekosse, 2005). Based on Figure 4.22, the XRD data of fresh and spent $K_2SiO_3$, also suggest that there is no major differences in both spectrum indicating that most element of $K_2SiO_3$ remained intact. The data was also proven to be in agreement with the FTIR data in Figure 4.21, in which the pattern of FTIR spectrum of fresh and spent $K_2SiO_3$ shows presence of –SiO band to remain intact. However, unobserved FTIR peaks at range of 1200-1500 $cm^{-1}$ for spent catalyst was found due to the presence of glycerol moiety that remained intact on the catalyst, which then interfered and broadened the FTIR signal (Figure 4.21). For record, the spent catalyst was subjected to washing with deionised water, thus remaining glycerol is expected. In the meantime, a slight difference in XRD pattern as shown in Figure 4.22 is due to dominant presence of $SiO_2$ in spent catalyst as an evident from FESEM-EDX analysis (Table 4.10). More dominant amorphous $SiO_2$ is expected to be present due to the loss of some potassium ion, thus the XRD diffractogram will closely resemble the diffraction pattern of pure $SiO_2$ (Musić, Filipović-Vinceković, & Sekovanić, 2011). Thus, resulting in the slight shift of the spent $K_2SiO_3$. Furthermore, the spent BA 900 (c) had comparable xrd pattern compared to spent $K_2SiO_3$ (b). The data of spent BA 900 which closely resembles spent $K_2SiO_3$ affirms that the catalytic basic site could be distributed similar to spent $K_2SiO_3$ (Figure 4.22).

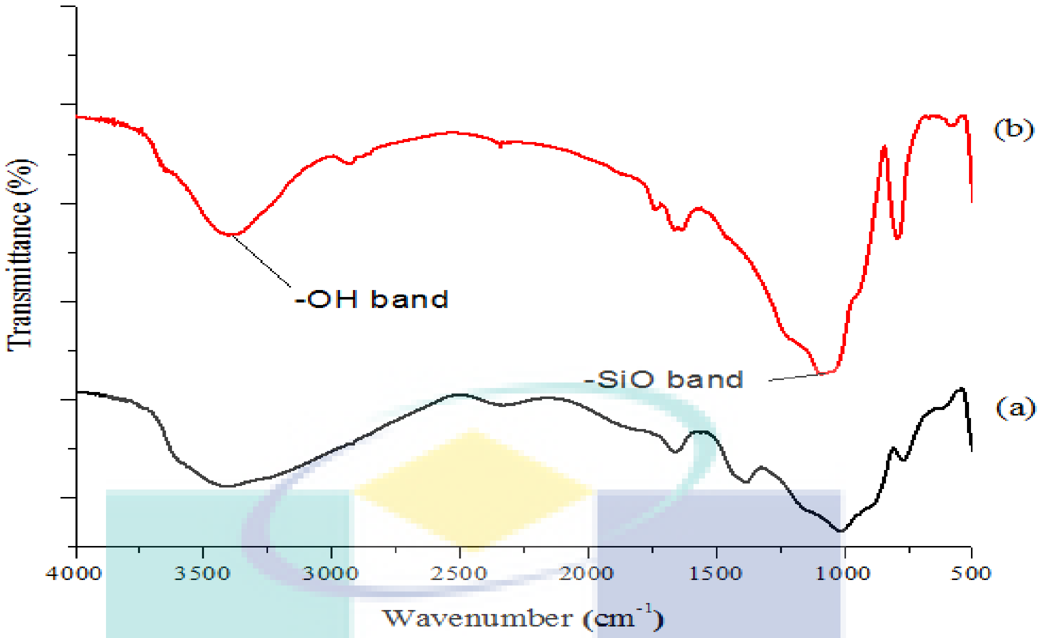


*Figure 4.21.* FTIR of (a) fresh $K_2SiO_3$ and (b) spent $K_2SiO_3$.

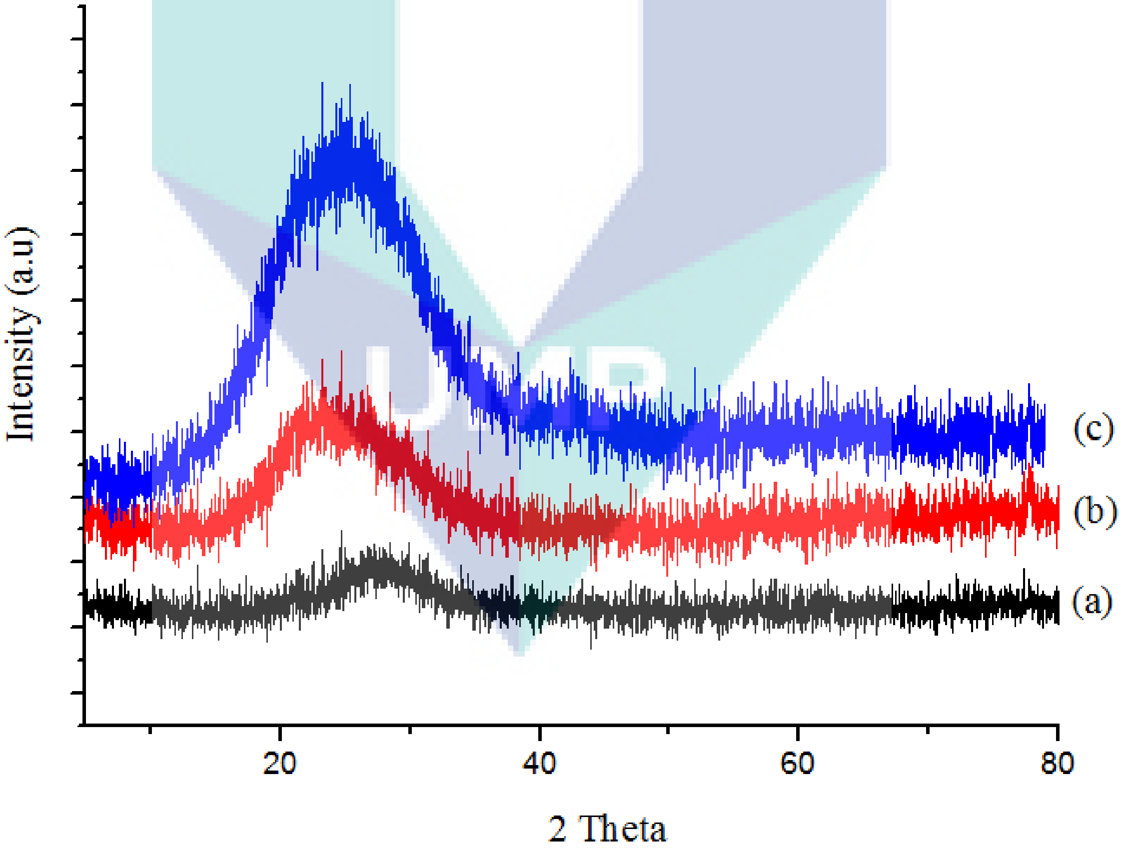


*Figure 4.22.* XRD of (a) fresh $K_2SiO_3$, (b) spent $K_2SiO_3$ and (c) spent BA 900.

On top of that, the morphology and elemental analysis of both fresh and spent $K_2SiO_3$ showed no significant difference (Figure 4.23, 4.24, 4.25 and 4.26). Besides, table 4.10 suggests that the elemental composition of fresh and spent $K_2SiO_3$ to be comparable. Only 3.62 % of potassium was lost during reaction which is a result of homogenisation of the metal ion in the solution. This result also correlated to findings by ICP-MS which was found that the total leaching of potassium ion was about 2.4 %. The $K^+$ ions are also expected to be loss during washing of catalyst before being dried for reusability.

Table 4.10

*Element and composition in weight percentage of fresh $K_2SiO_3$ and spent $K_2SiO_3$*

| Element | Weight % of fresh $K_2SiO_3$ | Weight % of spent $K_2SiO_3$ |
|---|---|---|
| O | 56.11 | 57.27 |
| Si | 26.01 | 28.47 |
| K | 17.88 | 14.26 |
| Totals | 100.00 | 100.00 |

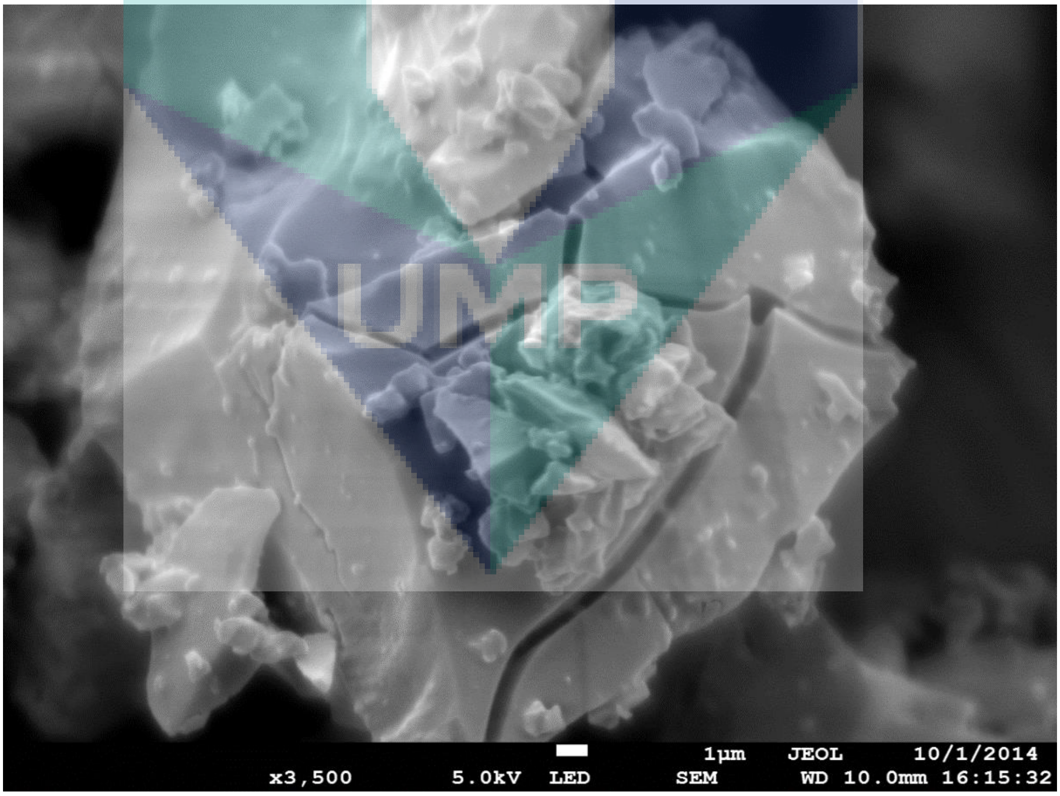


*Figure 4.23.* FESEM morphology of fresh $K_2SiO_3$.

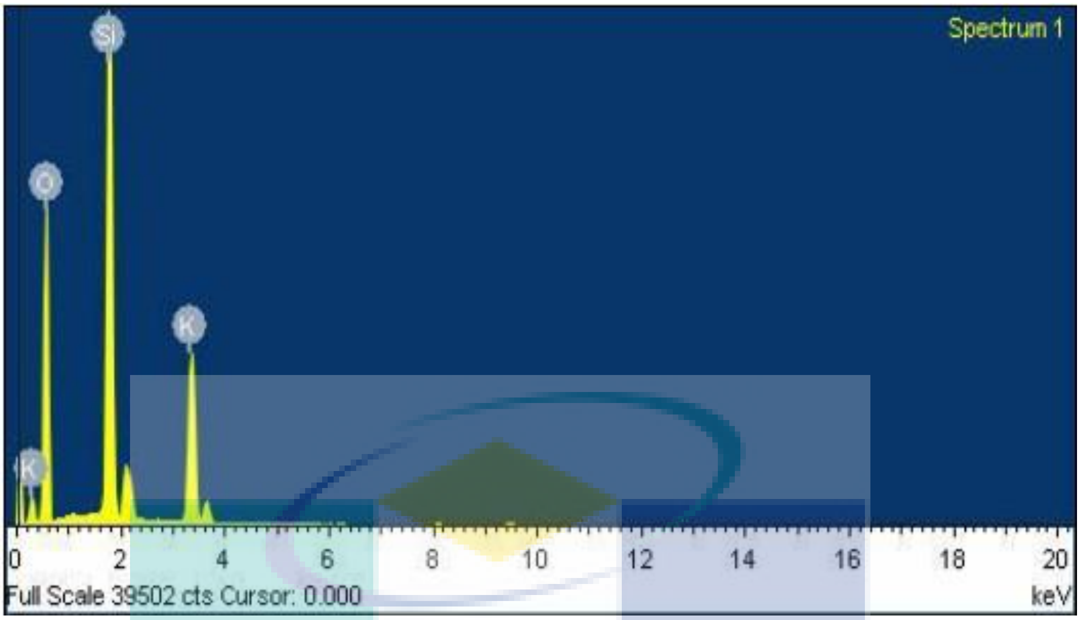


*Figure 4.24.* EDX spectrum of fresh $K_2SiO_3$.

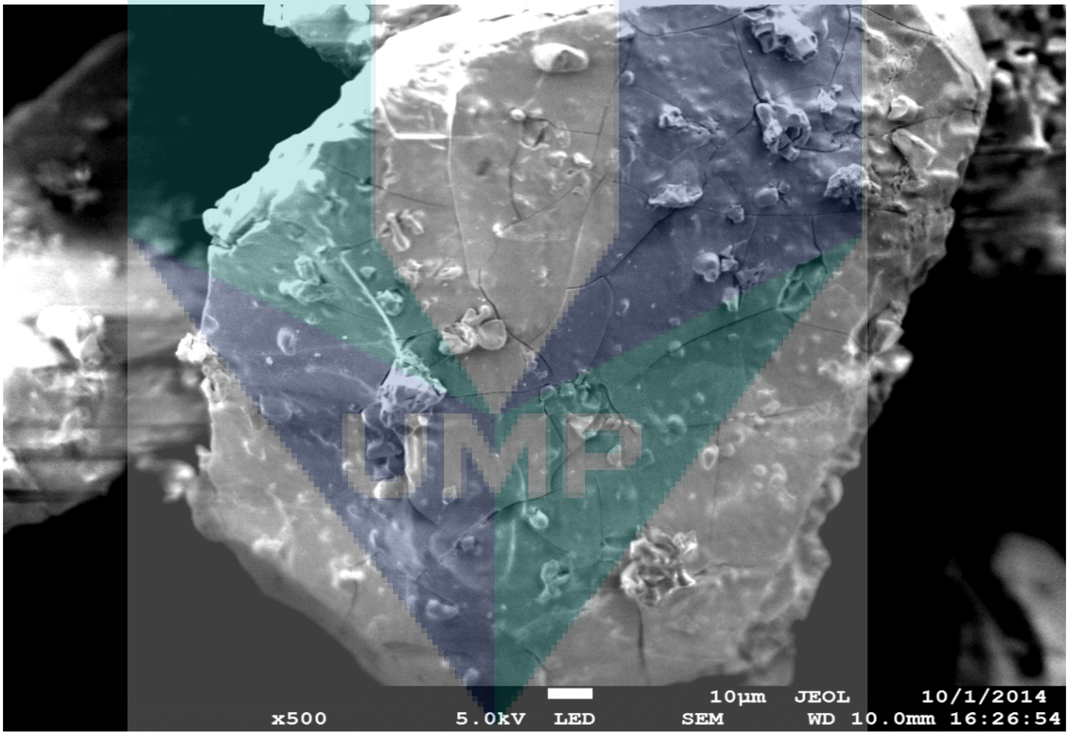


*Figure 4.25.* FESEM morphology of spent $K_2SiO_3$.

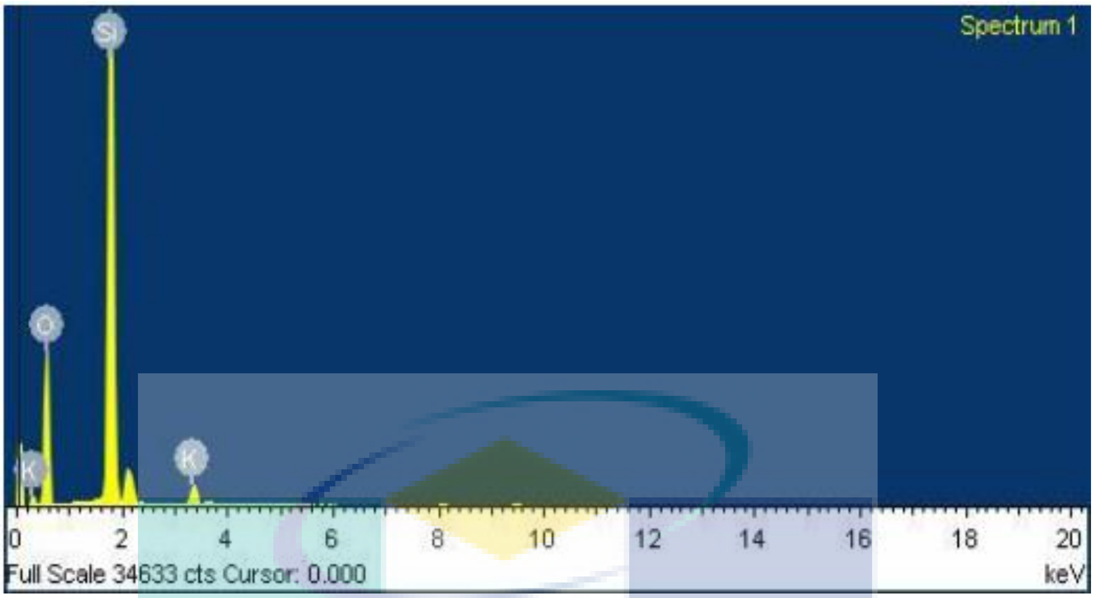


*Figure 4.26.* EDX spectrum of spent $K_2SiO_3$.

Based on Figure 4.27, the analysis of FTIR of Fresh BA 900, spent BA 900 and spent $K_2SiO_3$ revealed that both catalysts have almost similar properties after reusability study. Therefore, it was found that the activity of both spent catalyst were almost similar to each other. However, the FTIR analysis of fresh and spent BA 900 showed the catalyst has undergone a transformation due to loss of other minor elements as mentioned to be present previously in FESEM-EDX analysis tabulated in Table 4.3 section 4.2.6. It is also believed that loss of other elements during reusability study of BA 900 also correlated to the minor recovery of BA 900 compared to $K_2SiO_3$ as reported in section 4.5. In contrast, this did not affect the activity of boiler ash as it was found that the presence of potassium silicate majorly influenced the catalytic activity of boiler ash.

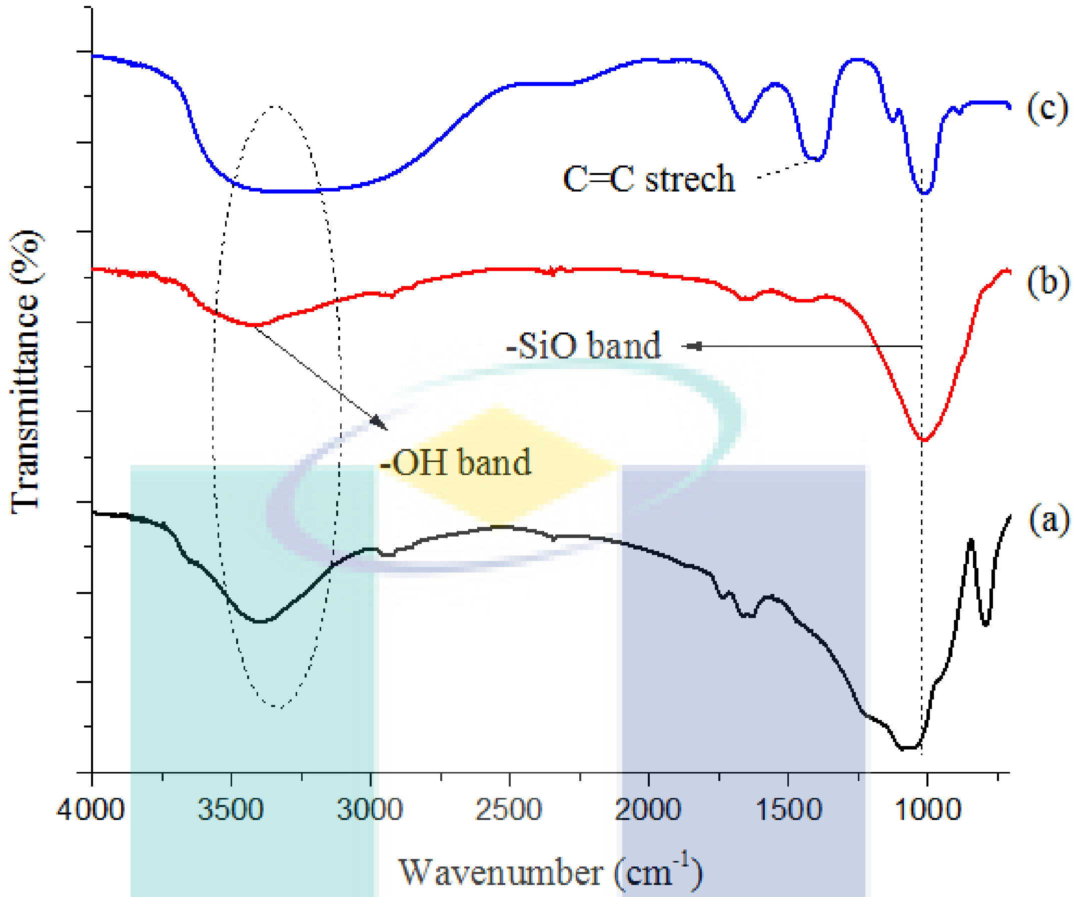


*Figure 4.27*. FTIR spectrum of (a) spent $K_2SiO_3$, (b) spent BA 900 and (c) fresh BA 900.

On the other hand, Hammett test also revealed similar findings on both spent catalysts BA 900 and $K_2SiO_3$ (Table 4.11). The findings suggested that both catalysts were mildly basic in nature as comparable to the fresh catalysts (BA 900 and $K_2SiO_3$). Besides, $CO_2$–TPD analysis (Figure 4.28) of both fresh and spent $K_2SiO_3$ reveals that the basic site of both fresh and spent catalyst to be equally comparable. The total basic site of fresh $K_2SiO_3$ was found to be 958.74 µmol/g while the total active site of spent $K_2SiO_3$ was 923.67 µmol/g. Therefore, the catalytic activity of catalyst towards, yield and selectivity of glycerol carbonate is not essentially altered.

Table 4.11

*Hammett test of spent catalyst*

| **Catalyst** | **Methyl Red (H_=4.8)** | **Phenolphthalein (H_=8.2)** | **2, 4 – Dinitroaniline (H_=15)** | **4 – Nitroaniline (H_=18.4)** |
|---|---|---|---|---|
| Spent BA 900 | No changes | Colourless to pink solution | No changes | No changes |
| Spent $K_2SiO_3$ | No changes | Colourless to pink solution | No changes | No changes |

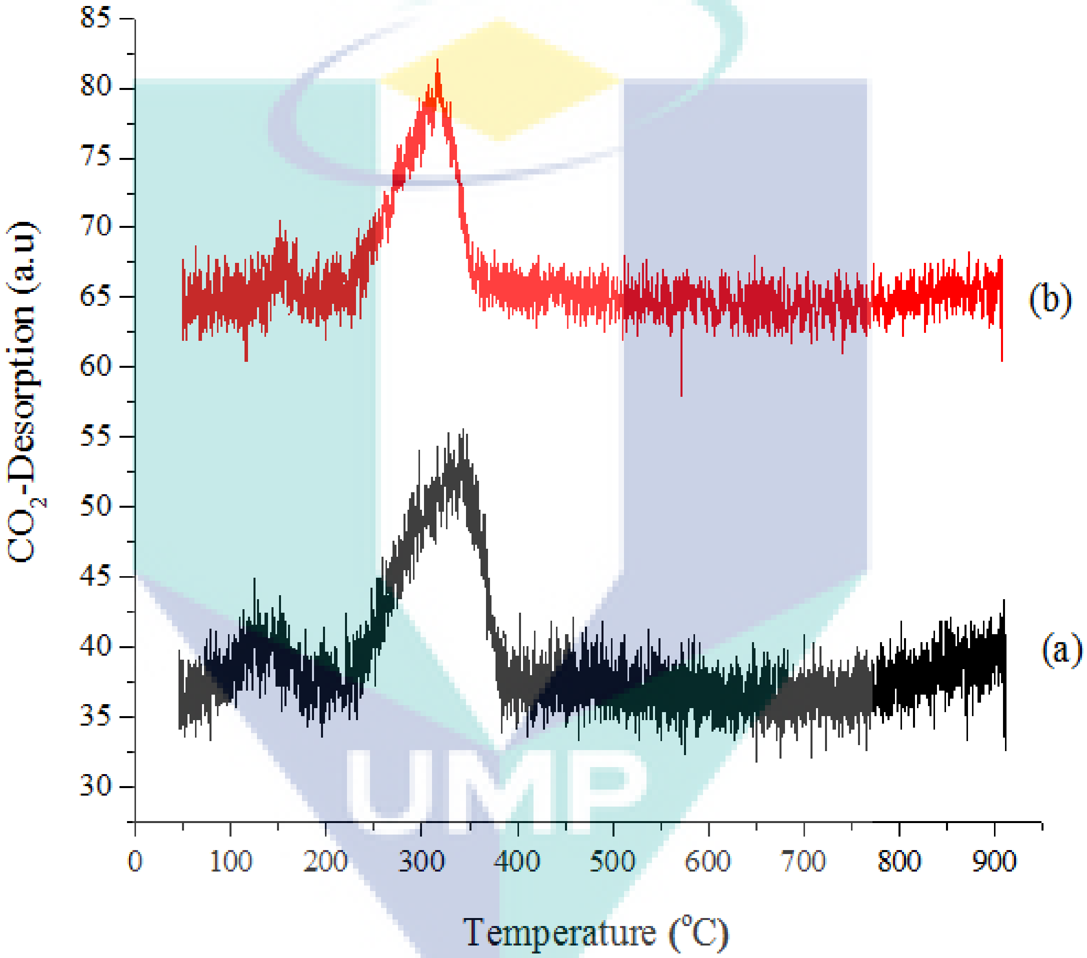


*Figure 4.28.* $CO_2$-TPD analysis of (a) fresh $K_2SiO_3$ and (b) spent $K_2SiO_3$.

On the other hand, the BET analysis of both fresh and spent $K_2SiO_3$ revealed that the surface area of both these catalysts were closely comparable to BA 900 (Table 4.12). However, spent catalyst contains larger pore volume and pore size. This scenario is expected to occur due to the loss of some potassium ion embedded to the silicate that allows larger pore of silicate to be present. As aforementioned, it was found that potassium ion and silicate ions majorly plays an important role in the catalytic mechanism. Therefore, the variation of catalyst surface area, porous structure and morphology are less significant. The mass transfer of reactants are not entirely effected by these physical characteristic of boiler ash due to the catalyst activity being influenced by the soluble potassium ion and silicates.

Table 4.12

*BET Surface area, pore size and pore volume of fresh and spent $K_2SiO_3$*

| **Catalyst** | **BET Surface area ($m^2/g$)** | **Pore Volume ($cm^3/g$)** | **Pore Size (Å)** |
|---|---|---|---|
| Fresh $K_2SiO_3$ | 2.50 | 0.003 | 45.14 |
| Spent $K_2SiO_3$ | 2.54 | 0.021 | 342.06 |
| BA 900 | 2.00 | 0.002 | 38.01 |

## 4.9 Summary

In short it can be summarised that calcination temperature of boiler ash towards glycerol carbonate synthesis had significant effect and BA 900 calcined at 900 °C gave the best catalytic activity and selectivity. On the other hand, the reaction conditions studied using a set of various reaction parameters such as temperature, stirring rate, mass of catalyst loaded and duration of reaction showed that the suitable parameters were 150 °C, 340 rpm, 0.25 g of catalyst with 4 h reaction time respectively. Moreover, flowing different type of gas (i.e. nitrogen or compress air) did not show any significant differences. This is because the gas flowed was essentially used for removal of excess ammonia formed. The effect of metal on catalytic activity showed that the most effective element in boiler ash which was proven to have played the role is potassium silicate. Moreover, the reusability study of potassium silicate as well as boiler ash resulted in comparable reaction results with no loss of activity spotted up to three consecutive cycles. In addition, glycerol carbonate synthesis pathway was also confirmed to be through decomposition of intermediate carbamate compound while the catalytic mechanism route of potassium silicate was also identified. $K^+$ ion acted as weak Lewis acid which activated the urea while the $SiO_3^{2-}$ acted as the conjugate basic site which activated the hydroxyl group of glycerol.

# CHAPTER 5

# RESULTS AND DISCUSSION: UTILISATION OF INDUSTRIAL CRUDE GLYCEROL AS A FEEDSTOCK FOR THE SYNTHESIS OF GLYCEROL CARBONATE

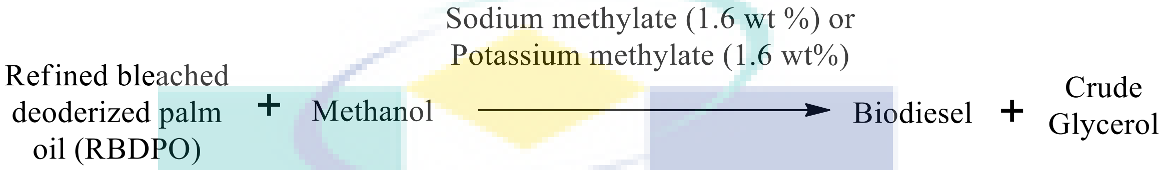
## 5.1 Introduction

This chapter is an elaboration to meet the second objective of the research which divided into two main sections. Firstly the study focused on synthesis of glycerol carbonate using different source of industrial crude glycerol obtained from commercial biodiesel plant (Artistic Support Sdn. Bhd.). Then, second part of the chapter covered the effect of other impurities present in the crude glycerol that effects glycerol conversions as well as the glycerol carbonate selectivity and yield.

## 5.2 Analysis of Crude Glycerol

As mentioned in chapter 3, there are two different sources of crude glycerol obtained from the commercial biodiesel plant. The main difference is due to the different type of catalysts used for the biodiesel transesterification process. The catalysts are sodium methylate, (crude glycerol denoted as Gly NaM) and potassium methylate (crude glycerol denoted as Gly KM). Sodium methylate and potassium methylate are the catalysts used in Artistic Support Sdn. Bhd. at 1.6 wt % respectively in the synthesis of biodiesel. Scheme 3, illustrates the biodiesel synthesis route of Artistic Support Sdn.

Bhd.. It is believed that the crude glycerol typically contained several compounds and impurities which originated from the parent feedstock used such as refined bleached deodorised palm oil, methanol and catalyst (sodium methylate or potassium methylate) in the biodiesel production process. Thus, an analysis carried out on that particular crude glycerol was necessary. The information should be obtained before any meaningful catalytic testing can be carried out.



Scheme 3. Feedstocks and catalysts used for synthesis of biodiesel in Artistic Support Sdn. Bhd.

The detailed analysis involving total glycerol content, moisture, soap, methanol, ester, ash and matter of organic content non-glycerol (MONG) has been carried out in Artistic Support Sdn Bhd and summarised in Table 5.1. It was also found that the catalyst present in both crudes were 1.6 wt % respectively for both Gly NaM and Gly KM.

Table 5.1
*Certificate of analysis (COA) from Artistic Support Sdn. Bhd.*

| **Test** | **Specification (%)** | **Result (%)** |
|---|---|---|
| Glycerol content | 75 Min. | 81.0 |
| Moisture | 10 Max. | 3.15 |
| Soap Content | 25 Max | 22.0 |
| Methanol | 5 Max | 0.80 |
| Oil (as Ester) | 5 Max | 0.29 |
| Ash content | 15 Max | 4.0 |
| MONG | 15 Max | 13.0 |

*Note: Min is minimum and Max is maximum. Specification of the report is that the allowable limit of the content of glycerol and impurities in Artistic Support Sdn. Bhd. The results show the real value obtained through analysis of both crude glycerol Gly NaM and Gly KM.

## 5.3 Catalytic Synthesis of Glycerol Carbonates Using Different Sources of Crude Glycerols

The development of catalytic system whereby the direct utilisation of industrial crude glycerol without any pretreatment step will significantly contribute to a more economical process, and subsequently reduce the total production cost of glycerol carbonate. For that purpose, two different sources of crude glycerol obtained from the commercial biodiesel plant were tested as a feedstock for the production of glycerol carbonate as target product. It is worthy to note that that very limited studies have been reported to directly use crude glycerol for the synthesis of glycerol carbonate. (Nguyen & Demirel, 2011) reported that crude glycerol eluted in the biodiesel plant can be converted into value added glycerol carbonate using glycerolysis reaction with urea. However, the study reported use of non-economical catalyst such as $La_2O_3$ calcined at 600 °C and under reduced pressure. On the other hand, Teng and co-workers in 2014, reviewed that the use of microwave assisted glycerolysis gives prominent results with crude glycerol. However, fundamentally the application has not been used in industry yet due to the limitations of microwave technology that cannot penetrate through larger volume of samples as reported by Sturm, Verweij, Stankiewicz and Stefanidis, (2014). In this case, respective BA 900 and $K_2SiO_3$ were used as catalyst in direct glycerolysis of crude glycerol with urea. Besides, the blank reaction without presence of any of the aforementioned catalysts was carried out to establish the baseline reaction data.

### 5.3.1 Synthesis of Glycerol Carbonate using Crude Glycerol (Gly NaM)

#### 5.3.1.1 Blank Reaction

Figure 5.1 illustrates the time online analysis of crude glycerol (Gly NaM) in blank reaction without presence of any catalyst compared with the study of blank with purified glycerol. From the analysis it was found that blank reaction of crude glycerol (Gly NaM) with urea showed maximum conversion of glycerol at 88.3 ± 0.5 %, selectivity of glycerol carbonate at 40.2 ± 0.7 %, and yield of glycerol carbonate at 35.5 ± 0.9 % with 4 h reaction time. In contrast, similar reaction with purified commercial glycerol showed lower glycerol conversion and glycerol carbonate yield. The value of conversion of purified glycerol was 78.7 ± 0.6 %, selectivity and yield of glycerol carbonate was 32.8

± 0.9 % as well as 25.8 ± 0.7 %. It is believed that the sodium methylate catalyst contained in crude glycerol NaM might have contributed to the reactions to have higher conversion, selectivity and yields. For record, there is no available published works reported for the non-catalysed reaction with crude glycerol as feedstock to synthesise glycerol carbonate.

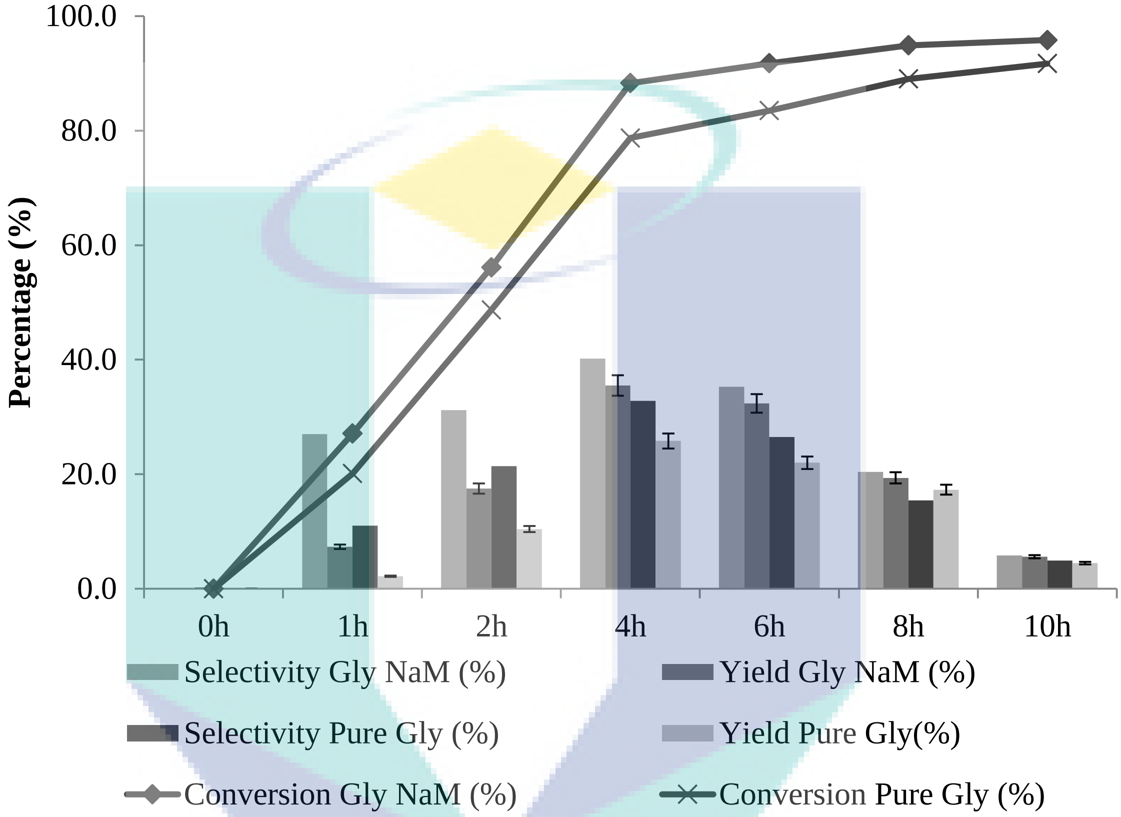


*Figure 5.1.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of crude Gly NaM blank and pure glycerol blank. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Standard stirring rate, 340 rpm.

### 5.3.1.2 Catalysed Reaction

Figure 5.2 and 5.3 clearly showed the significant role of BA 900 and $K_2SiO_3$ catalysts in improving the glycerol conversion and yield of glycerol carbonate. On top of that, it was found that crude Gly NaM with BA 900 and $K_2SiO_3$ showed almost similar catalytic data and TOL pattern, thus further confirmed the previously claimed findings in chapter 4 in which the catalytic activity and selectivity of boiler ash is mainly influenced by potassium silicate as active site. However, the results of selectivity and yield reported are lower than previous catalyst testing conducted using purified glycerol which can be compared in Figures 5.2 and 5.3. The presence of other substances in crude glycerol as summarised in Table 5.1 contributed to the inferior catalytic data. The lower glycerol conversion observed for crude glycerol at the beginning of reaction compared to analogue reaction using pure glycerol is believed to occur due to the presence of moisture in crude glycerol. In the later stage of reaction, the moisture is subsequently lost through heating, thus allowing conversion of glycerol to be almost similar with purified glycerol. The effect of moisture in affecting the glycerolysis reaction with urea is discussed in section 5.4.1.

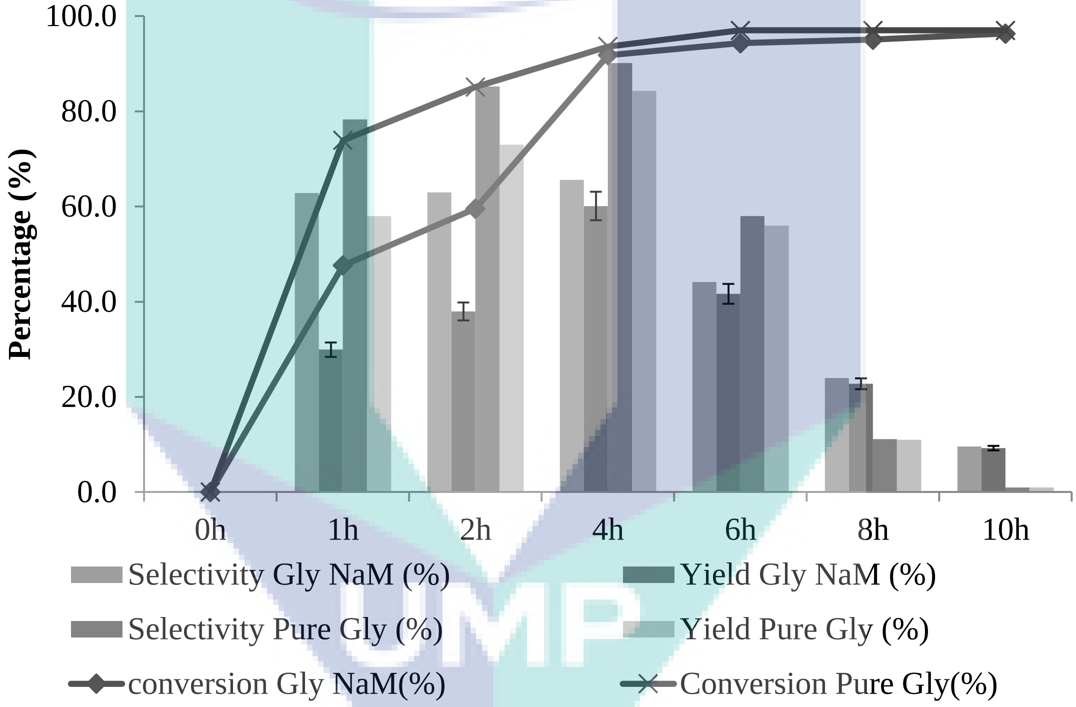


*Figure 5.2.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of crude Gly NaM as well as pure glycerol (Pure Gly) with BA 900. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

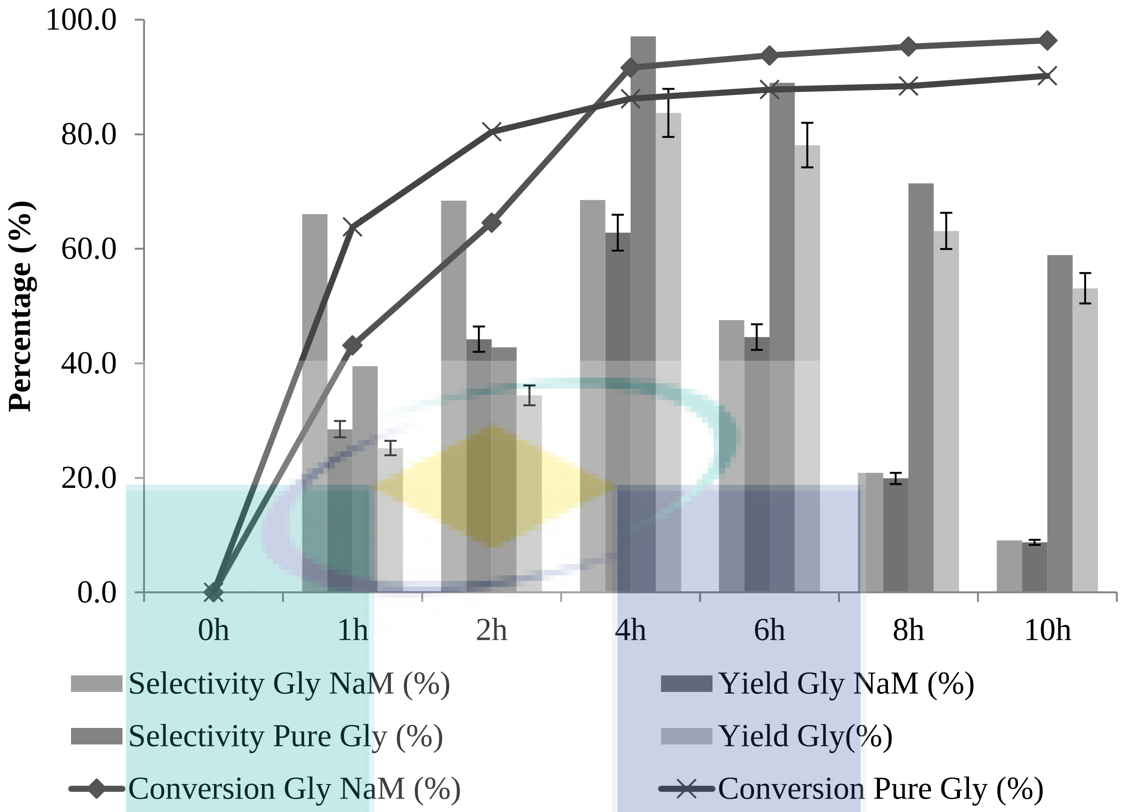


*Figure 5.3.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of crude Gly NaM as well as pure glycerol (Pure Gly) with $K_2SiO_3$. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

### 5.3.2 Synthesis of Glycerol Carbonate using Crude Glycerol (Gly KM).

#### 5.3.2.1 Blank reaction

Figure 5.4 illustrates the time online analysis of crude glycerol (Gly KM) without presence any catalyst. From the analysis it was found that blank reaction of crude glycerol (Gly KM) with urea showed maximum conversion of glycerol at 84.3 ± 0.6 %, selectivity of glycerol carbonate at 68.1 ± 0.3, and yield of glycerol carbonate at 57.5 ± 0.5 with 4 h reaction time. These results of selectivity and yield were comparably higher than analogue reaction with crude Gly NaM. It is also believed that potassium methylate expresses better catalytic activity compared to sodium methylate. Potassium has an electron further from the nucleus compared to sodium. Therefore, the electron is easily lost to form $K^+$ which acts as weak Lewis acid to catalyse the reaction. Besides, the strength of bond between potassium and methoxy group is also relatively weaker than sodium. Therefore, the higher ability of potassium ion to delocalise in the homogeneous reaction gives better conversion, yield and selectivity.

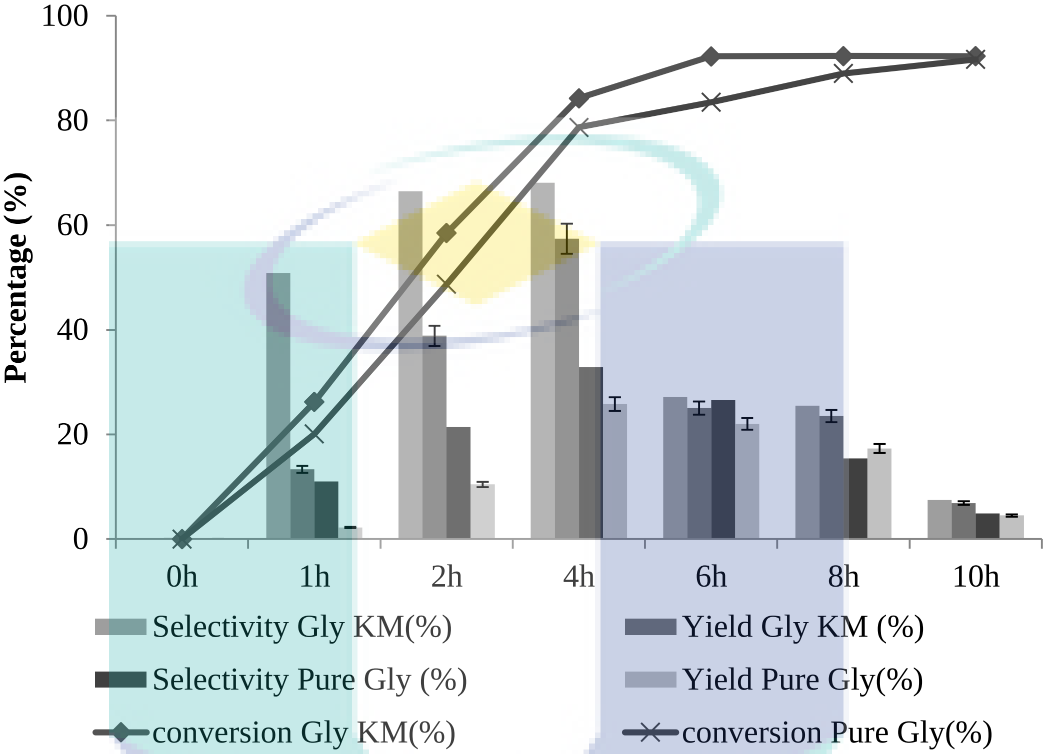


*Figure 5.4.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of crude Gly KM blank and pure glycerol blank. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Standard stirring rate, 340 rpm.

### 5.3.2.2 Catalysed Reaction

As shown in section 5.3.1.2 above, both BA 900 and $K_2SiO_3$ show beneficial effect on enhancing the productivity of glycerol carbonate from crude glycerol (Gly NaM) and urea (Figures 5.5 and 5.6). Similar effect and TOL trend were also observed with utilisation of Gly KM. However, glycerol conversion and glycerol carbonate yield for Gly KM as a starting feedstock are 20% higher than as observed with Gly NaM. This phenomenon is likely due to the similar activity of the potassium ion contained in the crude Gly KM as discussed earlier in section 5.3.2.1. However, the results of selectivity and yield reported are still lower than previous catalyst testing using purified glycerol.

Similar to crude glycerol (Gly NaM) the moisture present in crude glycerol (Gly KM) effects the conversion of glycerol at the beginning of the reaction which is gradually lost through heating. As mentioned earlier the stability of glycerol carbonate is disturbed by presence of moisture which decomposes it to glycerol.

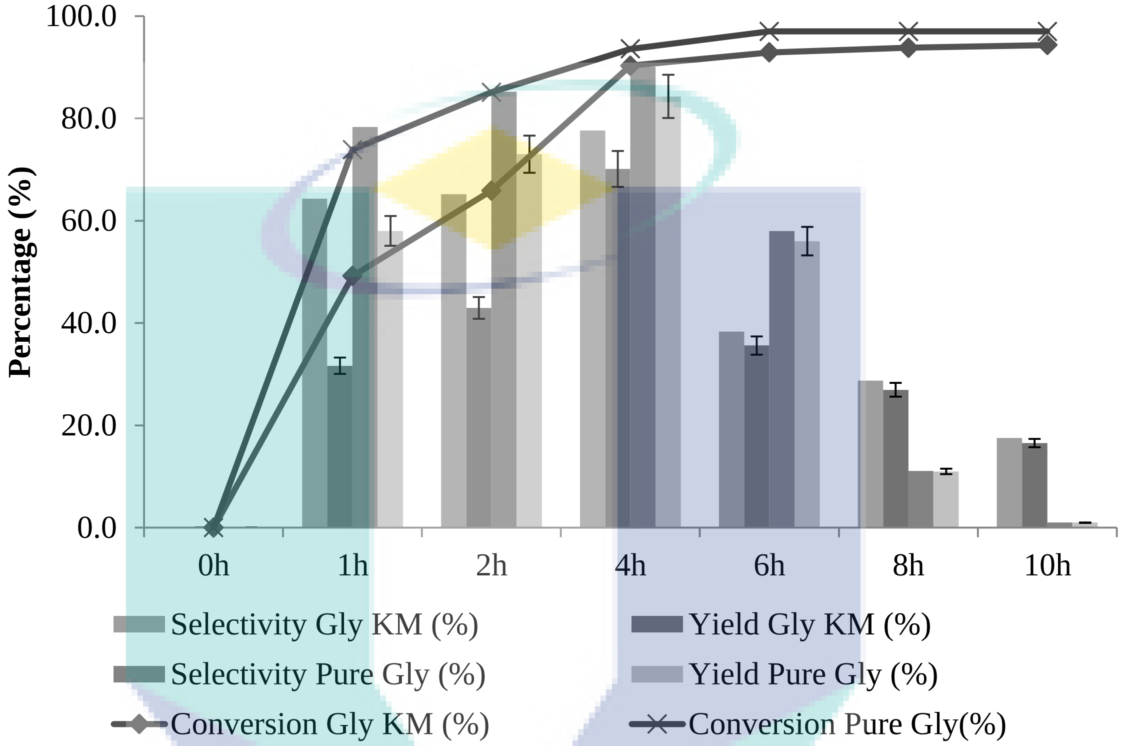


*Figure 5.5.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of crude Gly KM as well as pure glycerol (Pure Gly) with BA900. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

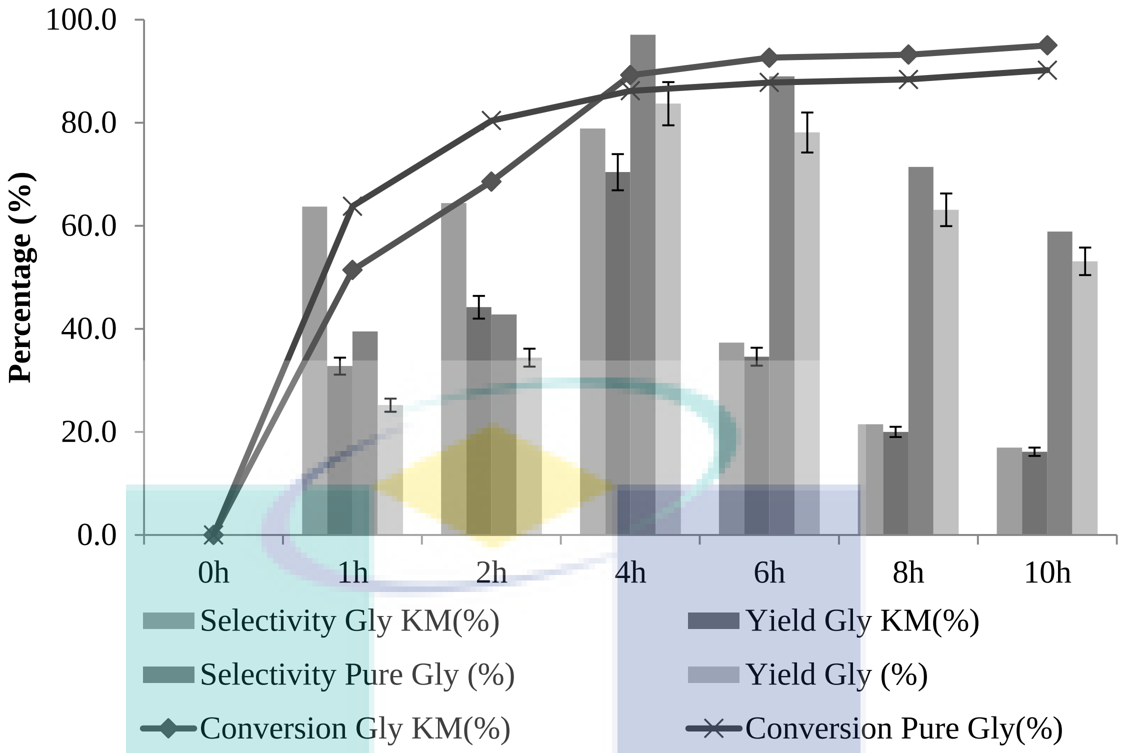


*Figure 5.6.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of crude Gly KM as well as pure glycerol (Pure Gly) with $K_2SiO_3$. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

## 5.4 Simulated Crude Glycerol Analysis

These analyses were conducted by mimicking pure glycerol with 10 wt % of moisture, 5 wt % of methanol, 1.6 wt % of potassium methylate and 1.6 wt % of sodium methylate. The values of mimicking conditions for moisture and methanol content were extracted from certificate of analysis (COA) as listed in Table 5.1.

### 5.4.1 Glycerol Mimicked with 10 wt % of Water

Based on the certificate of analysis details in Table 5.1, it was found that the maximum content of moisture specification was 10 wt % of water ($H_2O$). Therefore, in order to understand the level of interference of water in the reaction mechanism and catalytic performance, pure glycerol was mimicked with 10 wt % of water. It is evident from figure 5.7 that presence of 10 wt % water influences the catalytic reaction whereby the conversion of glycerol was effected by almost 50 % drop comparing with the pure glycerol (Table 5.2).

Table 5.2
*Analysis of glycerol conversion, glycerol carbonate selectivity and yield of pure glycerol and glycerol mimicked with 10 wt % water*

| **Reaction** | **Glycerol Conversion (%)** | **Gly C Selectivity (%)** | **Gly C Yield (%)** |
|---|---|---|---|
| Pure Glycerol | 93.6 ± 0.4 | 90.1 ± 1.0 | 84.3 ± 1.1 |
| Glycerol + 10 wt % water | 49.5 ± 0.4 | 69.5 ± 0.4 | 34.4 ± 0.5 |

Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

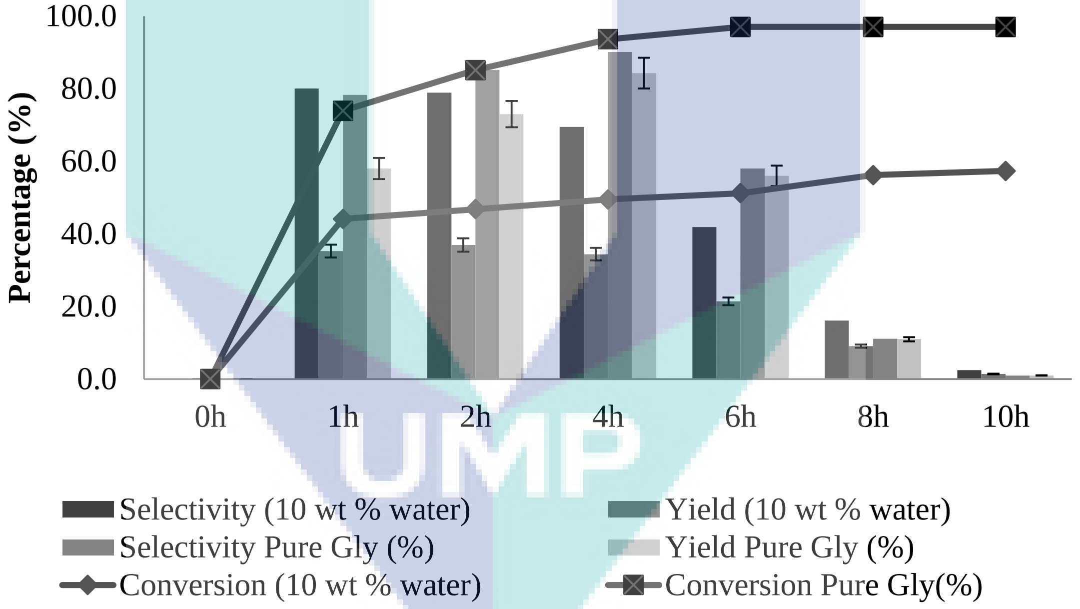


*Figure 5.7.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimic with 10 wt % water compared with the pure glycerol results. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

Figure 5.7 illustrates the selectivity towards glycerol carbonate increased from 0 h to 3 h. However, the poor conversion of glycerol causes selectivity towards glycerol carbonate to decline after 3 h due to decomposition of glycerol carbonate into glycerol.

Therefore, the yield of glycerol was affected by drop in conversion. Similar observation also reported by previous researchers (Nohra et al., 2012; Tudorache et al., 2013). This phenomenon can be explained through the stability of glycerol carbonate which is affected by water content. Glycerol carbonate containing water at prolonged time will transforms into glycerol. This is clearly proven by the qualitative stability analysis of glycerol carbonate carried out using GC-FID (Figure 5.8 and 5.9). From the analysis, 0.4 M of glycerol carbonate containing in water transformed to glycerol after 1 week in storage at 8 °C. Besides, it is also reported that presence of water can cause equilibrium shift in the glycerol carbonate reaction due to hydrolysis (Cushing & Peretti, 2013).

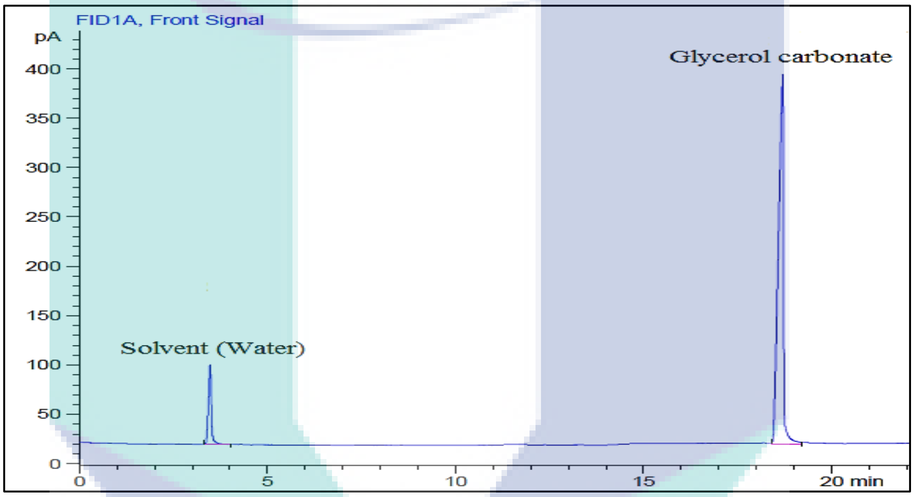


*Figure 5.8.* GC chromatogram of freshly prepared 0.4 M glycerol carbonate in water.

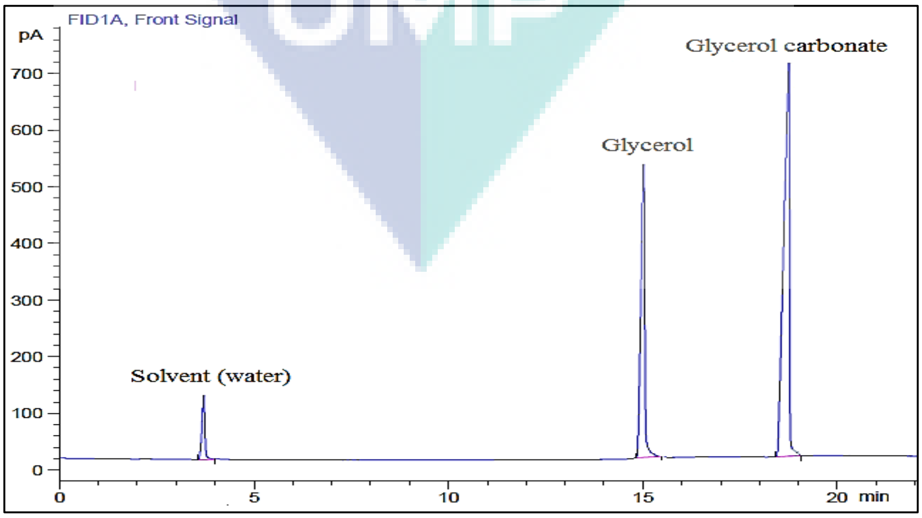


*Figure 5.9.* GC chromatogram of 0.4 M glycerol carbonate standard prepared in water and analysed after one week.

Even though the reaction is conducted at temperature higher than 100 °C, presence of water is still detected at 10 h as analysed using Mehtrohm Moisture Analyser (Table 5.3). Therefore, it can be expected that there is no complete loss of moisture. However, moisture content in both crude glycerol were reported to be 3.15 wt % only. Hence, this lower amount of moisture could be pertinent factor which could attribute to the conversion of glycerol to be higher in both crudes tested (section 5.2). In contrast, the presence of water at lower amount may have resulted in the slight drop in yield of Gly C synthesised using crude glycerol as reviewed by Teng et al., (2014).

Table 5.3

**Moisture Content Analysis*

| **Sample** | **Percentage of moisture (%)** |
|---|---|
| 10 wt % $H_2O$ | 10.0 ± 0.01 |
| 0 h | 9.2 ± 0.2 |
| 10 h | 5.6 ± 0.07 |

* Analysed using Mehtrohm Moisture Analyser

Based on the ATR-FTIR analysis in the Figure 5.10, the moisture band –OH observed at 10 wt % of $H_2O$ gradually decreases as duration of reaction increase from 0 h to 10 h. Note that 0 h reading is taken after flowing nitrogen gas for 20 minutes at 150 °C. Thus, the loss of –OH band at range of (3200-3400 $cm^{-1}$) due to loss of moisture is clearly evident. However, the formation of glycerol carbonate (1790 $cm^{-1}$) was not clearly evident due to the poor conversion of glycerol inhibited by moisture in the sample.

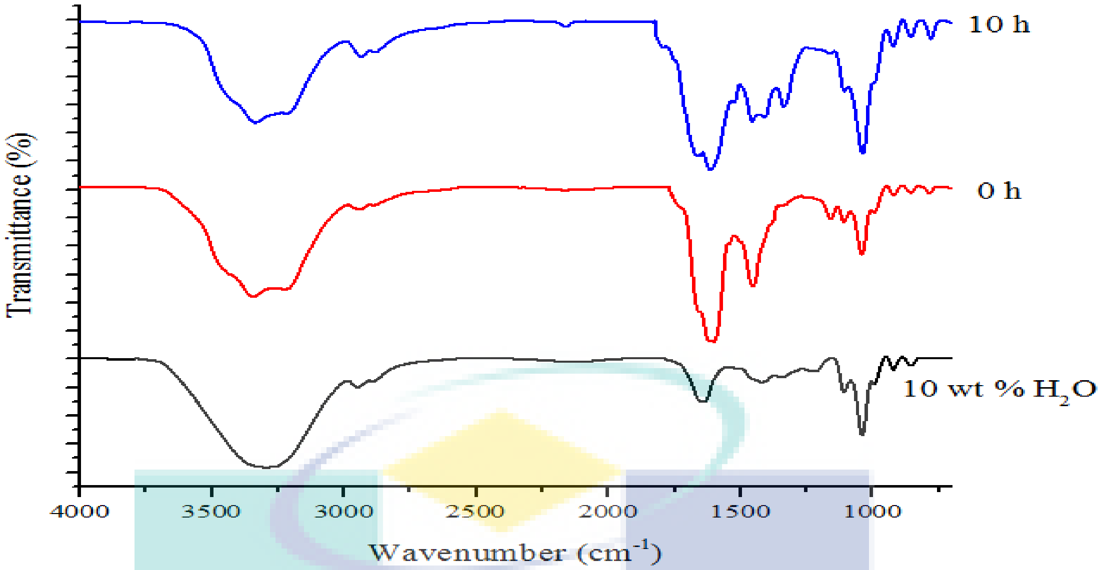


*Figure 5.10.* ATR-FTIR analysis spectrum of 10 wt % $H_2O$, 0 h and 10 h.

### 5.4.2 Glycerol Mimicked with 5 wt % of Methanol

Figure 5.11 illustrates the effect of methanol content towards synthesis of glycerol carbonate. 5 wt % of pure methanol was mimicked in pure glycerol following specification of COA in Table 5.1. The 5 wt % methanol content in glycerol alters selectivity of glycerol carbonate as depicted in Figure 5.11 but does not significantly affect conversion of glycerol in the overall process. However, slight drop in conversion compared with the pure glycerol is expected as mass transfer of reactant is limited in presence of methanol that could possibly alter the basic strength of catalyst. Thus, limiting conversion of the glycerol, Maximum selectivity of the glycerol carbonate found was 75.4 ± 0.4 % at 4 h reaction time which was slightly lower than the pure glycerol. This scenario is due to the formation of by-products such as glycidol.

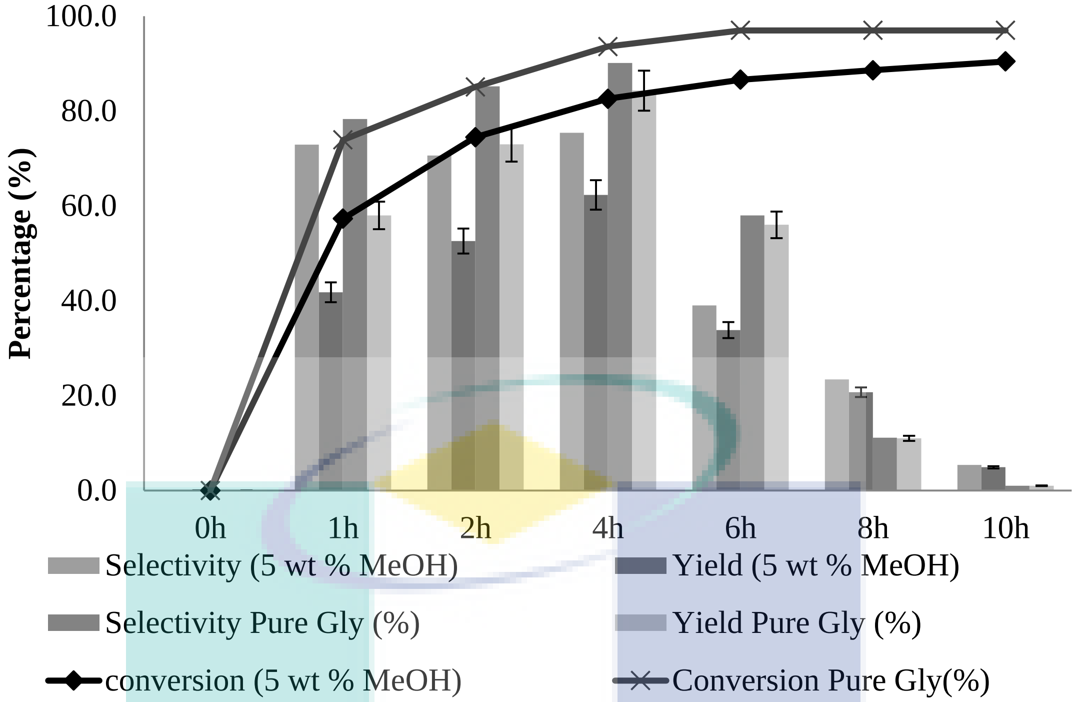
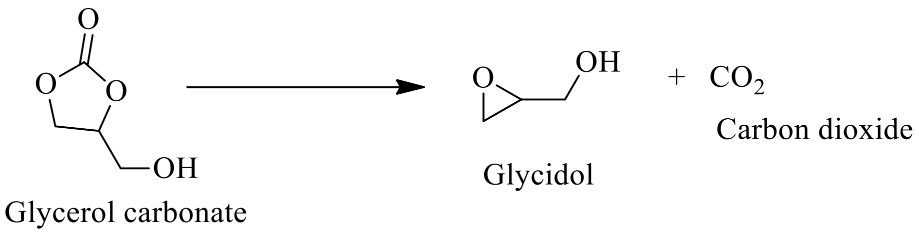


*Figure 5.11*. Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimic with 5 wt % methanol compared with pure glycerol results. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

Based on review reported by Teng et al., (2014), presence of methanol can cause decomposition of glycerol carbonate into glycidol. Besides, study by González, Cabanelas and Baselga, (2012), peak of epoxide belonging to glycidol should be observed at 1254 $cm^{-1}$, stretching of C-O of oxirane group at 909 $cm^{-1}$ and stretching of C-O-C of oxirane group at 846 cm. In analysis of mimicking glycerol with 5 wt % of methanol using ATR-FTIR the formation of glycidol was detected at 10 h but with weak peak absorptions (Figure 5.12). Therefore, it can be expected that only minimal level of glycidol could be present in the glycerol simulated with 5 wt % methanol. The formation of glycidol is as discussed in scheme 4. Moreover, in ATR-FTIR analysis using direct crude glycerol the formation of glycidol was not detected (Figure 5.13). This is because very minimal amount of methanol is present in both crudes about 0.8 wt %. Thus, the formation of glycidol from decarboxylation of glycerol carbonate is not possible when very low amount of methanol is present. However, the reduction in glycerol carbonate selectivity is effected by the increased formation of other by-products similar to those reported in chapter 4.



Scheme 4. Decarboxylation of glycerol carbonate to glycidol.

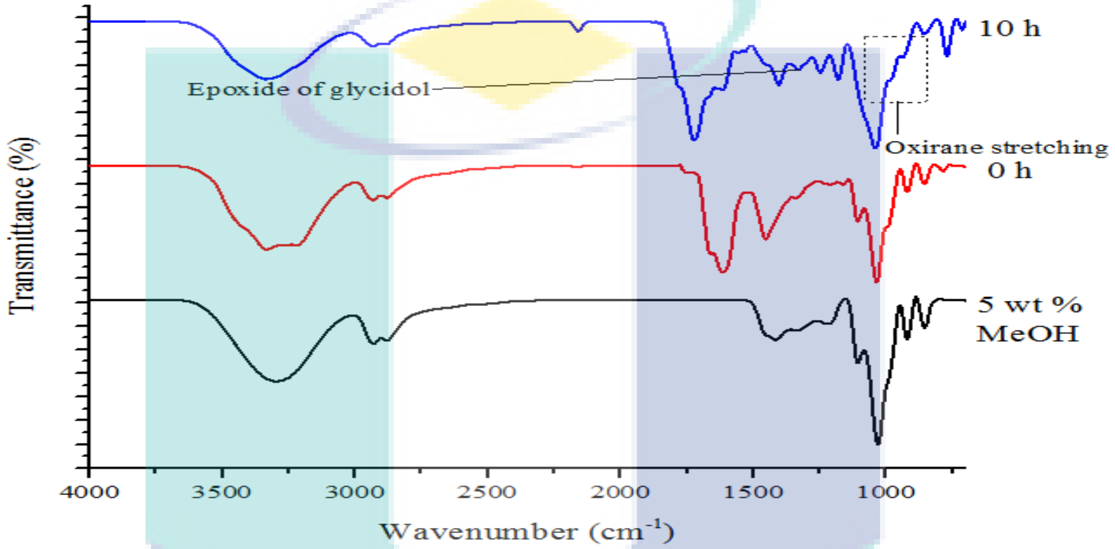


*Figure 5.12.* ATR-FTIR spectrum analysis of 5 wt % MeOH, 0 h and 10 h.

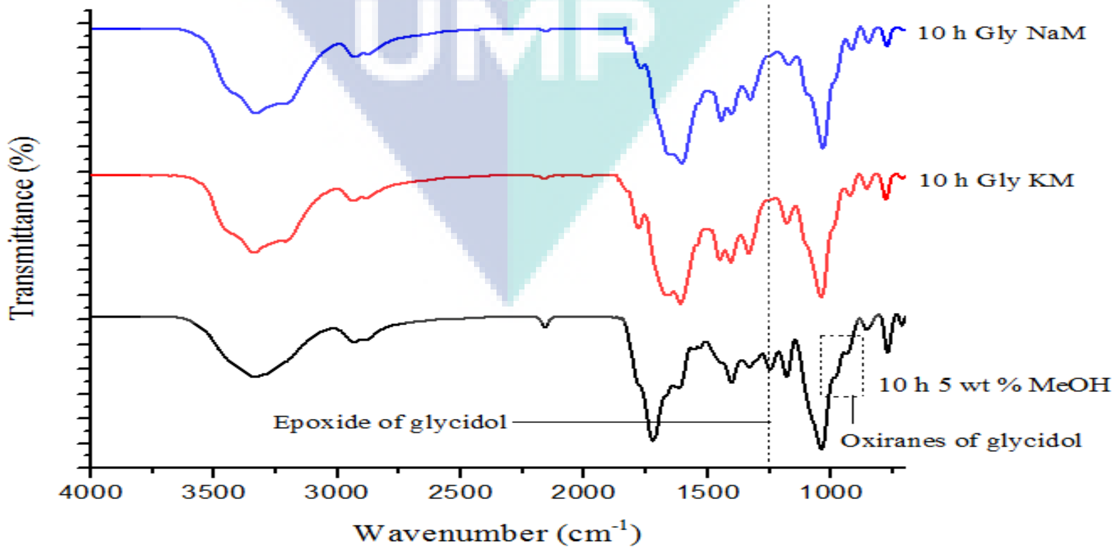


*Figure 5.13.* ATR-FTIR spectrum analysis of 10 h 5 wt % MeOH, 10 h Crude Gly NaM and 10 h Crude Gly KM.

### 5.4.3 Glycerol mimicked with 10 wt % moisture and 5 wt % methanol

In order to understand the level of interference of mixture of moisture and methanol, these substances were mimicked in glycerol at 10 wt % and 5 wt % respectively. From the analysis it was found that conversion of glycerol to glycerol carbonate was significantly affected which directly reduced yield of desired product (Figure 5.14). The effect of the data obtained was influenced by the stability of glycerol carbonate in moisture and formation of by-product glycidol which was evident in the ATR-FTIR analysis depicted in Figure 5.15 where functional groups of oxirane stretching and epoxide of glycidol were present.

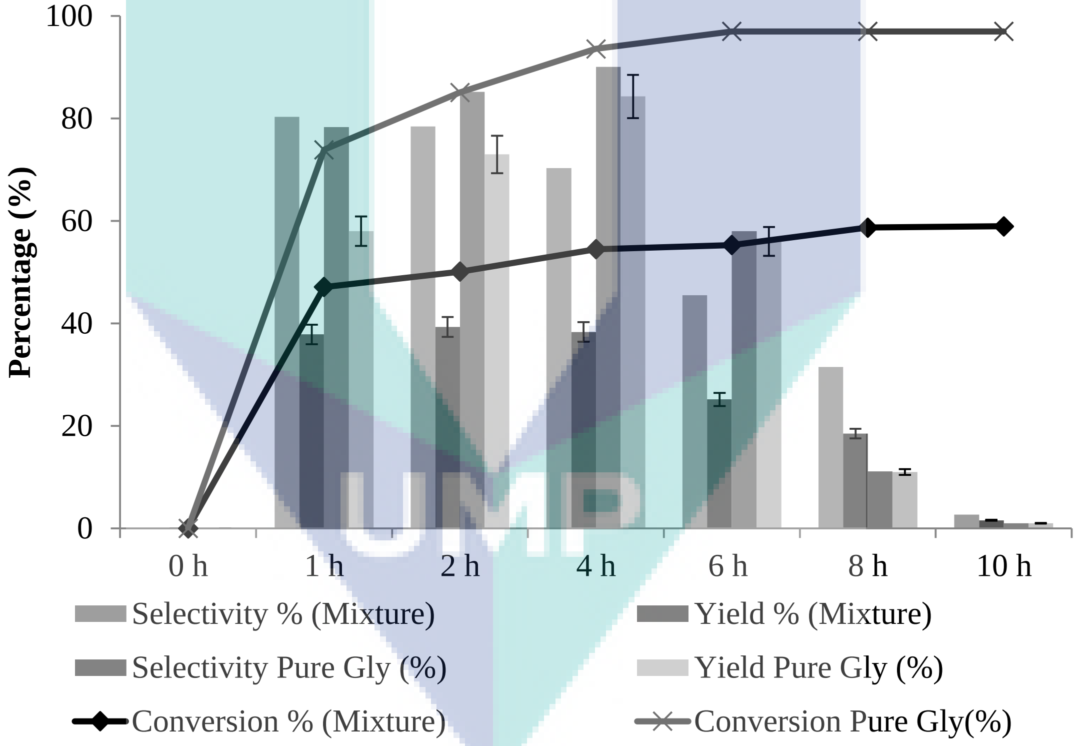


*Figure 5.14.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimic with 10 wt % moisture and 5 wt % methanol compared with pure glycerol results. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

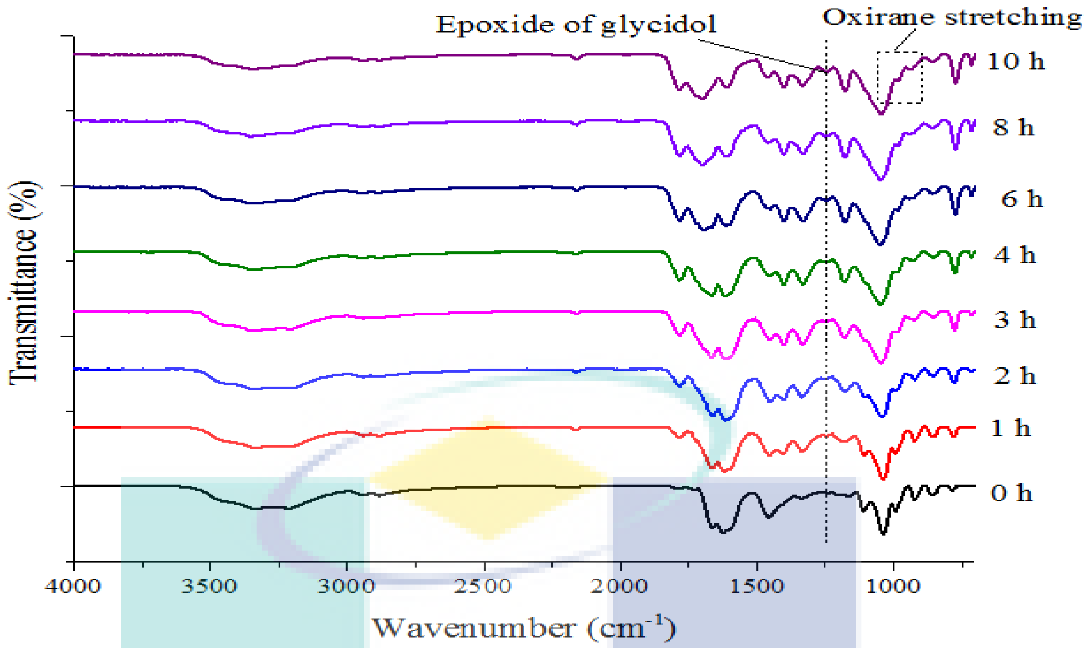


*Figure 5.15*. Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimic with 10 wt % moisture and 5 wt % methanol using ATR-FTIR.

### 5.4.4 Glycerol mimicked with 3.15 wt % moisture and 0.8 wt % methanol

As illustrated in Figure 5.16, it was found that the catalytic data of glycerol simulated with mixture of moisture and methanol at 3.15 wt % and 0.8 wt % does not have significant impact towards glycerol carbonate yield. Only slight drop in conversion, selectivity and yield was noted. However, mixing of moisture and methanol at higher rates directly effects the conversion, selectivity and yield drastically as depicted in Figure 5.14. About 78.3 % yield glycerol carbonate was found to be present in this study in which the result of simulated mixture dropped to about 6 % from the yield percentage when compared with the pure glycerol reaction with BA 900. Therefore, the crude containing moisture and methanol at lower amounts as shown in the certificate of analysis does not show major interference on the glycerol carbonate formation.

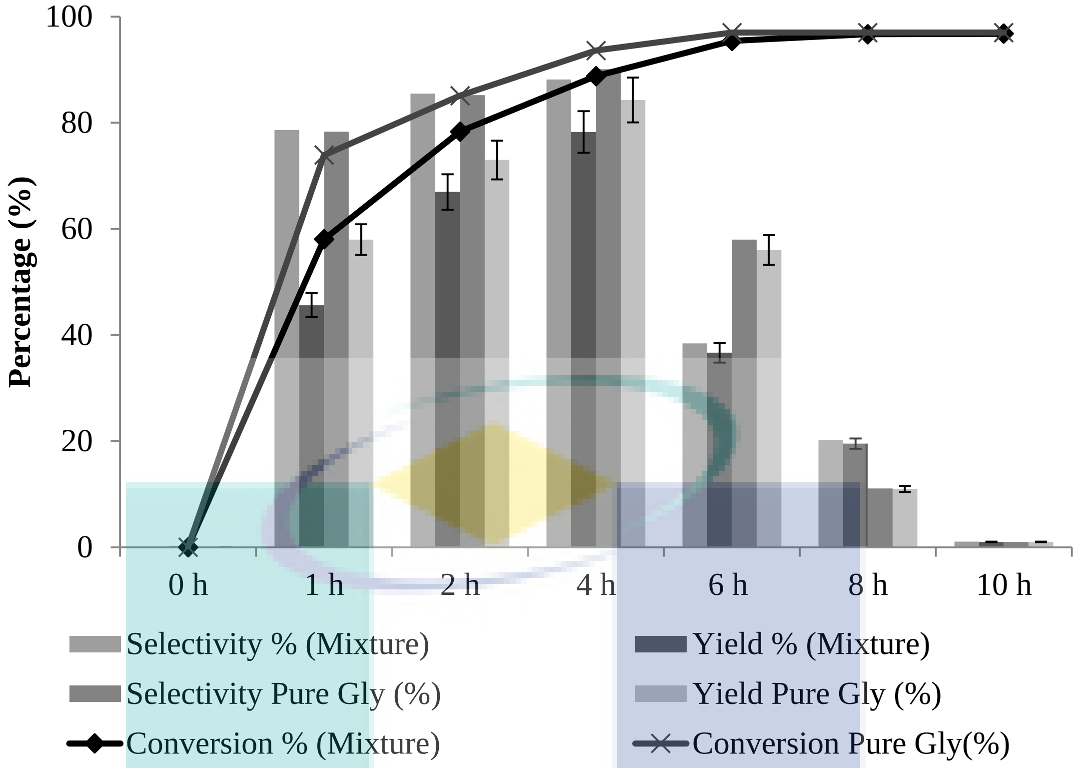


*Figure 5.16.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimic with 3.15 wt % moisture and 0.8 wt % methanol compared with pure glycerol results. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

### 5.4.5 Glycerol Mimicked with 1.6 wt % of Potassium methylate

As introduced earlier in section 5.1, there are two different source of glycerol obtained from Artistic Support Sdn. Bhd. In the biodiesel production plant there are mainly two sources of catalyst used which are potassium methylate and sodium methylate. According to the process about 1.6 wt % of these catalysts are loaded respectively in to different processing tanks to obtain biodiesel. The final glycerol extracted along with other impurities contains the initial catalyst loaded. Therefore, the effect of the catalyst loaded towards glycerol carbonate synthesis was also investigated.

Pure glycerol was mimicked with 1.6 wt % of potassium methylate. From Figure 5.17, maximum yield and selectivity of glycerol carbonate was observed at 4 h with 95.5 ± 0.6 % and 86.4 ± 1.1 % respectively. The conversion of glycerol was 95.4 ± 0.6 %. From this study it was found that potassium ion attached to any form of conjugate basic site is highly active for glycerolysis of urea. Besides, potassium methylate showed higher yield and selectivity compared to crude glycerol mimicked with sodium methylate.

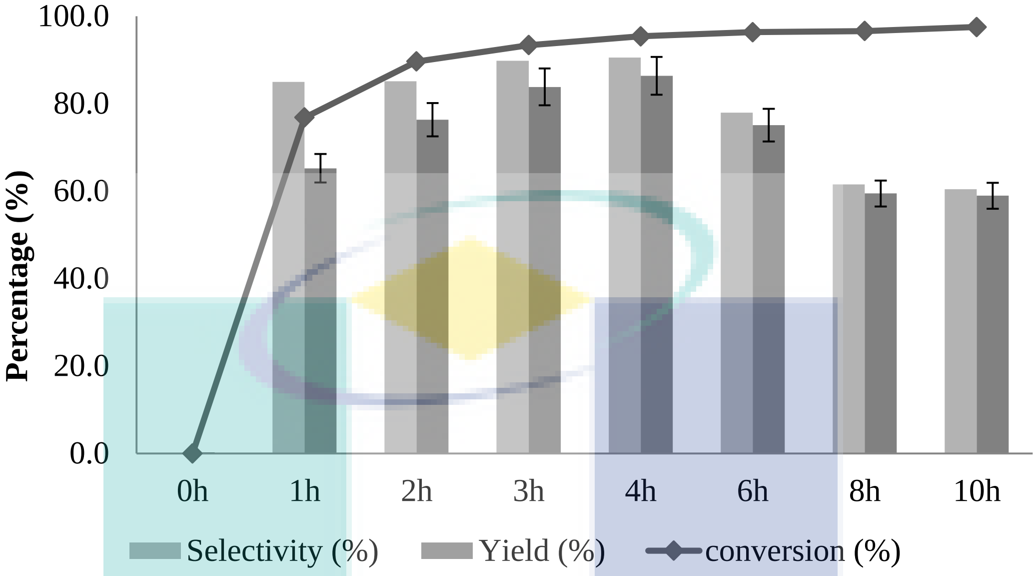


*Figure 5.17*. Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimicked with 1.6 wt % potassium methylate. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

The Hammett test also indicates that potassium methylate and sodium methylate is basic in nature which is relatively similar to the property of boiler ash (Table 5.4). To add on, all catalyst containing potassium exhibited comparable results with one another.

Table 5.4
*Hammett Test*

| **Catalyst** | **Methyl Red (H_=4.8)** | **Phenolphthalein (H_=8.2)** | **2, 4 – Dinitroaniline (H_=15)** | **4 – Nitroaniline (H_=18.4)** |
|---|---|---|---|---|
| Potassium methylate | No changes | Colourless to pink solution | No changes | No changes |
| Sodium methylate | No changes | Colourless to pink solution | No changes | No changes |

From Figure 5.18, the ATR-FTIR time online analysis of glycerol mimicked with 1.6 wt % potassium methylate shows the decomposition pattern of urea from 0 h to 10 h and formation of glycerol carbonate along with other by-products as discussed earlier in chapter 4. Similarly like synthesis of glycerol carbonate using boiler ash (BA 900) as catalyst, the formation of glycerol carbonate in this study also occurred from rapid decomposition of intermediate glycerol carbamate into glycerol carbonate. Therefore, this study also proposes an effective use of potassium methylate as bifunctional catalyst for the synthesis of both biodiesel and glycerol carbonate in biodiesel industry.

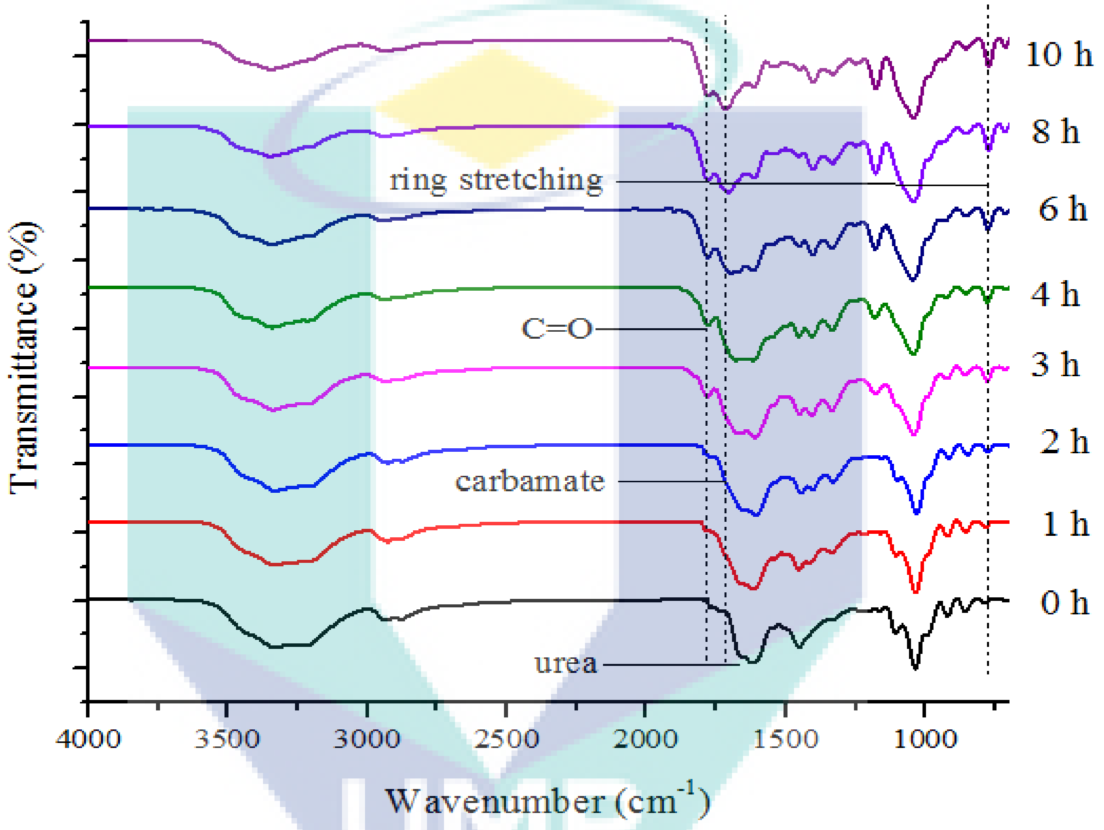


*Figure 5.18.* ATR-FTIR spectrum for time online analysis of reaction mimicked with 1.6 wt % potassium methylate from1 h to 10 h.

### 5.4.6 Glycerol Mimicked with 1.6 wt % of Sodium methylate

Figure 5.19 illustrates the time online analysis (TOL) of glycerol mimicked with 1.6 wt % sodium methylate. At 4 h of reaction time, maximum selectivity and yield of glycerol carbonate observed were 82.5 ± 0.7 % and 79.0 ± 0.7 %, respectively. The conversion of glycerol was 95.7 ± 0.2 %. Even though, the selectivity and yield of glycerol carbonate is reported to be slightly lower than using potassium methylate as catalyst, sodium methylate also can act as suitable catalyst for the synthesis of glycerol carbonate.

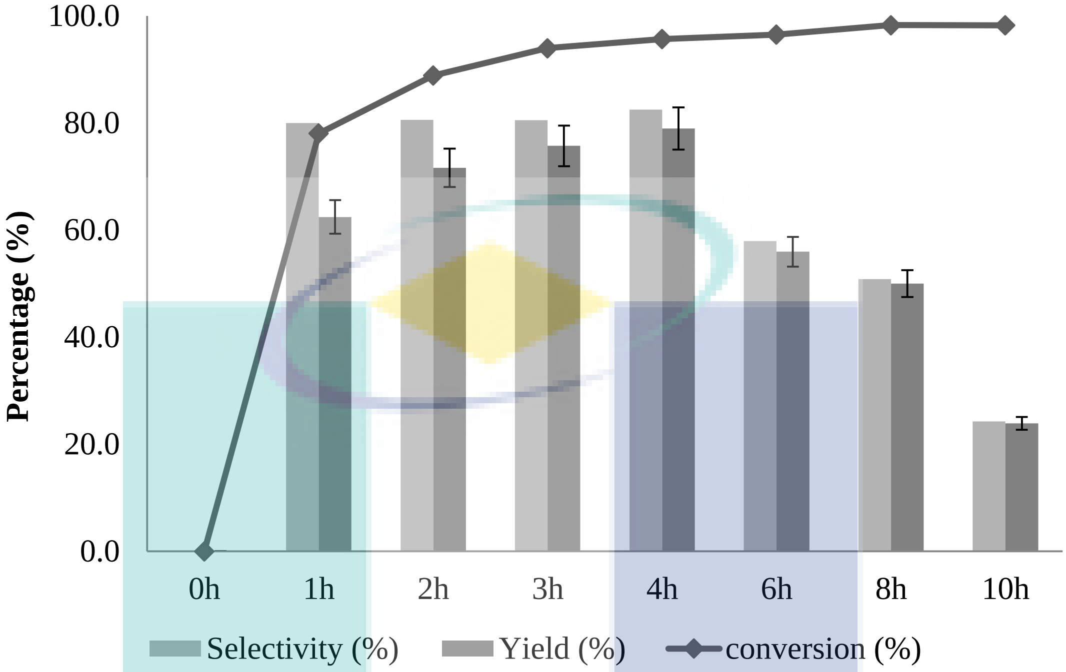


*Figure 5.19.* Time online analysis (TOL) of glycerol conversion (%), glycerol carbonate selectivity (%) and glycerol carbonate yield (%) of glycerol mimicked with 1.6 wt % sodium methylate. Reaction conditions: Temperature, 150 ˚C; Gas, Nitrogen; Glycerol: Urea, 1: 1.5 (Molar ratio); Catalyst mass, 0.25 g; Standard stirring rate, 340 rpm.

Property of sodium methylate which is found to be basic in nature through the Hammett test (Table 5.4) allows sodium to act as a Lewis acid to activate the carbonyl group of urea while the methoxy group activates the glycerol to form glycerol carbonate. Even though sodium methylate is less active than potassium methylate, the pattern of TOL from Figure 5.20 suggests that it still follows accelerated decomposition of glycerol carbamate into glycerol carbonate. The Lewis acidity of potassium is theoretically expected to be higher than sodium based on discussion in (section 5.3.2.1) which may be a relevant reason to the current scenario.

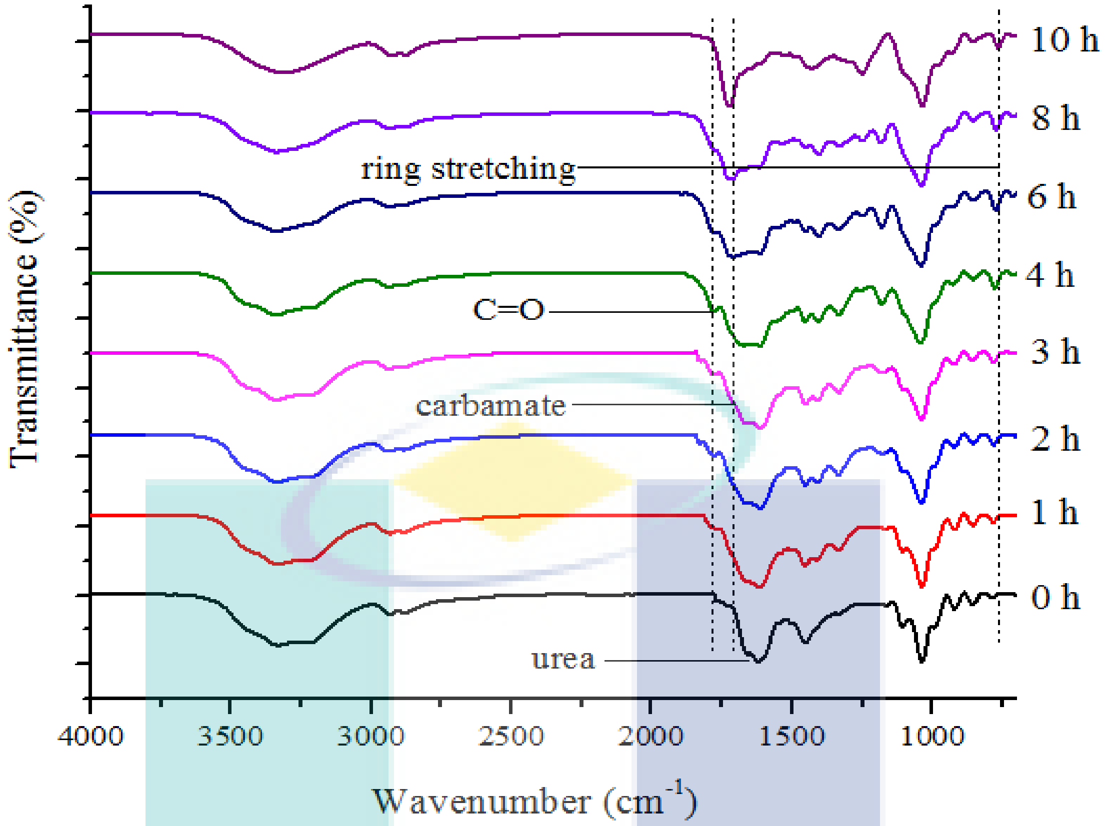


*Figure 5.20.* ATR-FTIR spectrum for time online analysis of reaction mimicked with 1.6 wt % sodium methylate from1 h to 10 h.

## 5.5 Summary

In concise, it can be summarised that the activity of crude glycerol is influenced by the presence of moisture and methanol content. However, in this study the lower content of moisture and methanol in crude glycerol allowed transformation of direct crude glycerol into glycerol carbonate. It was also found that moisture at 10 wt % significantly effects the conversion of glycerol due to instability of glycerol carbonate in water. On the other hand, methanol at 5 wt % influences catalyst basicity in selectivity of glycerol carbonate. However, maximum yield of glycerol carbonate can be achieved if the crude glycerol is pretreat for purification. Nevertheless, the current findings suggest that the crude glycerol can be used directly without purification using boiler ash as catalyst. Even though, optimum yield of glycerol carbonate cannot be achieved, crude glycerol Gly KM achieved promising yield of 70.1 ± 0.9 % which is industrially favoured value. Thus, purification of the crude before use may not be susceptible as it will only increase yield by 14 % approximation. The overall study suggests that both potassium methylate and sodium methylate used in the biodiesel industry as catalysts for biodiesel production can also be used as catalysts for the glycerolysis reaction with urea. On the other hand, a recent study by Nguyen and Demirel, (2013) suggests a co-production plant of biodiesel along with glycerol carbonate using glycerolysis route with urea as an economical plant. However, they propose the use of two different catalysts for biodiesel synthesis and glycerol carbonate synthesis which involved use of calcined eggshells majorly containing calcium oxide and synthetically derived lanthanum oxide, respectively. Therefore, in our view similar catalyst used in Artistic Support Sdn. Bhd. for the synthesis of biodiesel fuels can also be used for the synthesis of glycerol carbonate concurrently.

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# CHAPTER 6

# FEASIBILITY OF BOILER ASH AND $K_2SIO_3$ AS CATALYST FOR THE SYNTHESIS OF OTHER ORGANIC CARBONATES

## 6.1 Introduction

This chapter discusses the feasibility of boiler ash (BA 900) and $K_2SiO_3$ in synthesising other organic carbonates such as ethylene carbonate and propylene carbonate from ethylene glycol and propylene glycol respectively as a proof of concept study. The chapter is later elaborated to discuss the synthesis mechanistic pathway of ethylene carbonate and propylene carbonate using BA 900 as catalyst.

## 6.2 Synthesis of Ethylene Carbonate and Propylene Carbonate

In this section of the chapter, the feasibility of the catalyst to synthesise ethylene carbonate (EC) and propylene carbonate (PC) is discussed. This specific carbonates were chosen due to their adverse use in many industries. Ethylene carbonate and propylene carbonate have variety of applications in many major industries such as polymers, gas separation membranes, paints, agrochemicals, batteries as well as supercapacitors (Barreto et al., 2012; Perricone et al., 2013; Wagner et al., 2014).

The cyclisation of ethylene glycol (EG) and propylene glycol (PG) to form their respective carbonate was possible through the use of boiler ash catalyst and it was reported for the first time herein. It was found that potassium silicate ($K_2SiO_3$) contained in boiler ash could aid in the selective carbonylation of ethylene glycol and propylene glycol to their respective carbonates. As shown in Table 6.1, at 8 h reaction time, maximum yield of ethylene carbonate of 80.1 ± 0.6 % was obtained while at 10 h, yield of propylene carbonate was 73.2 ± 0.7 %. It is important to note that catalytic activity for both ethylene carbonate and propylene carbonate show almost identical turnover frequency (TOF) indicating the amount of active species responsible for the transcarbonylation reaction to be equal (Boudart, 1995). Apart from that, reaction involving the use of $K_2SiO_3$ alone instead of boiler ash produced almost similar yield of respective carbonates of EC (79.9 ± 0.3 %) and PC (72.8 ± 0.7 %) correspondingly. Thus, this study further confirms the role of $K_2SiO_3$ as active sites in boiler ash in carbonylation of polyol similar to study conducted for the synthesis of glycerol carbonate in chapter 4. Thus, this scenario suggested that the catalytic activity was due to the presence of $K^+$ which acted as weak Lewis acid to activate urea while the conjugate basic site $SiO_3^{2-}$ activated the hydroxyl group of the polyols to form the respective carbonates.

Table 6.1
*Reaction conditions and yield of ethylene carbonate and propylene carbonate*

| **Catalyst** | **Molar Ratio of Polyol to Urea** | **Conversion % of polyol** | **Duration (h)** | **Yield % of Organic Carbonate** | **TOF (mmol/ g cat.h$^{-1}$)** |
|---|---|---|---|---|---|
| **EC** | | **Ethylene Carbonate** | | | |
| Blank | 1.5:1 EG: Urea | 60.5 | 8 | 17.9 | - |
| BA 900 | | 92.7 | 8 | 80.1 | 120.2 |
| $K_2SiO_3$ | | 92.7 | 8 | 79.9 | 119.8 |
| **PC** | | **Propylene carbonate** | | | |
| Blank | 4:1 PG: Urea | 78.4 | 10 | 36.3 | - |
| BA 900 | | 89.2 | 10 | 73.2 | 117.1 |
| $K_2SiO_3$ | | 89.4 | 10 | 72.8 | 116.5 |

Reaction conditions: Temperature, 150 °C; Catalyst mass, 0.25 g; gas, $N_2$; Standard stirring rate, 340 rpm. TOF: calculated based on mmol of initial polyols multiply by yield percentage of carbonate per gram catalyst per total reaction time (h). Note: EG is ethylene glycol while PG is propylene glycol.

In general, this study was carried out to prove the feasibility of the catalyst in synthesis of other organic carbonates using similar synthesis approach. Therefore, various reaction condition parameters study was not carried out for both EC and PC synthesis.

Instead, reaction conditions obtained from literatures were used to study the feasibility of the catalyst BA 900 with slight modification (Sharma et al., 2013; Du et al., 2014). This is because reaction parameters found suitable for the synthesis of glycerol carbonate using BA 900 did not suite the reaction of EC and PC while poorer yields of 21.3 ± 0.6 % and 41.7 ± 0.4 % were obtained, respectively (Table 6.2). Since the reaction conditions study proposes suitable reaction time, the current study resulted in a longer duration for both EC and PC synthesis compared to glycerol carbonate (Gly C) synthesis using the same catalyst. Besides, higher molar ratio of glycols to urea was favoured in both EC and PC synthesis as proposed in previous literatures. Even though, study by several researchers suggest higher yield of ethylene carbonate at 83 % (Peng et al. 2012) and propylene carbonate at 93.1 % (D. Wang et al., 2014), the turnover frequency of the catalyst resulted in poor values of 26.7 mmol/g.cat.h$^{-1}$ and 81.7 mmol/g.cat.h$^{-1}$ respectively.

Table 6.2

*Synthesis of EC and PC using similar reaction conditions of glycerol carbonate synthesis*

| **Catalyst** | **Molar Ratio of Polyol to Urea** | **Conversion % of polyol** | **Duration (h)** | **Yield % of Organic Carbonate** | **TOF (mmol/ g cat.h$^{-1}$)** |
|---|---|---|---|---|---|
| **EC** | | **Ethylene carbonate** | | | |
| Blank | 1:1.5 EG: Urea | 68.6 | 4 | 10.1 | - |
| BA 900 | | 65.8 | 4 | 21.3 | 32.0 |
| **PC** | | **Propylene carbonate** | | | |
| Blank | 1:1.5 PG: Urea | 90.6 | 4 | 29.4 | - |
| BA 900 | | 98.1 | 4 | 41.7 | 62.6 |

Reaction conditions: Temperature, 150 °C; Catalyst mass, 0.25 g; gas, $N_2$; Standard stirring rate, 340 rpm. TOF: calculated based on mmol of initial polyols multiply by yield percentage of carbonate per gram catalyst per total reaction time (h). Note: EG is ethylene glycol while PG is propylene glycol.

It can be seen from Figure 6.1 oxazolidin-2-one (denoted as compound 10) and 3-(2-hydroxyethyl) oxazolidin-2-one (denoted as compound 11) increases as duration of reaction is increased from 0 h to 10 h. In addition, the by-products detected in this study was also found in previously reported literature by Bhanage, Fujita, Ikushima, and Arai, (2003) as well as Zhao et al., (2008). On the other hand, decomposition of 2-hydroxyethyl carbamate (denoted as compound 9) was observed from 0 h to 10 h. It was found that the decomposition of intermediate carbamate did not directly correspond to the selectivity of ethylene carbonate which suggested the second step of the reaction occurred at an accelerated manner as previously found in synthesis of glycerol carbonate using BA 900. On the other hand, the current study proposes that the use of BA 900 is a feasible catalyst at atmospheric pressure for the synthesis of ethylene carbonate. Qiu et al., (2012), reported that the reaction cannot occur at atmospheric pressure and resulted in poor value of EC yield. This may suggest an economical route for the industry to conduct experiment at lower pressures using BA 900 as catalyst.

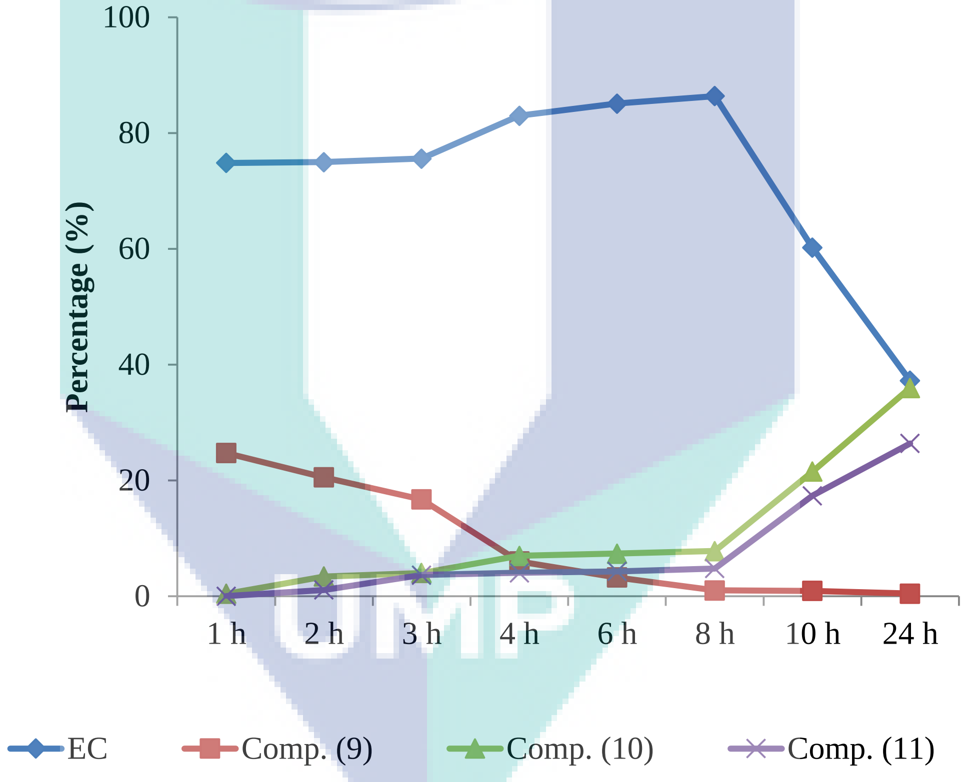


*Figure 6.1*. TOL of selectivity of EC, Comp. 9, Comp. 10 and Comp. 11 from 1 h to 24 h. Reaction conditions: Temperature, 150 °C; Catalyst mass, 0.25 g; gas, $N_2$; Standard stirring rate, 340 rpm.

Similar trend in product selectivity (Figure 6.2) were witnessed for the synthesis of propylene carbonate (PC) suggested both starting material (EG and PG) followed similar mechanistic pathways. For TOL of propylene glycol as starting polyol, the amount of by-products 4-methyloxazolidin-2-one (comp. 15) and 3-methyloxazolidin-2-one (comp. 16) increases as duration of reaction is increased from 0 h to 10 h. On the other hand, decomposition of 2-hydroxyproyl carbamate (comp. 14) was observed from 0 h to 10 h. It was found that the decomposition of intermediate carbamate did not directly correspond to the selectivity of propylene carbonate which suggested the second step of the reaction occurred at an accelerated manner as previously found in synthesis of glycerol carbonate and also in synthesis of EC using BA 900. Detailed discussion on reaction mechanism is included in the following section 6.3.

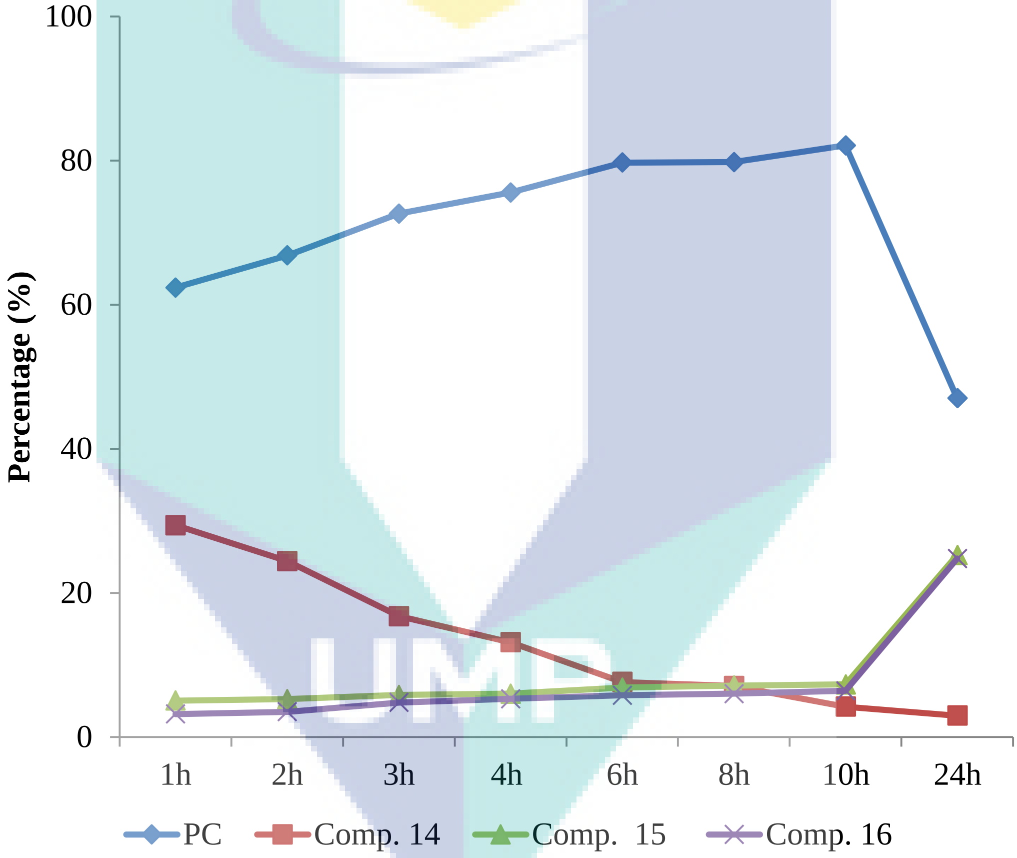


*Figure 6.2.* TOL of selectivity of PC, Comp. 14, Comp. 15 and Comp. 16 from 1 h to 24 h. Reaction conditions: Temperature, 150 °C; Catalyst mass, 0.25 g; gas, $N_2$; Standard stirring rate, 340 rpm.

In contrast, the percentages of conversion between the non-catalysed and boiler ash catalysed reaction for EG and PG is slightly different whereby the percentage conversion of EG in the presence of catalyst is more significant compared to less than 10 % conversion value difference for PG.

The products yield and by-products yield for the synthesis reaction of both ethylene carbonate and propylene carbonate is tabulated in Table 6.3 and Table 6.4.

Table 6.3
*Product yield and by-product selectivity from synthesis of ethylene carbonate using BA 900*

| **Catalyst** | **EG conversion %** | **Selectivity %** | | | | **EC Yield %** |
|---|---|---|---|---|---|---|
| | | **EC** | **Comp. (9)** | **Comp. (10)** | **Comp. (11)** | |
| **Blank** | 60.5 | 29.6 | 10.1 | 36.1 | 24.2 | 17.9 |
| **BA 900** | 92.7 | 86.4 | 1.0 | 7.8 | 4.58 | 80.1 |

Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; EG: Urea, 1.5: 1 (Molar ratio); Catalyst mass, 0.25 g; Time, 8 h; Standard stirring rate, 340 rpm. Note: EG, ethylene glycol; EC, ethylene carbonate; Comp. (9), 2-hydroxyethyl carbamate; Comp. (10), oxazolidin-2-one; Comp. (11), 3-(2-hydroxyethyl) oxazolidin-2-one.

Table 6.4
*Product yield and by-product selectivity from synthesis of propylene carbonate using BA 900*

| **Catalyst** | **PG conversion %** | **Selectivity %** | | | | **PC Yield %** |
|---|---|---|---|---|---|---|
| | | **PC** | **Comp. (14)** | **Comp. (15)** | **Comp. (16)** | |
| **Blank** | 78.4 | 46.3 | 5.8 | 26.2 | 21.7 | 36.3 |
| **BA 900** | 89.2 | 82.1 | 4.2 | 7.3 | 6.2 | 73.2 |

Reaction conditions: Temperature, 150 ˚C; Gas, $N_2$; PG: Urea, 4: 1 (Molar ratio); Catalyst mass, 0.25 g; Time, 10 h; Standard stirring rate, 340 rpm. Note: PG, propylene glycol; PC, propylene carbonate; Comp. (14), 2-hydropropyl carbamate; Comp. (15), 4-methyloxazolidin-2-one; Comp. (16), 3-methyloxazolidin-2-one.

It is essential to note that the current study proposes better yield of ethylene carbonate than previously reported study (Zhao et al., 2008; Sharma et al., 2013). However, for the synthesis of propylene carbonate, the PG catalysed by boiler ash showed lower yield than the previous reported work. Nonetheless, their reaction operated at higher temperature (170 $^{o}$C and 180 $^{o}$C) which could contributed to relatively non cost effective process (Wang, D. et al., 2014; Qiu et al., 2012; Du et al., 2014). In addition, use of higher temperature more than 150 °C was not favoured due reported decomposition of urea into isocyanic acid (HCNO) (Lundström et al., 2011).

It is also worthy to note that there has been no available study reported on the use of potassium as active catalyst for the cyclisation of polyols with aid of urea apart from the current work. In industry, the synthesis of EC and PC is favoured using ethylene oxide and propylene oxide with carbon dioxide where by the reaction is conducted at very high temperatures (160-200 °C) and pressures (50-150 atm) as patented by Tsang, Ainsworth and Raines, (1985) as well as reported by Clements, 2003 from Huntsman corporation. Besides, Liteplo et al., (2003) reported in the World Health Organization (WHO), Geneva that ethylene oxide is hazardous and carcinogenic while (Institute for Health and Consumer Protection European Chemicals Bureau, 2002) reported that propylene oxide is also toxic and carcinogenic. Therefore, the current route is more economical and safe route for the synthesis of ethylene carbonate. In short, it can be concluded that synthesis of EC and PC has an accelerated route in second step using BA 900 similarly to synthesis of Gly C. Quantitative analysis was carried out using GC-FID for both ethylene carbonate and propylene carbonate (refer appendix C).

## 6.3 Analysis of Mechanistic Pathway of Ethylene Carbonate and Propylene Carbonate

One of the methods to monitor and propose the mechanistic pathway for the catalytic reaction is by performing the time online study. In this case, both catalytic synthesis of EC and PC using boiler ash as catalyst is carried out at prolong reaction time with time interval sampling. The obtained liquid product was then subjected to ATR-FTIR analysis and validated by $^{13}$C NMR and GC-MS analysis.

### 6.3.1 ATR-FTIR of Time Online Analysis of Ethylene and Propylene Carbonate

The mechanistic pathway for both ethylene carbonate and propylene carbonate through respective carbamate intermediate was confirmed via time online study (TOL) monitored by ATR-FTIR (Figure 6.3 and 6.4). Both analysis showed the presence C=O group of 2-hydroxyethyl carbamate and 2-hydroxypropyl carbamate at around 1715 cm$^{-1}$ which later cyclised into their respective carbonates. As duration of reaction was prolonged the intermediate carbamate peak deformed as increase in EC and PC was observed. Besides, there were also no sign N-C-O stretching of isocyanic acid peak observation at 2210 cm$^{-1}$ indicating the reaction solely dependent on carbamate as intermediate compound. The decomposition of urea from 0 h to 10 h is visible from being consumed in the reaction where the peak for urea labelled in Figure 6.3 and Figure 6.4 which gradually deforms and disappears. Based on Figure 6.3, the band at 1801 cm$^{-1}$and 1788 cm$^{-1}$ indicate the symmetrical C=O stretching of EC (Zhao, Zhang, & Wang, 2004). The ring stretching peak of EC and PC were visible as duration or reaction increased and was present at range of (770-785 cm$^{-1}$). In case of TOL of PC the methyl group was also observed to be formed at 1352 cm$^{-1}$ and 1380 cm$^{-1}$.

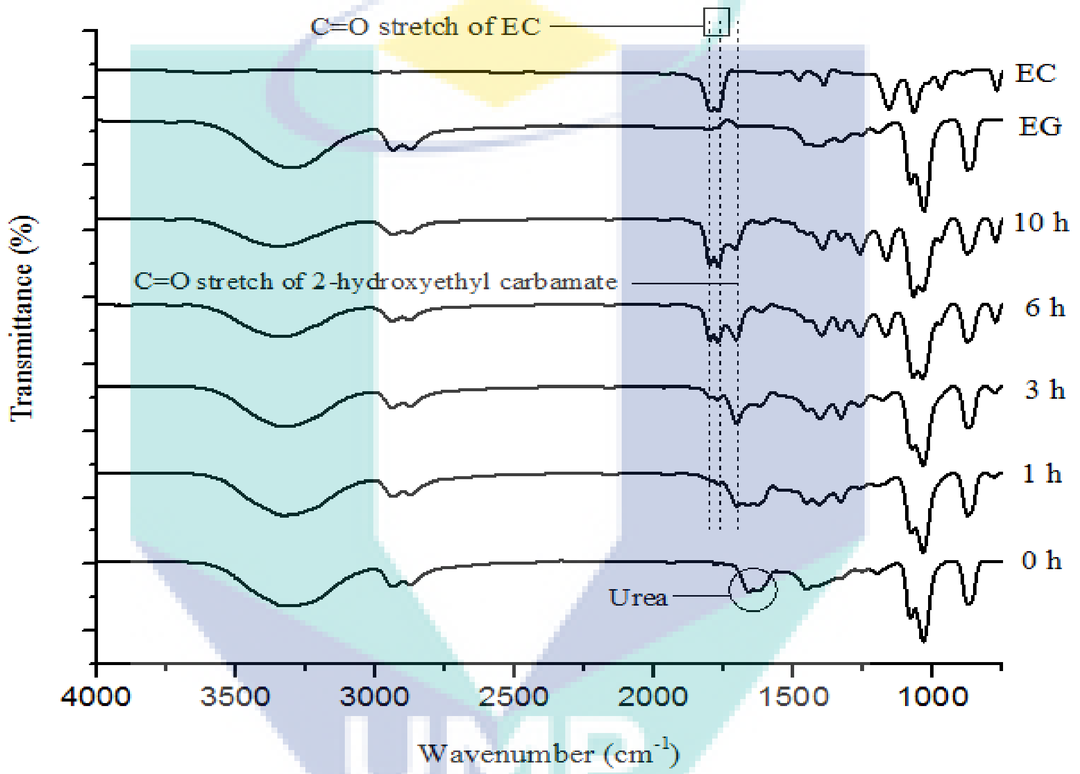


*Figure 6.3.* ATR-FTIR of time online analysis of ethylene carbonate.

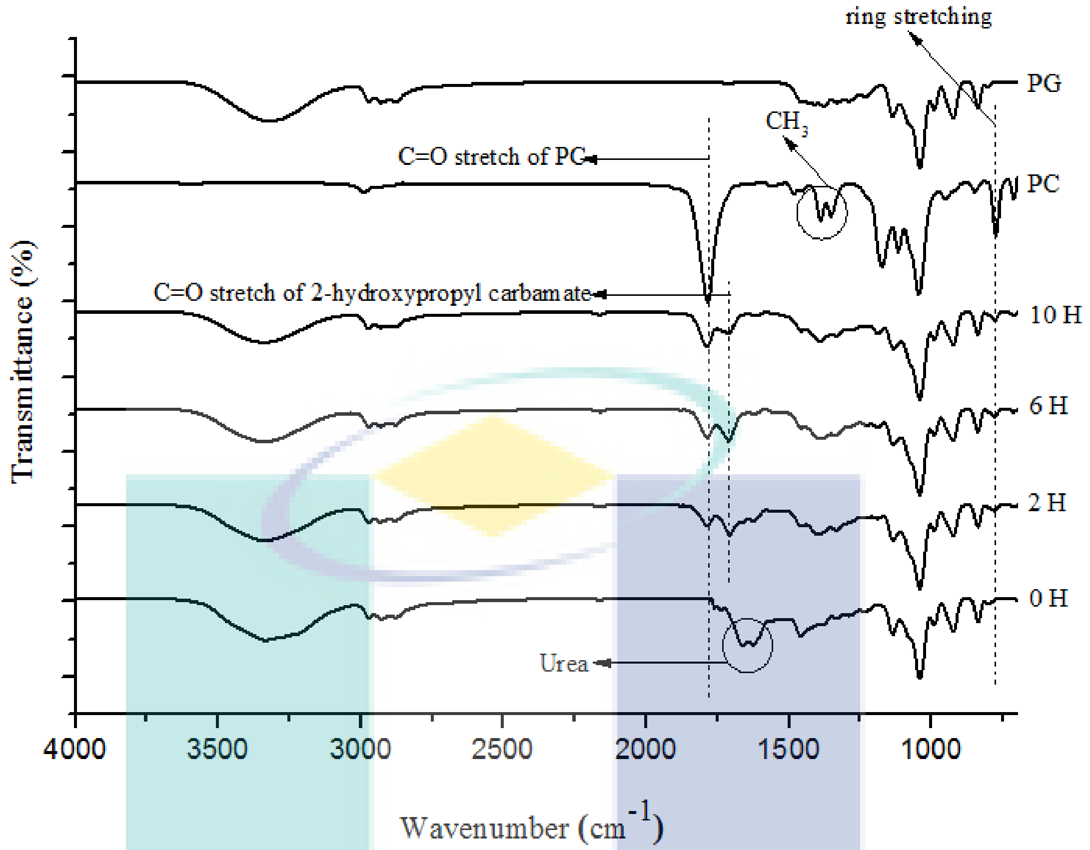
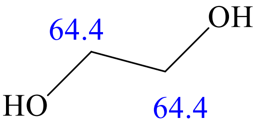


*Figure 6.4.* ATR-FTIR of time online analysis of propylene carbonate.

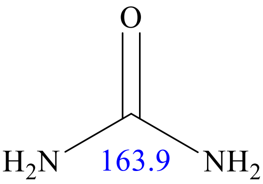
### 6.3.2 $^{13}$C NMR of Time Online Analysis of Ethylene Carbonate and Propylene Carbonate

Figure 6.5 and 6.7 illustrates the compound and their respective $^{13}$C NMR labelling of δ ppm. Ethylene glycol $^{13}$C NMR ($CD_3OD$, 125MHz) δ 64.4 (-$CH_2$-OH); Ethylene carbonate $^{13}$C NMR ($CD_3OD$, 125MHz) δ 158.1(C=O, carboxy), 66.7(-$CH_2$-O-); 2-hyoxyethyl carbamate $^{13}$C NMR ($CD_3OD$, 125MHz) δ 156.9 (C=O, amides) , 65.9 (-$CH_2$-O-), 59.7 (-$CH_2$-OH); oxazolidin-2-one $^{13}$C NMR ($CD_3OD$, 125MHz) δ 162.7 (C=O, amides), 66.4 (-$CH_2$-O-), 43.4 (-$CH_2$-N<); 3-(2-hydroxyethyl) oxazolidin-2-one $^{13}$C NMR ($CD_3OD$, 125MHz) δ 160.1 (C=O, amides), 65.5 (-$CH_2$-O-), 61.0 (-$CH_2$-OH), 55.8 (-$CH_2$-N<), 46.9 (-$CH_2$-N<); Urea $^{13}$C NMR ($CD_3OD$, 125MHz) δ 163.9 (C=O, amides); propylene glycol $^{13}$C NMR ($CD_3OD$, 125MHz) δ 69.3 (-$CH_2$-OH), 68.6 (>CH-OH), 19.9 (CH3-CH<, C primary); propylene carbonate $^{13}$C NMR ($CD_3OD$, 125MHz) δ 157.4 (C=O, carboxy), 75.7 (>CH-O-), 72.3 (-$CH_2$-O-), 19.6 (CH3-CH<, C primary); 2-hydroxypropyl carbamate $^{13}$C NMR ($CD_3OD$, 125MHz) δ 156.9 (C=O, amides), 70.7 (-

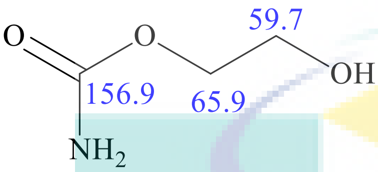
$CH_2$-O-), 66.4 (-CH-OH), 30.3 (CH3-CH<, C primary); 4-methyloxazolidin-2-one $^{13}C$ NMR ($CD_3OD$, 125MHz) δ 159.0 (C=O, amides), 73.7 (>CH-N<), 66.9 (-$CH_2$-O-), 21.1 ($CH_3$-CH<, C primary); 3-methyloxazolidin-2-one $^{13}C$ NMR ($CD_3OD$, 125MHz) δ 158.9 (C=O, amides), 61.8 (-$CH_2$-O-), 46.8 (-CH2-N<), 30.8 (CH3-N<). The time online analysis using $^{13}C$ NMR (figure 6.6 and 6.8) was carried out for both syntheses of EC and PC from 0 to 10 h. From the analysis the peak of urea at δ ppm 163.9 in both EC and PC synthesis gradually declined from 0 h to 10 h indicating urea being consumed in the reaction. Presence of intermediate carbamate of both EC and PC synthesis were also detected which supports the reaction mechanistic pathway of EC and PC proposed which occurs through decomposition of the intermediate carbamate in the second step. The compounds present in syntheses of ethylene carbonate and propylene carbonate using reaction conditions as listed in Table 6.1 and BA 900 as catalyst were also validated by GC-MS (refer appendix C).



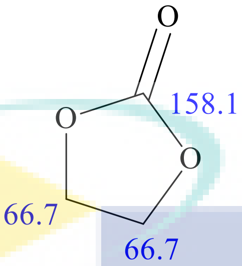
ethylene glycol
(Compound 7)



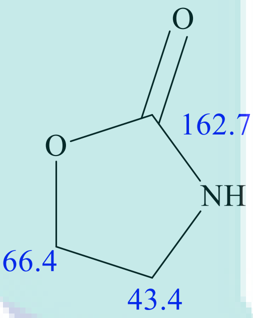
urea
(Compound 2)



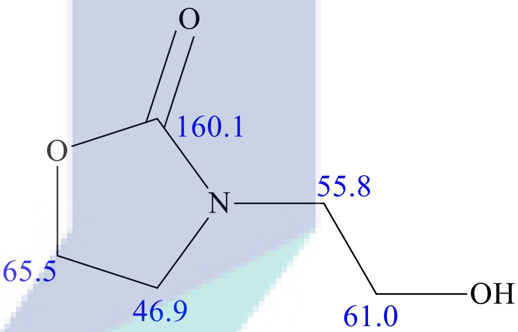
2-hydroxyethyl carbamate
(Compound 9)



ethylene carbonate
(Compound 8)



oxazolidin-2-one
(Compound 10)



3-(2-hydroxyethyl)oxazolidin-2-one
(Compound 11)

*Figure 6.5.* $^{13}$C NMR of reactants, intermediate and products labelled in ppm for ethylene carbonate synthesis.

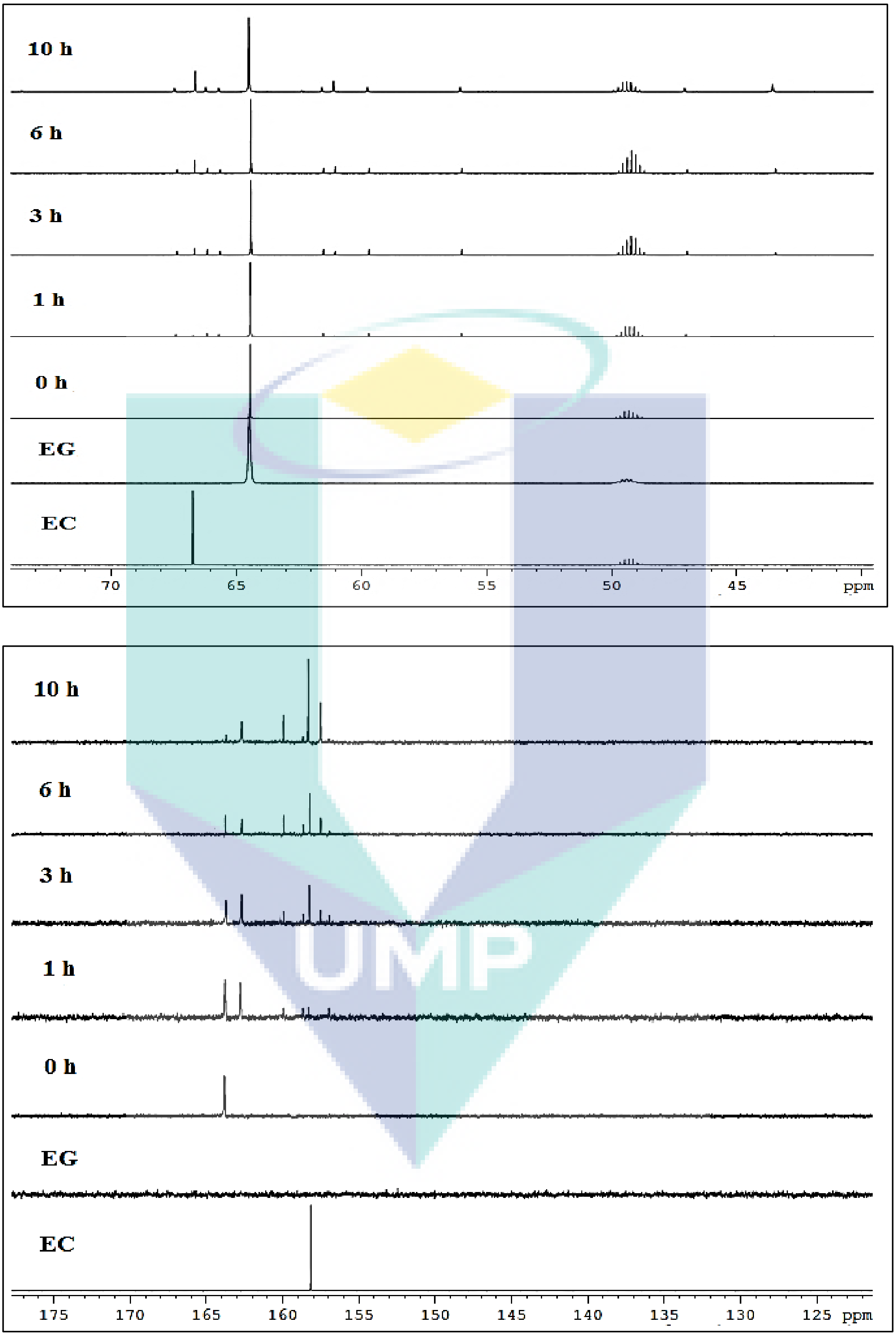
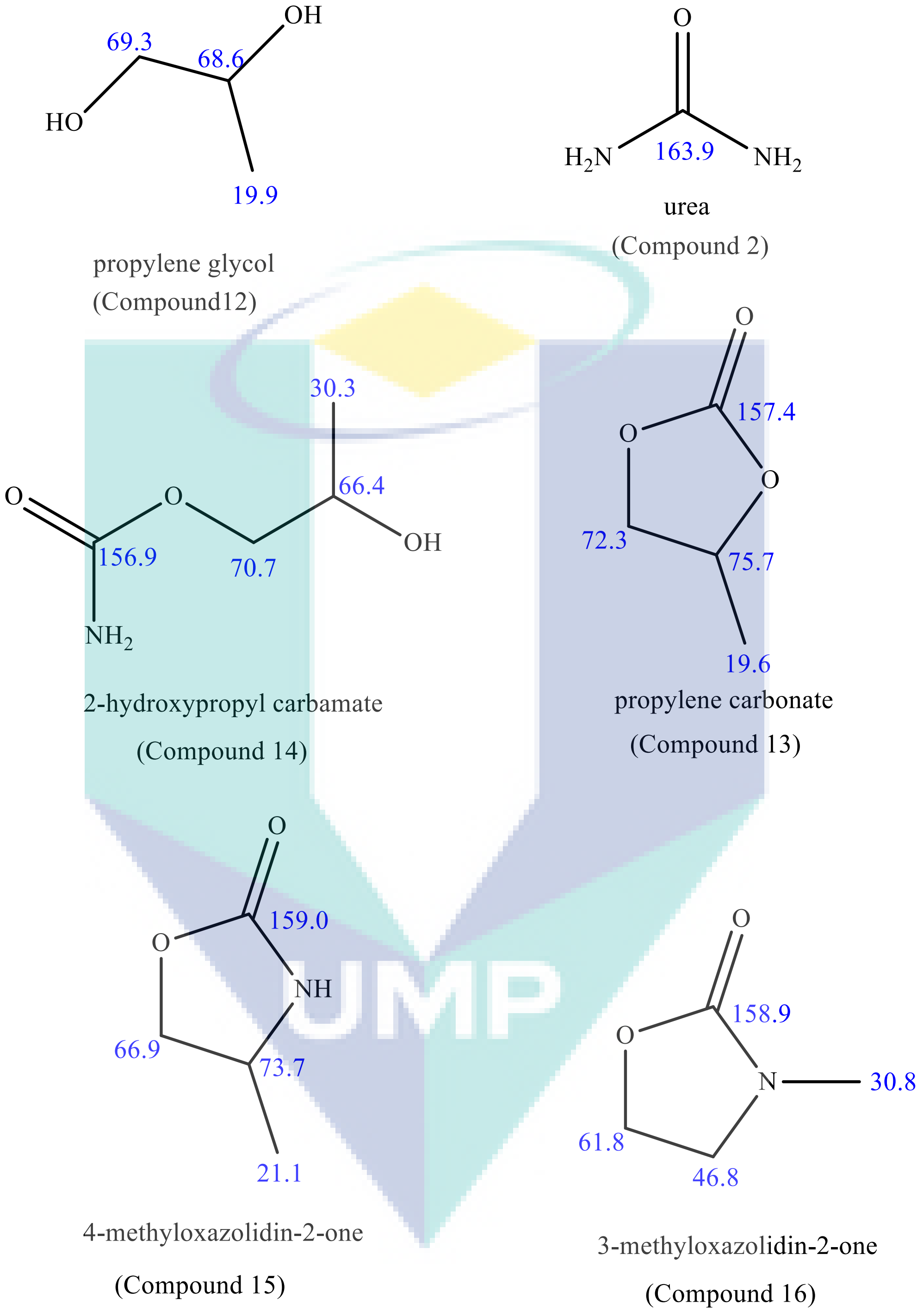


*Figure 6.6.* $^{13}$C NMR overlay of time online analysis of ethylene carbonate synthesis using ethylene glycol and urea.



propylene glycol (Compound12)

urea (Compound 2)

2-hydroxypropyl carbamate (Compound 14)

propylene carbonate (Compound 13)

4-methyloxazolidin-2-one (Compound 15)

3-methyloxazolidin-2-one (Compound 16)

*Figure 6.7.* $^{13}$C NMR of reactants, intermediate and products labelled in ppm for propylene carbonate synthesis.

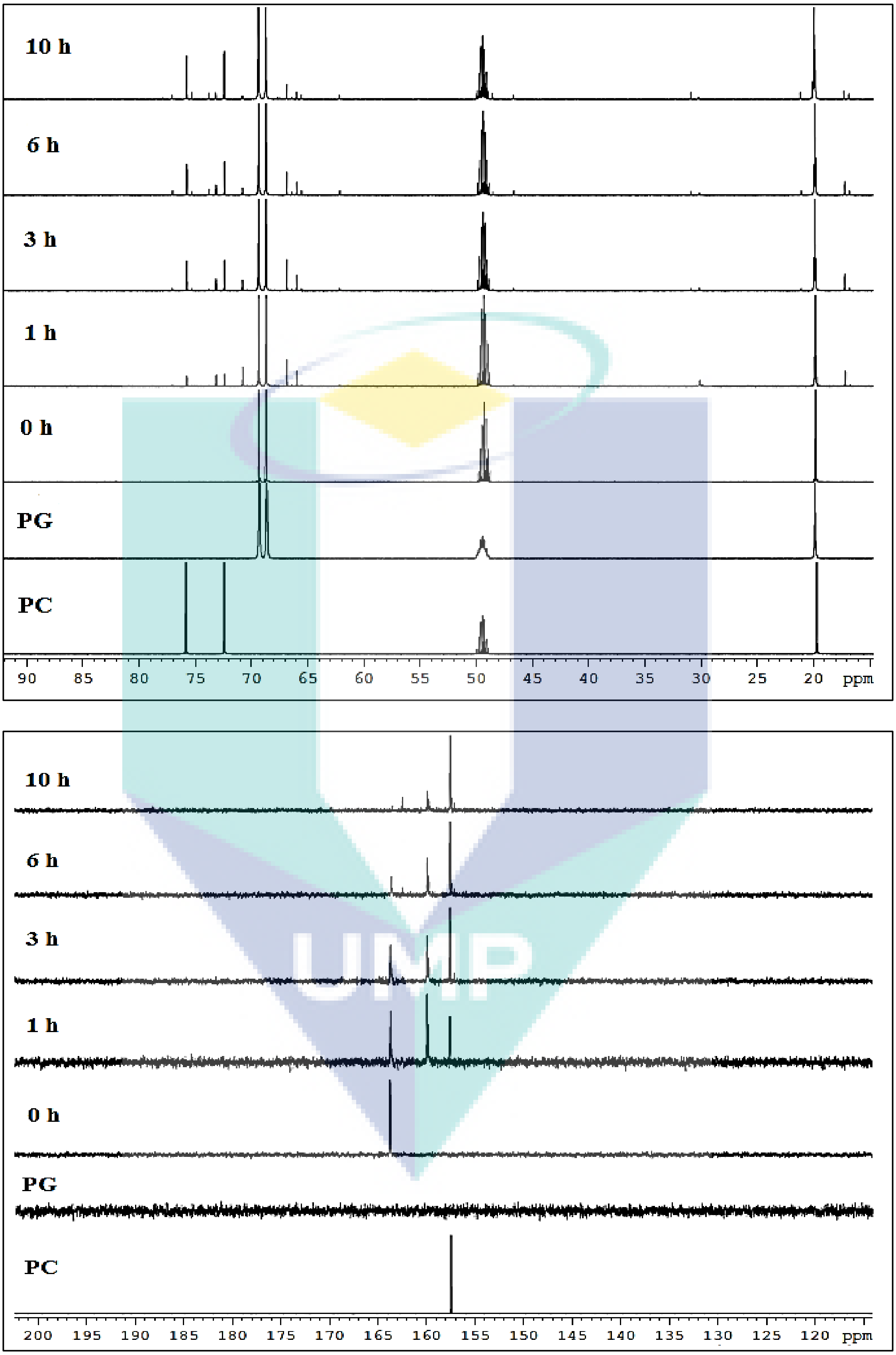
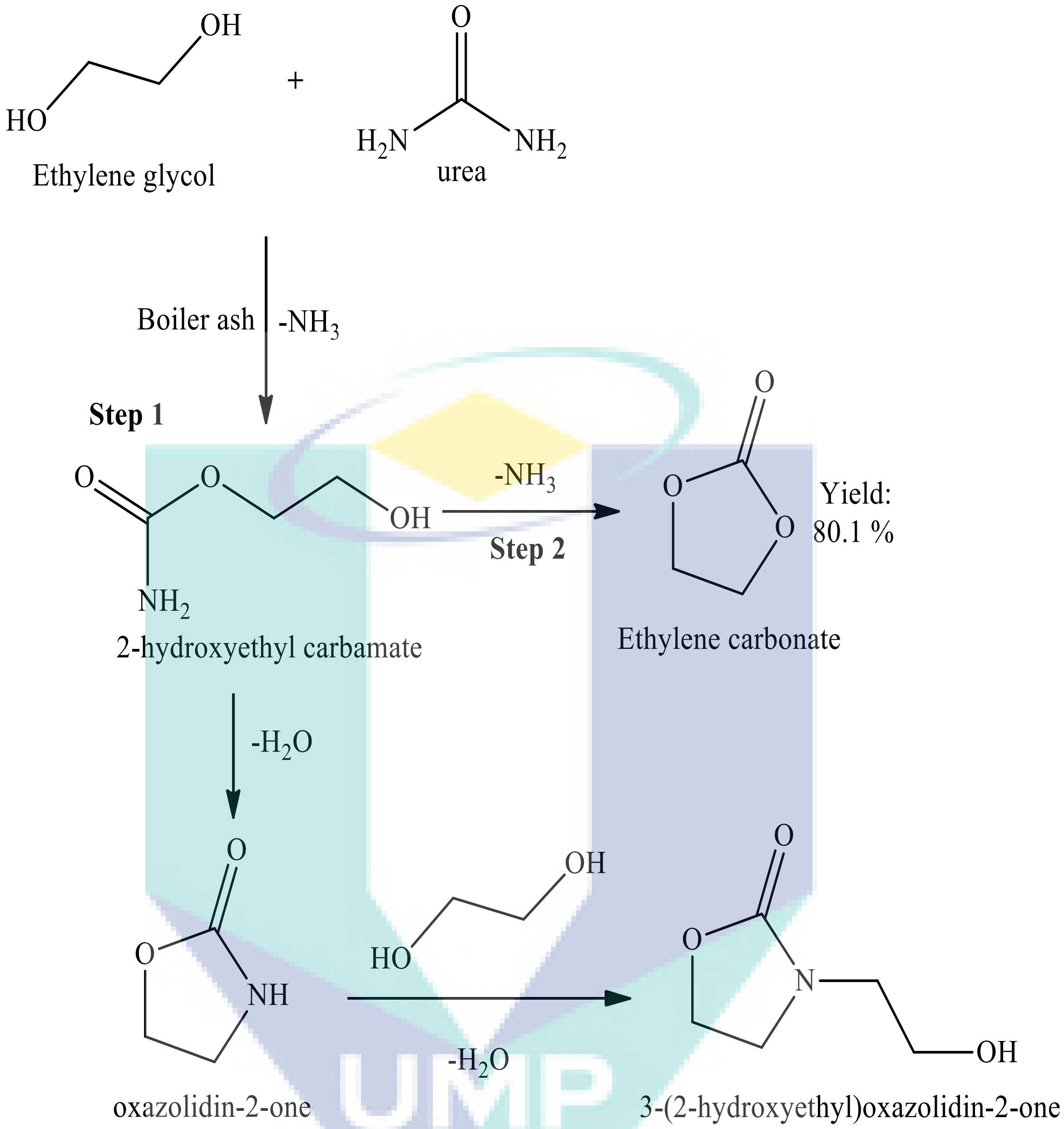


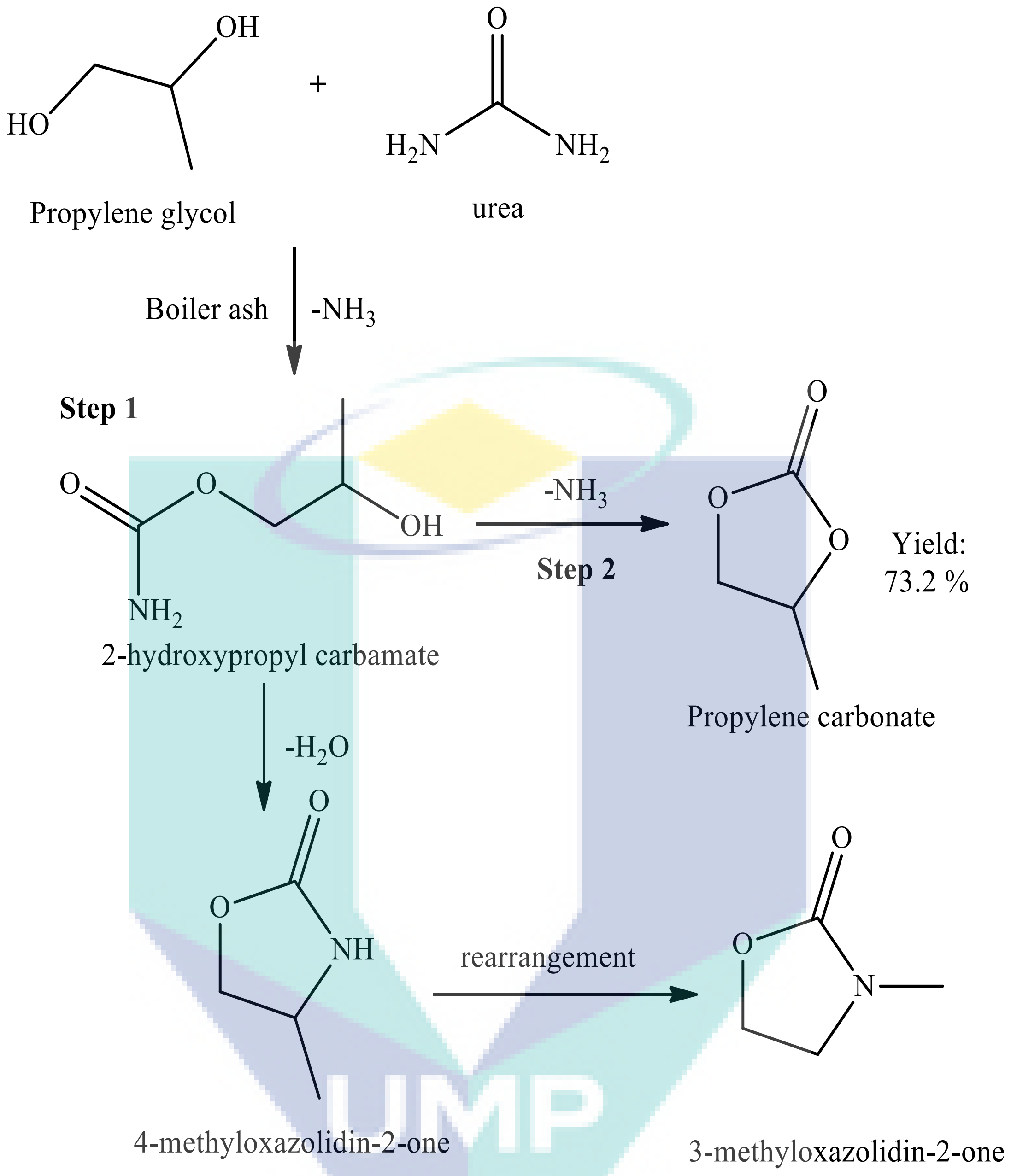
*Figure 6.8.* $^{13}$C NMR overlay of time online analysis of propylene carbonate synthesis using propylene glycol and urea.

### 6.3.3 Propose Mechanistic Pathway of Ethylene Carbonate and Propylene Carbonate

Based on TOL analysis conducted using ATR-FTIR and $^{13}$C NMR, the mechanistic pathway for both EC and PC corresponds to the similar pathway of observed for glycerol carbonate, where the formation of glycerol carbonate originated through selective transformation of respective carbamate intermediate. Even though similar route was observed in related literature (Bhanage et al., 2003; Wang, D. et al., 2014), a slight difference was perceived with boiler ash as catalyst, whereby the conversion of carbamate into respective carbonate occurred in an accelerated manner. However, some of the by-products detected in prior-art experiments were not detected in this study such as biuret also known as carbamylurea (Zhao et al., 2008). Bhanage, and co-workers in 2003 as well as Zhao et al., 2008 reported similar finding on the reaction pathway which involved decomposition of intermediate carbamate into EC. On the other hand, D. Wang et al., (2014) proposed the formation of propylene carbonate was due decomposition of intermediate carbamate, 2-hydroxypropyl carbamate which was similar to the current findings. However, Wang, D. and co-workers also reported presence of isocyanic acid which later forms the intermediate compound. This scenario is expected since the reaction was carried out at temperature higher than 150 °C, thus increase the possibility of urea to decompose into isocyanic acid. The cyclisation pathway of ethylene glycol and propylene glycol along with their by-products formation using boiler ash as catalyst is proposed in Scheme 5 and Scheme 6, respectively.

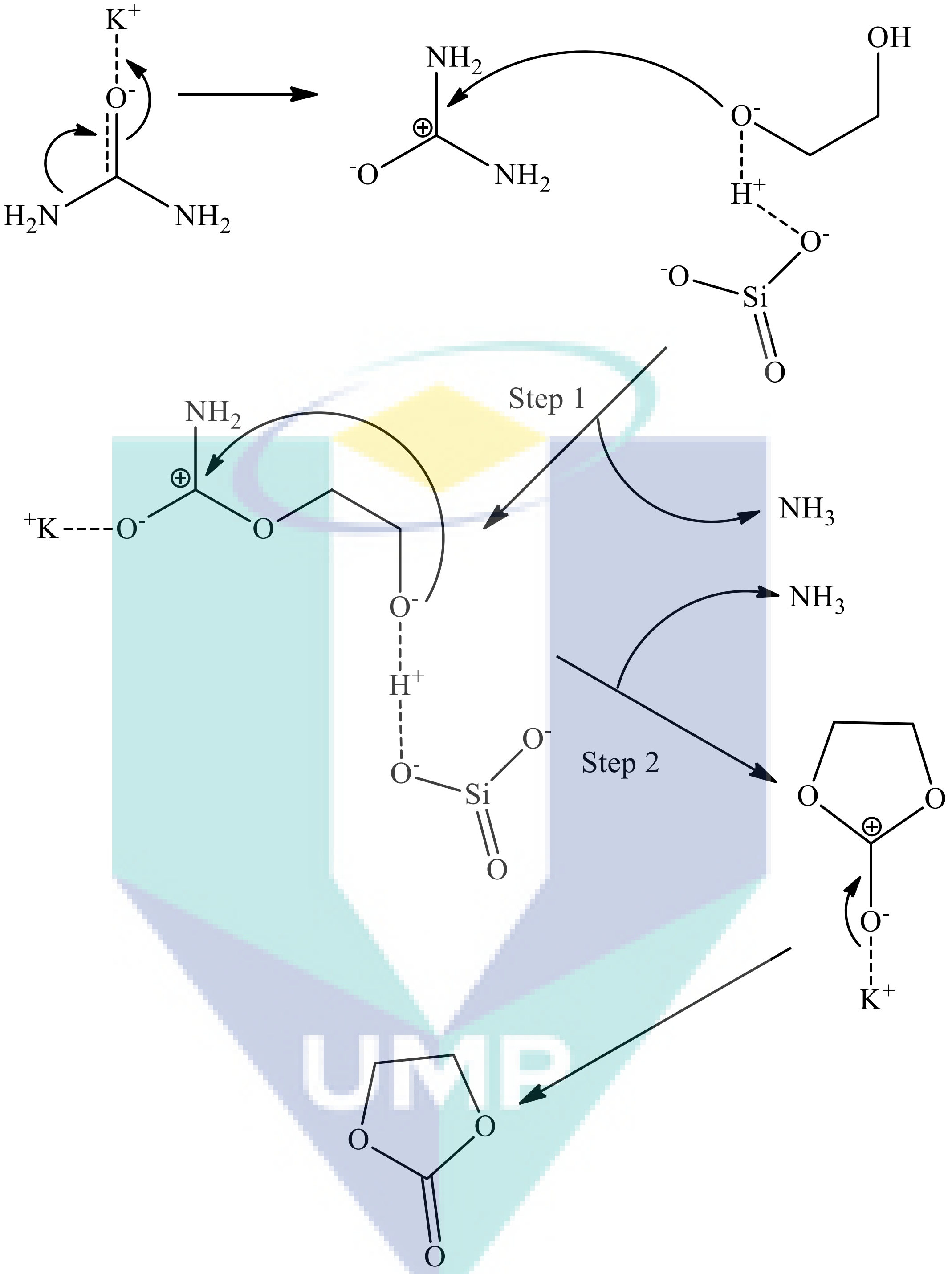


Scheme 5. Mechanistic pathway of ethylene carbonate.

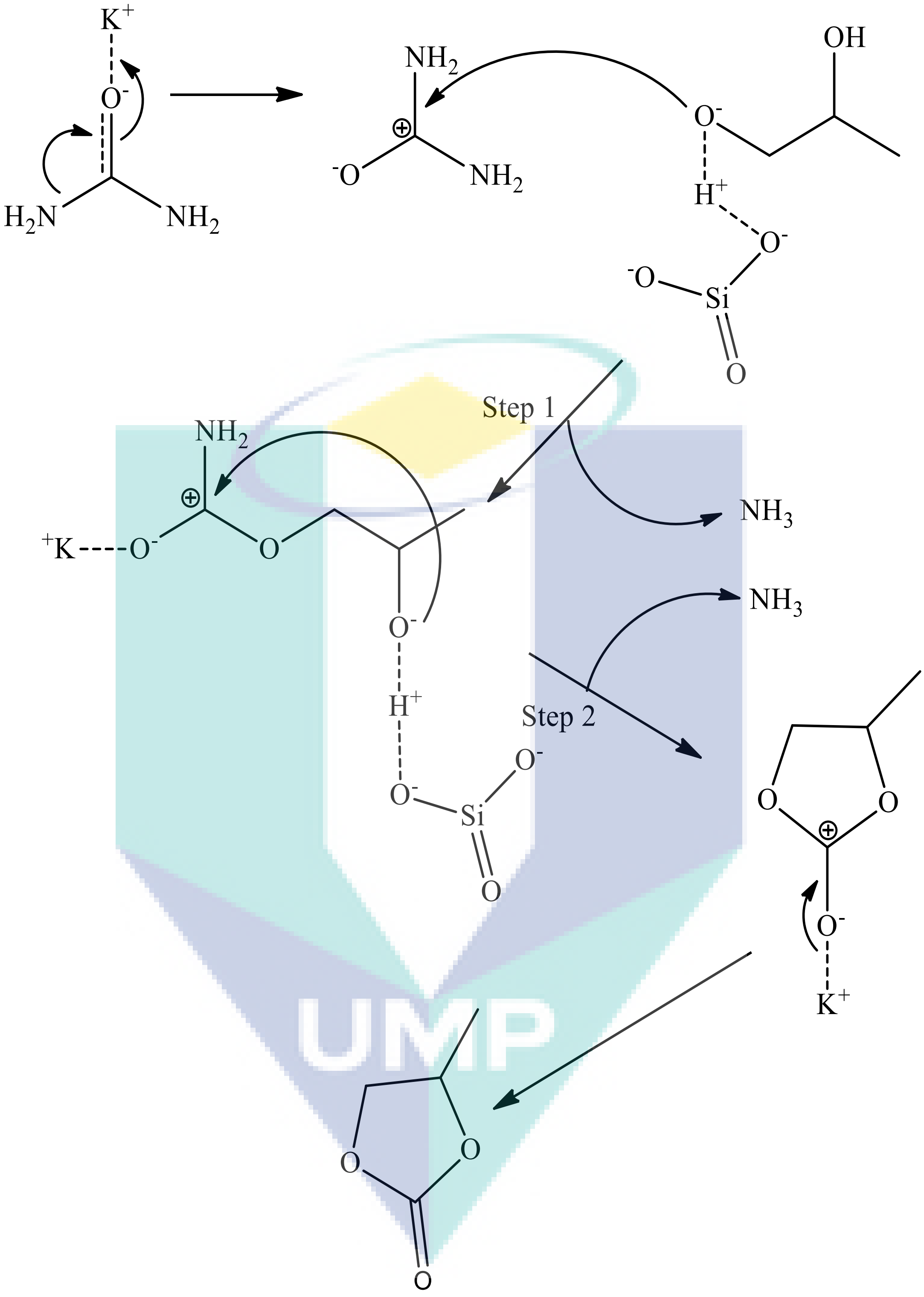


Scheme 6. Mechanistic pathway of propylene carbonate.

On the other hand, Scheme 7 and 8 illustrates the catalytic mechanism of $K_2SiO_3$ contained in boiler ash in synthesis of ethylene carbonate and propylene carbonate respectively. Similarly, the catalytic mechanism of ethylene carbonate and propylene corresponds to the catalytic mechanism of glycerol carbonate. The potassium ion activates urea to form an electrophile in both EC and PC synthesis. In step 1, the nucleophilic attack of hydroxyl group towards the electrophilic carbonyl of urea forms the carbamate intermediate while releasing ammonia gas. In the step 2, the hydroxyl group of the carbamate intermediate of EC and PC synthesis reacts with conjugate basic site $SiO_3^{2-}$ to form the respective carbonates. Again, the cyclisation is completed by the loss of more ammonia gas, followed by ring formation and rearrangement of the carbonyl double bond to form EC and PC.



Scheme 7. Catalytic mechanism of $K_2SiO_3$ contained in boiler ash towards synthesis of ethylene carbonate.



Scheme 8. Catalytic mechanism of $K_2SiO_3$ contained in boiler ash towards synthesis of propylene carbonate.

## 6.4 Summary

In short, it can be concluded that boiler ash can be used as a feasible catalyst in synthesis of ethylene carbonate and propylene carbonate. In this chapter, the analysis of the mechanistic pathway correlates to the previous finding of glycerol carbonate synthesis elaborated in chapter 4. It is also found that the mechanistic activity of boiler ash is comparably similar in all three carbonates synthesised which involve decomposition of intermediate carbamates into their respective carbonates. Maximum yield of ethylene carbonate and propylene carbonates achieved were 80.1 % as well as 73.2 % respectively.

# CHAPTER 7

# CONCLUSION AND RECOMMENDATIONS

## 7.1 Introduction

This chapter is an elaboration of the overall summary of important findings from chapter 4, 5 and 6. This chapter is divided into to two sections which include conclusions, followed by limitations and recommendations of the study.

## 7.2 Conclusions

In general, the study was set out to explore the use of considered waste materials as a cost effective catalyst for the synthesis of glycerol carbonate using bio-renewable feedstock of glycerol. Currently there is a rampant increase in the numbers of biodiesel industry growing yearly which generates huge amount of glycerol as by-product. Hence, significantly the market of glycerol is under risk due to increase in production than demand. Besides, in 2013 the price of crude glycerol significantly dropped as a result of the growing industry of biodiesel. However, since the current regulation worldwide required the petroleum diesel to mix with biodiesel up to certain percent, the production of biodiesel is expected to be stabilised. Besides, the biodiesel industrial survey report from Malaysia Annual Biofuel 2014 reports that 7 % of biodiesel from palm oil is mixed in all petroleum based diesel and 10 % biodiesel is mixed starting 2015. Thus, the biodiesel industry in Malaysia is expected to grow. In order to overcome this problem, researchers have paved pathways by turning them into value added chemicals such as glycerol carbonate which has extensive applications. However, none of the previous research suggested use of waste as a catalyst. Therefore, this research was aimed at proposing a suitable catalyst derived from waste boiler ash from local palm oil industry as a measure to meet the current scenario.

In short, this problem was met through in chapter 4 whereby boiler ash introduced as a new catalyst from waste source for the first time in synthesis of glycerol carbonate. It was also found that the catalytic behaviour of boiler ash was mainly influenced by potassium silicate ($K_2SiO_3$) contained in boiler ash. The most optimum reaction conditions were found to be at 4 h, 150 °C, stirring rate at 340 rpm, molar ratio of glycerol to urea at 1: 1.5 and catalyst loading at 0.25 g achieving glycerol conversion of 93.6 ± 0.4 %, selectivity of glycerol carbonate of 90.1 ± 1.0 % and yield of glycerol carbonate of 84.3 ± 1.1%. Boiler ash calcined at 900 °C (BA 900) under static air at environmental conditions showed maximum catalytic performance in term of selectivity and yield of glycerol carbonate. A slightly different reaction mechanism was found in this study whereby the selective transformation of glycerol carbamate as intermediate into glycerol carbonate occurred in an accelerated mechanistic manner. Moreover, interesting Lewis acidic property of potassium silicate in BA 900 was investigated and catalytic mechanism of boiler ash was proposed. It was found that boiler ash and potassium silicate is reusable up to 3 cycles with no loss of activity which suggests that both catalysts can be used to meet the industrial need to synthesise glycerol carbonate from bio-renewable glycerol. Boiler ash can be classified as pseudo-homogeneous catalyst due to it partial recoverability property. In short, chapter 4 meets the main aim of the research whereby boiler ash was successfully introduced as catalyst for glycerolysis reaction of glycerol with urea to produce glycerol carbonate.

Direct utilisation of crude glycerol without any prior pretreatment will benefit the overall process. Therefore, the second objective of the study is met by introducing waste boiler ash as catalyst in direct glycerolysis of crude glycerol with urea into glycerol carbonate. From the study it was evident that from the two different sources of glycerol, crude glycerol potassium methylate (Gly KM) showed higher yield and selectivity of glycerol carbonate compared to crude glycerol sodium methylate (Gly NaM).  Besides, this scenario was expected due to presence of potassium ion. To add on, analysis of the level of interference of moisture and methanol in the crude glycerol revealed that moisture affects the conversion of glycerol at maximum specification of 10 wt % while methanol affects the selectivity of glycerol carbonate at maximum specification of 5 wt %. However, crude Gly NaM and crude Gly KM had lower amount of moisture and methanol. Therefore, the yield of glycerol carbonate obtained was relatively higher than pure glycerol mimicked with 10 % moisture and 5 wt % methanol. Furthermore, both catalysts used in industry for biodiesel production showed comparable yield for glycerol carbonate synthesis mimicked with potassium methylate and sodium methylate respectively. Potassium methylate catalyst demonstrated higher yield and selectivity which again attributes to the Lewis acidic property of potassium.

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Additionally, there has been no reported study analysing the feasibility of the same catalyst used in synthesis of glycerol carbonate to synthesise other organic carbonates such as propylene carbonate and ethylene carbonate which has adverse applications in industries similar to glycerol carbonate. Therefore, the study later expanded into proving that the concept study is true for the synthesis of other organic carbonate using similar synthesis approach with different polyol sources and boiler ash containing potassium silicate as catalyst. The feasibility of boiler ash in synthesis of ethylene carbonate and propylene carbonate is well defined in this study. Similar to synthesis of glycerol carbonate the mechanistic pathway of ethylene carbonate and propylene carbonate also corresponded accordingly. Besides, the catalytic mechanism of potassium silicate in boiler ash for the synthesis of ethylene carbonate and propylene carbonate was also proposed to be similar.

In a nutshell, it can be concluded that boiler ash containing potassium silicate is a versatile catalyst for the synthesis of cyclic organic carbonates. The use of boiler ash in biodiesel industries to convert excess glycerol formed into glycerol carbonate can be an economical approach while also being an environmentally friendly approach that allows alternative and proper disposal of waste.

## 7.3 Recommendations

In an overall view, the objectives of this study have been clearly met. However there is always room for improvisation in any study. Based on the study it was found that potassium silicate plays an important role in the catalytic behaviour of boiler ash towards synthesis of organic carbonates. However, potassium silicate was not entirely recoverable due to leaching. Besides, in this study further purification of final product was not conducted due to availability of instrument and limitation of the scope of study. Therefore, following are the several recommendations to the industry and future researchers:-

i. Catalyst optimisation study to stabilise potassium silicate from leaching should be carried out to improve recovery of catalyst.

ii. Other than that, in industrial point of view, instead of boiler ash, other wastes which contains potassium ion dominantly can be used in biodiesel industries for conversion of glycerol by-product into glycerol carbonate as cheap and alternative source of catalyst which will reduce overall operational cost. This is because potassium in any form with its conjugated basic site in this study showed high yield and selectivity towards glycerol carbonate.

iii. Besides, product purification in industry can be done by using vacuum distillation unit for separation of final products from its by-products. This is because, the boiling points of all by-products reported in this study are clearly different from one to another, and thus it is easy to facilitate the separation process.

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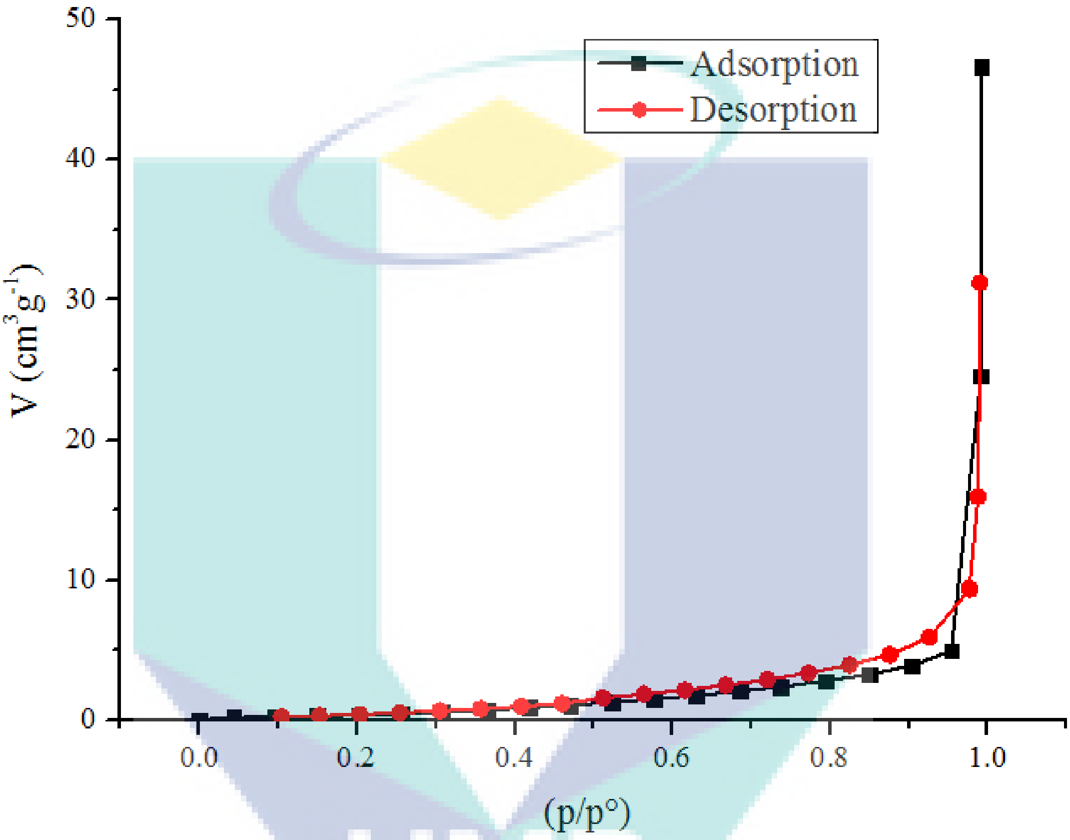
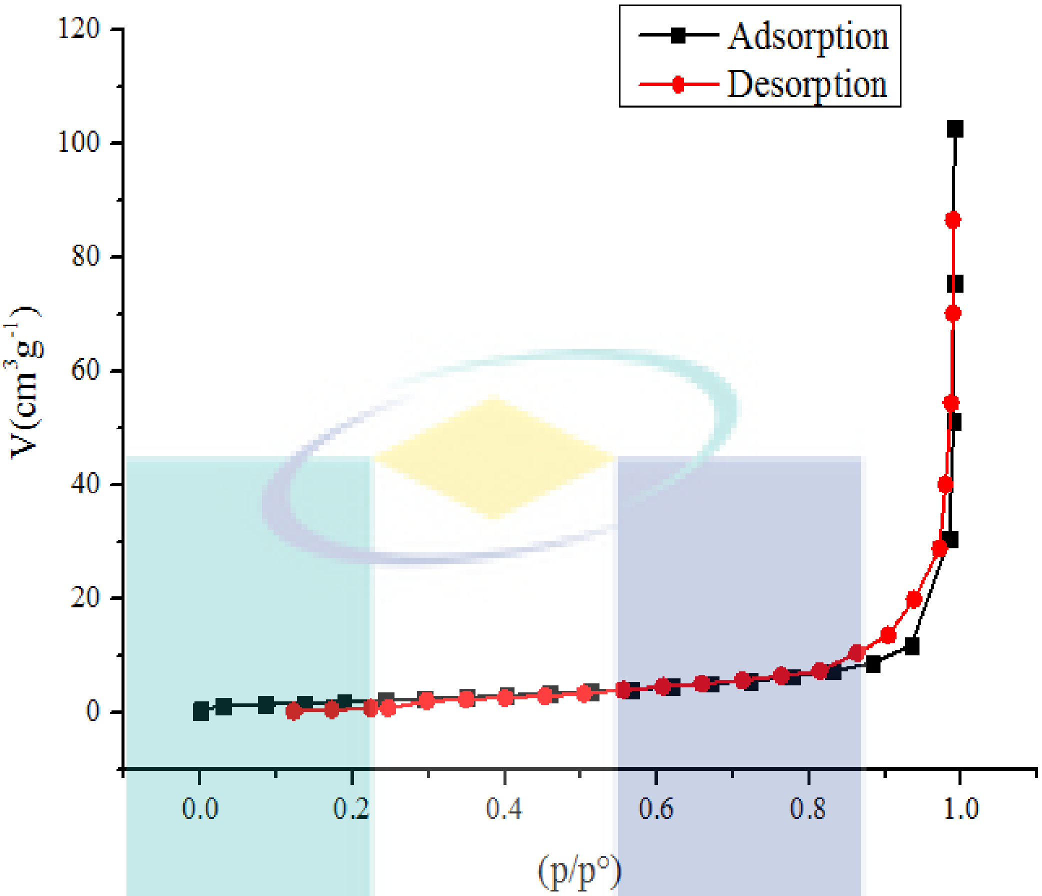
# APPENDICES

## APPENDIX A

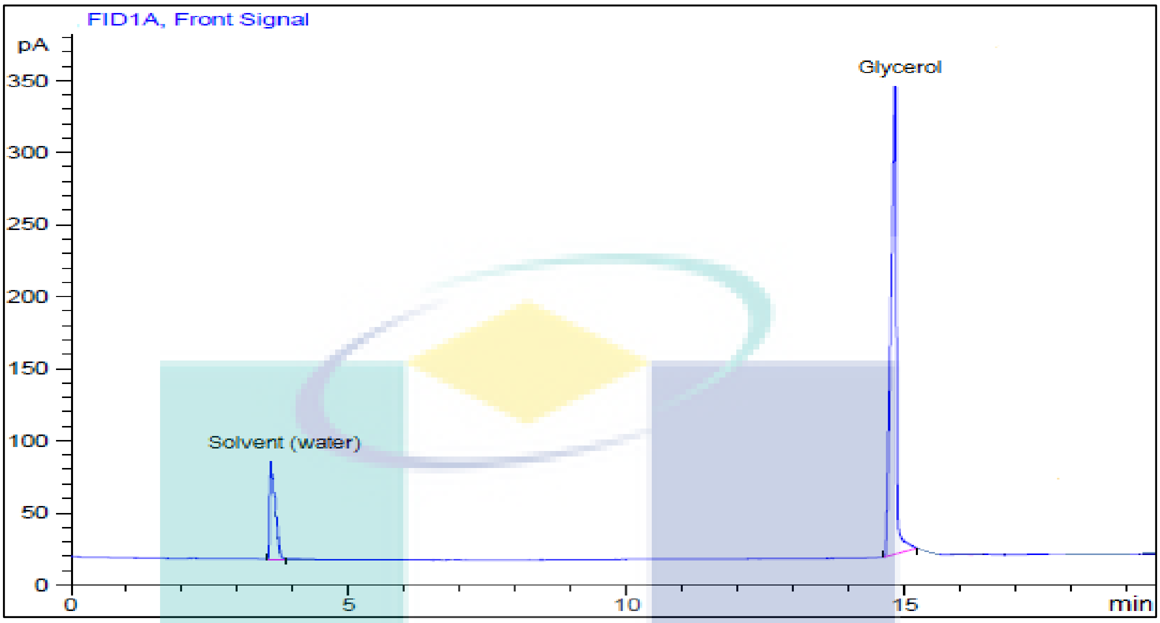


**Appendix A1:** BET Isotherm graph of BA 900.

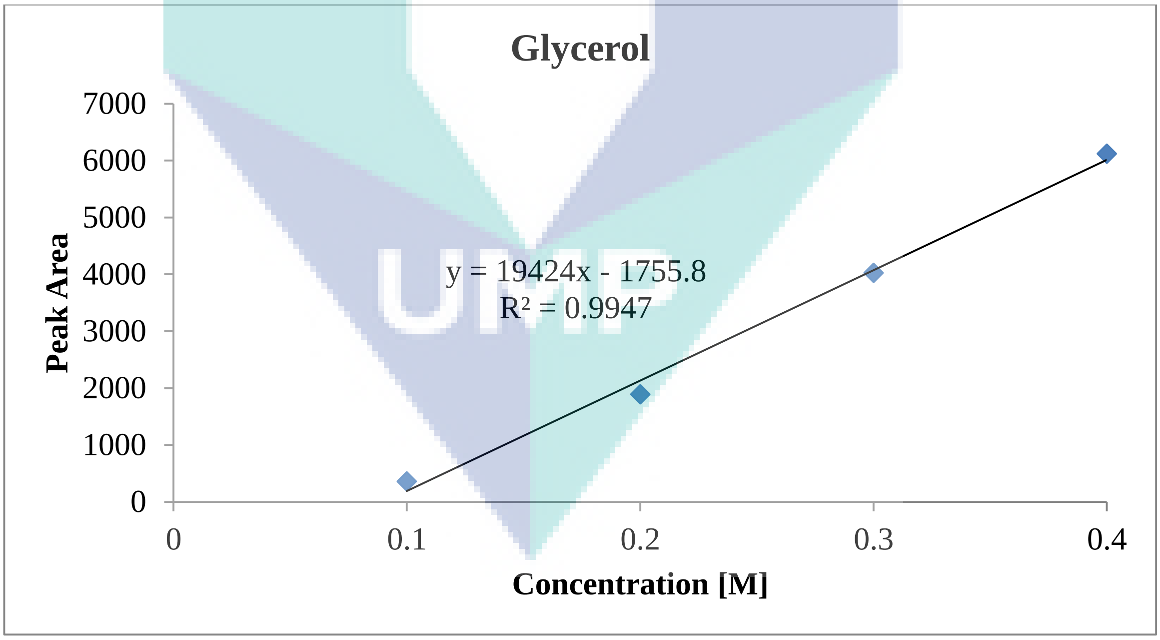


**Appendix A2:** BET Isotherm graph of BA 110.

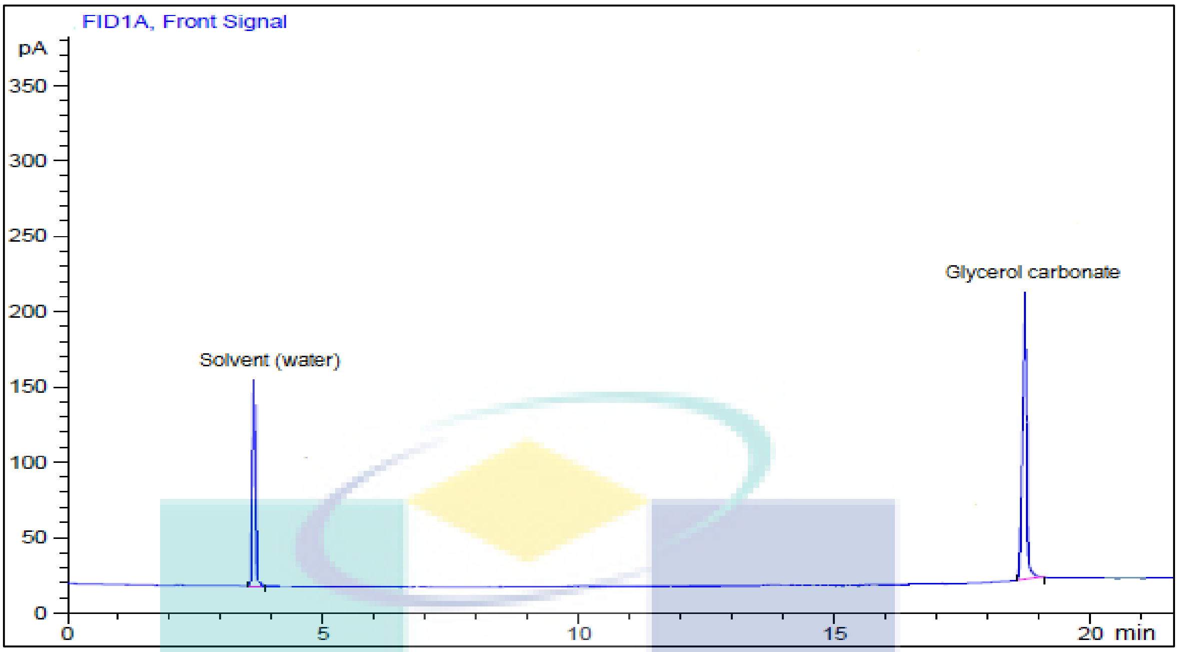
# APPENDIX B



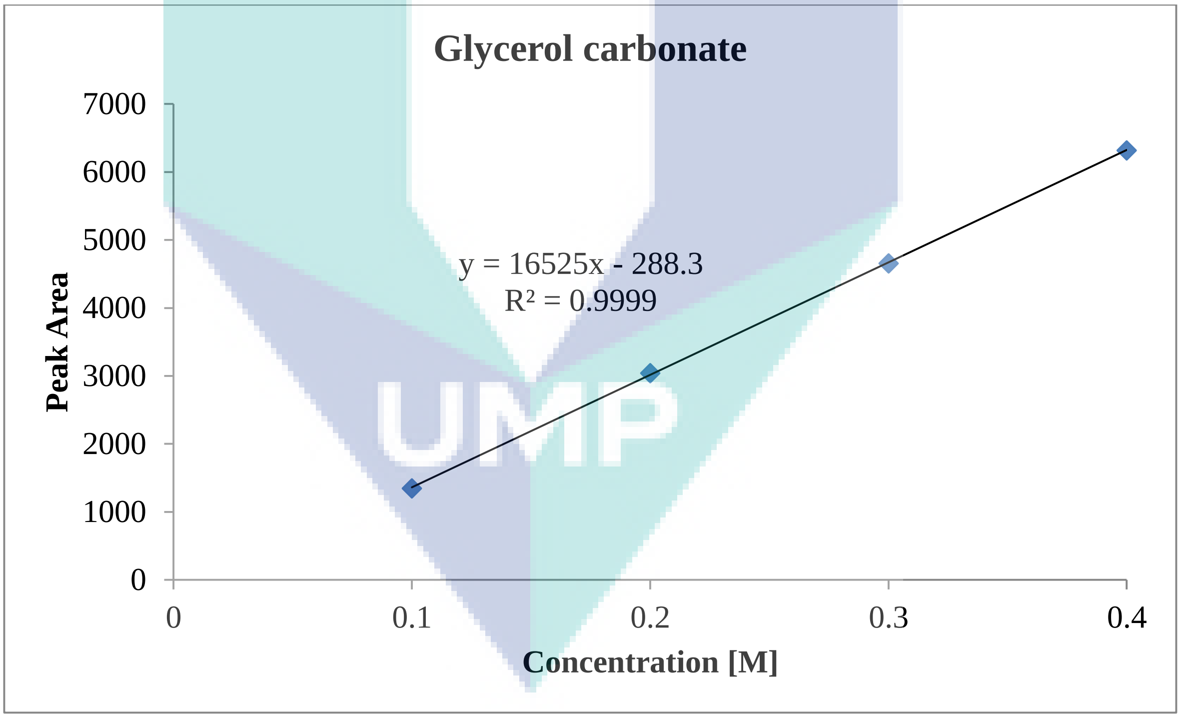
**Appendix B1**: GC-FID chromatogram of standard glycerol.



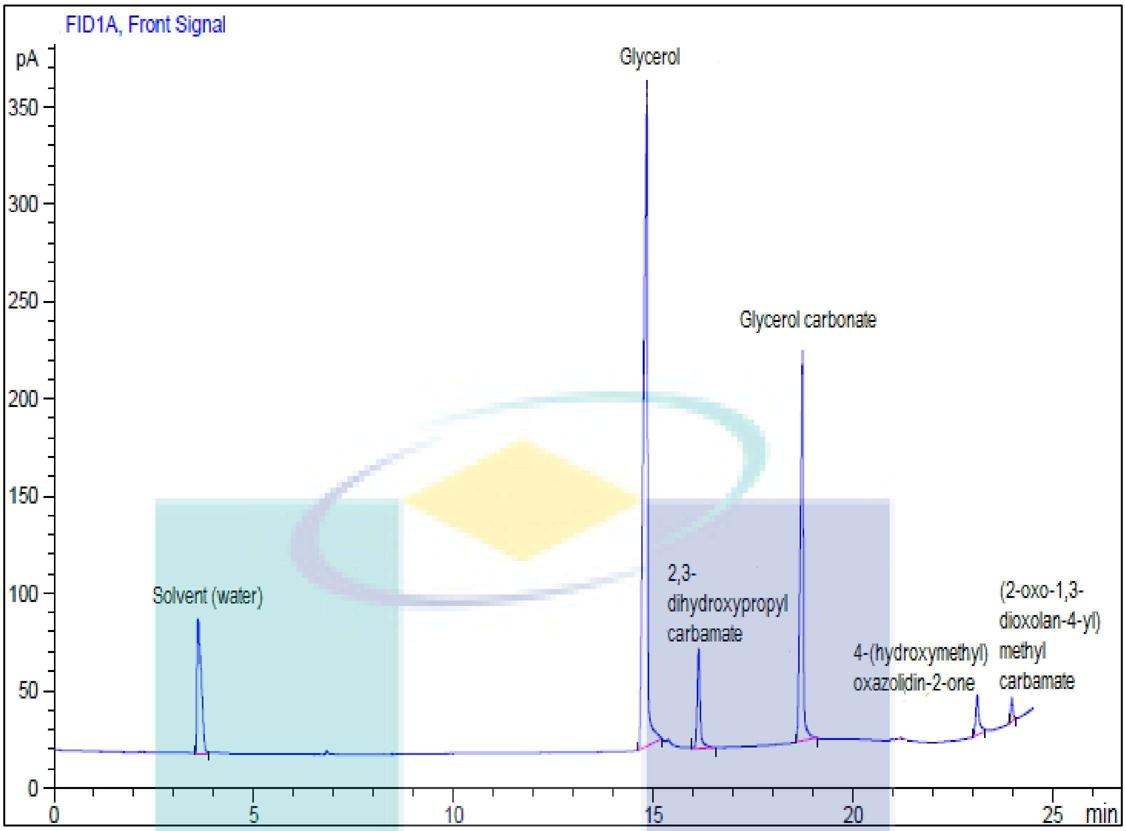
**Appendix B2**: Standard calibration curve of glycerol.



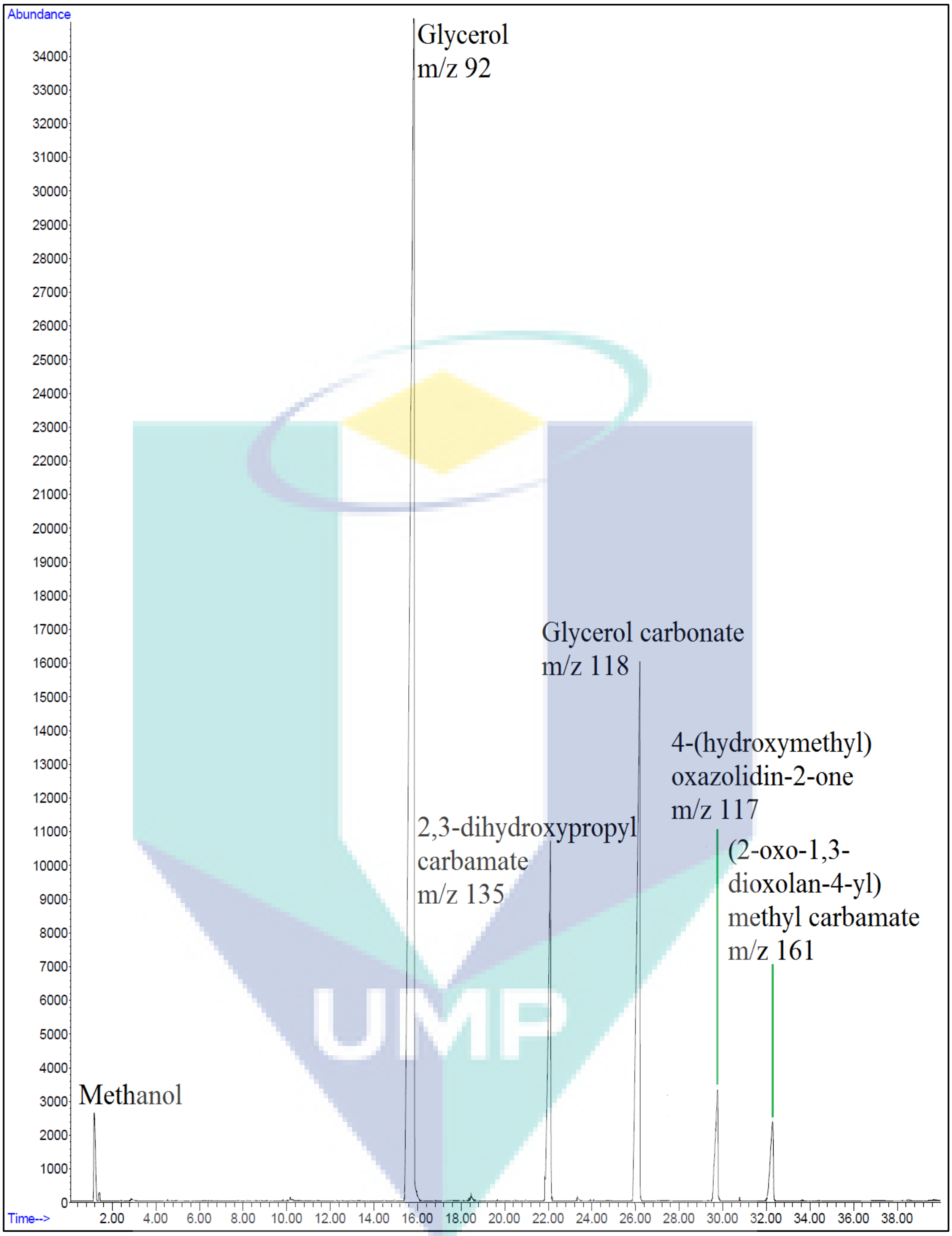
**Appendix B3**: GC-FID chromatogram of standard glycerol carbonate.



**Appendix B4**: Standard calibration curve of glycerol carbonate.

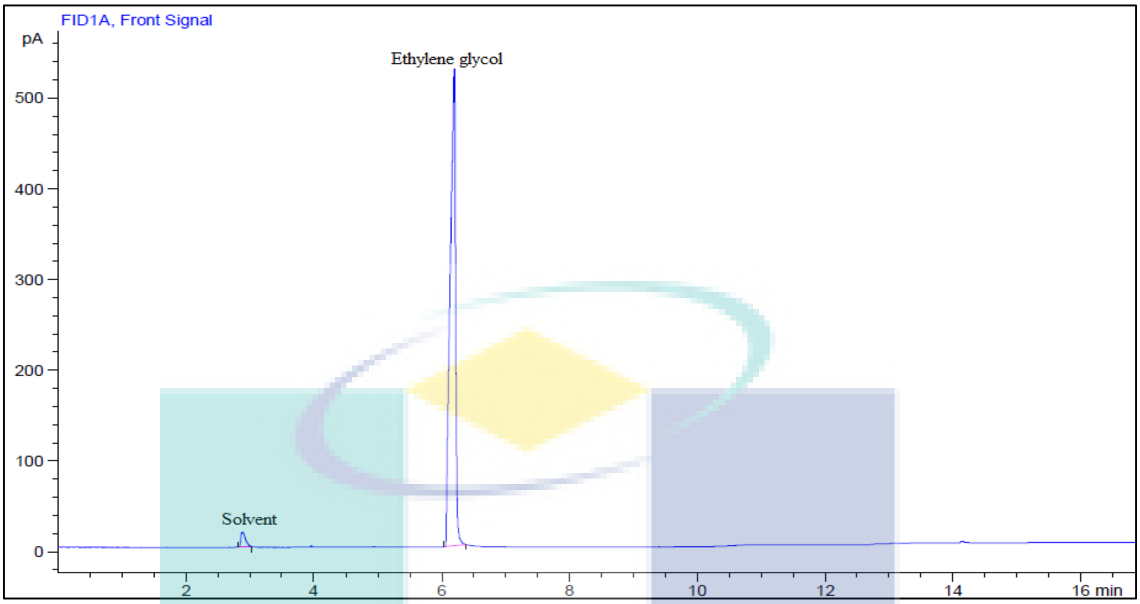


**Appendix B5:** GC-FID chromatogram of glycerol, glycerol carbonate, 2, 3-dihydroxypropyl carbamate, 4-(hydroxymethyl) oxazolidin-2-one and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate.

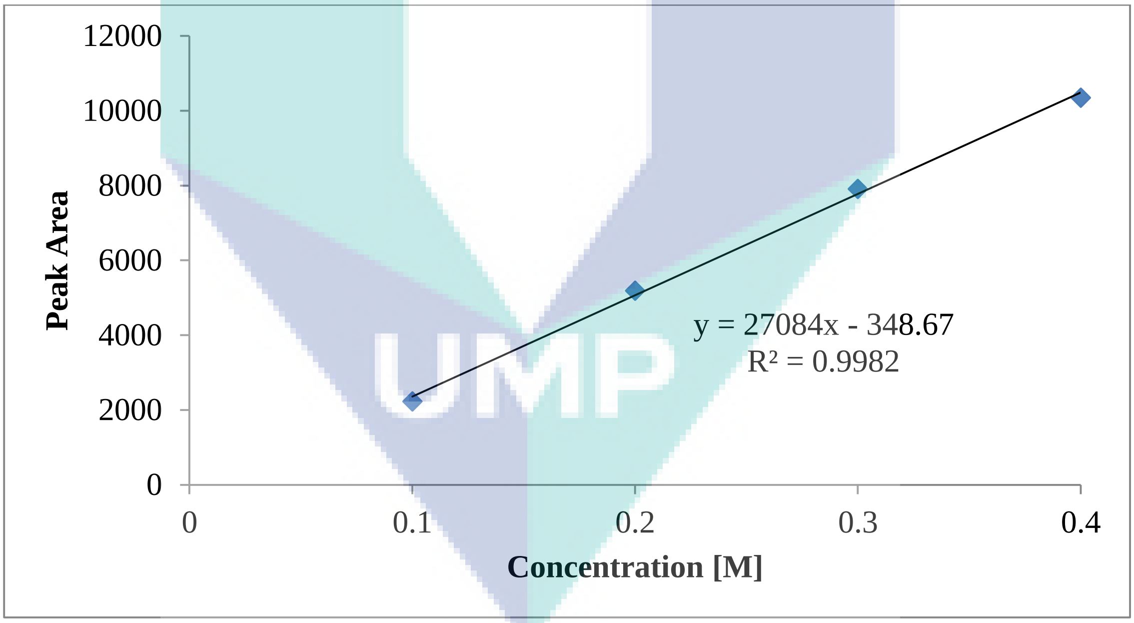


**Appendix B6:** GC-MS chromatogram of glycerol, glycerol carbonate, 2, 3-dihydroxypropyl carbamate, 4-(hydroxymethyl) oxazolidin-2-one and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate

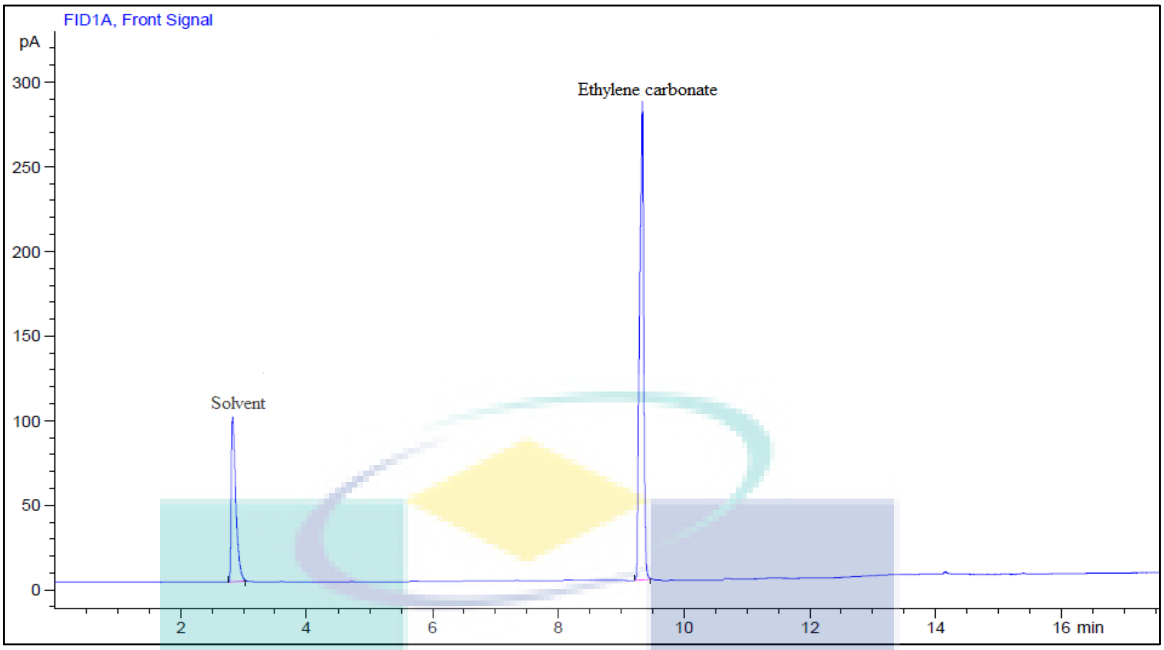
# APPENDIX C



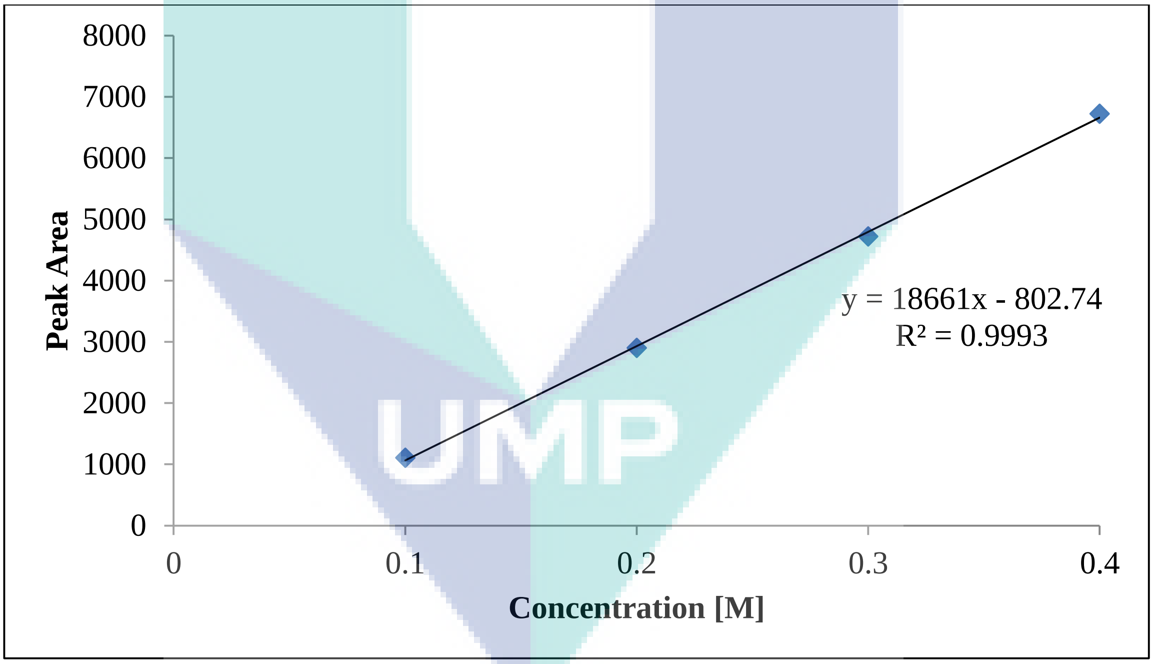
**Appendix C1:** GC-FID chromatogram of ethylene glycol.



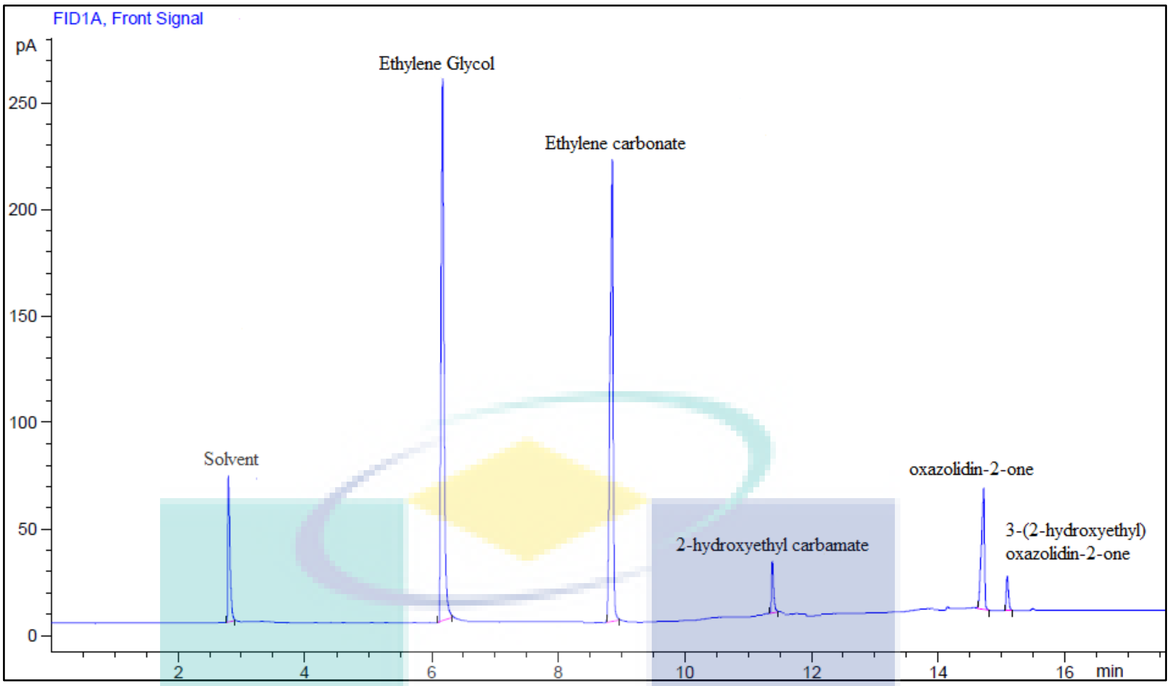
**Appendix C2:** Standard calibration curve of ethylene glycol.



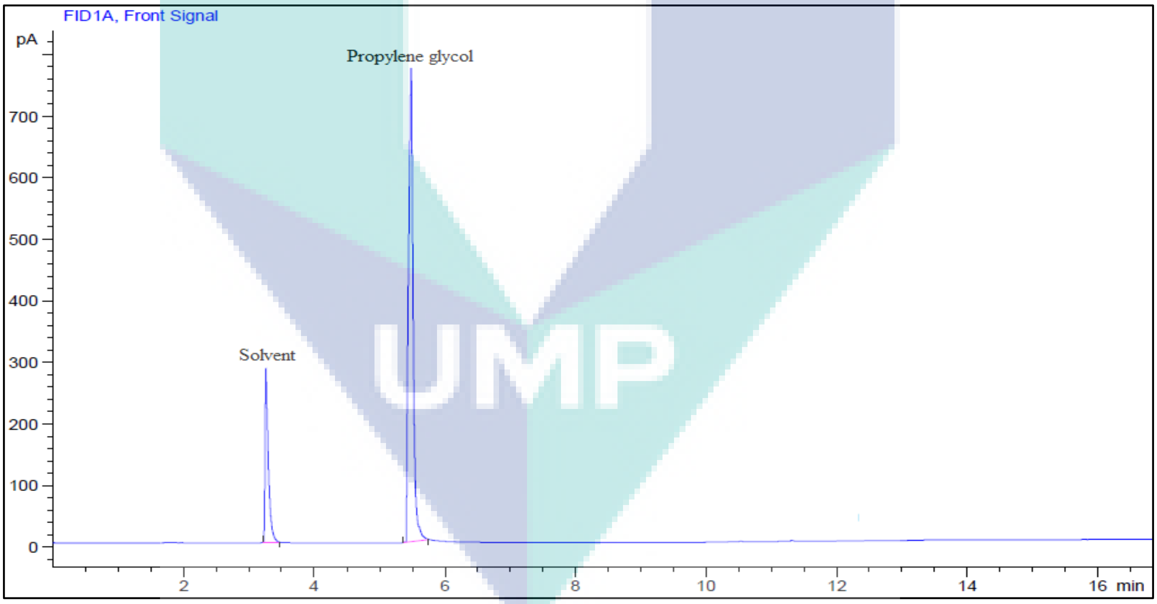
**Appendix C3:** GC-FID chromatogram of ethylene carbonate.



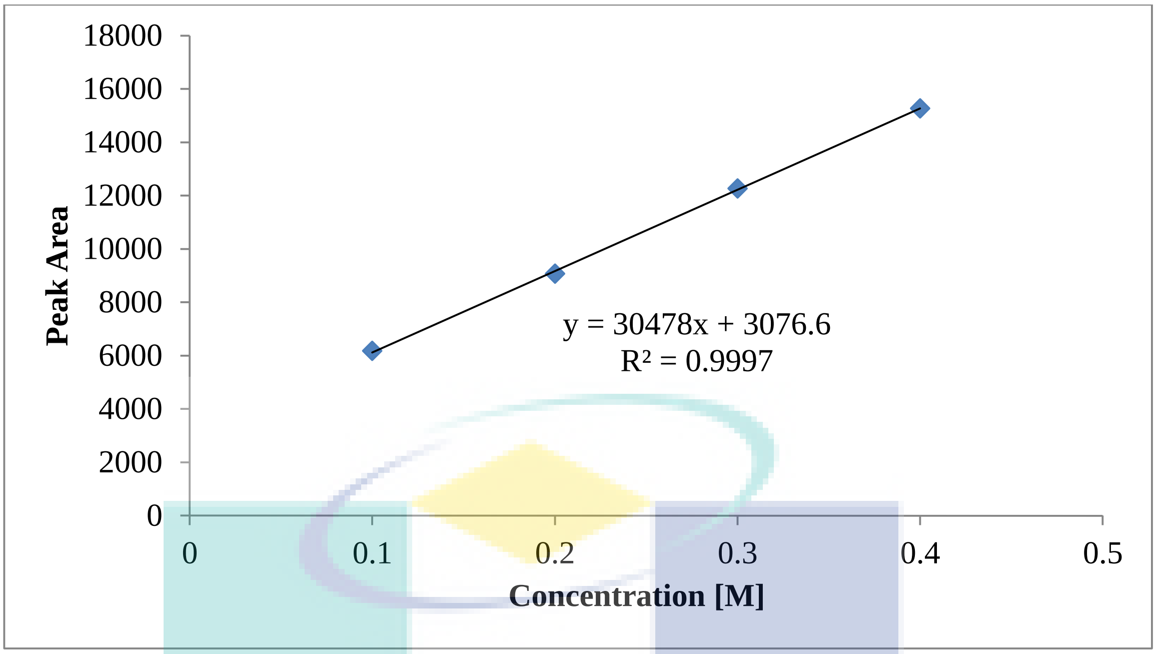
**Appendix C4:** Standard calibration curve of ethylene carbonate.



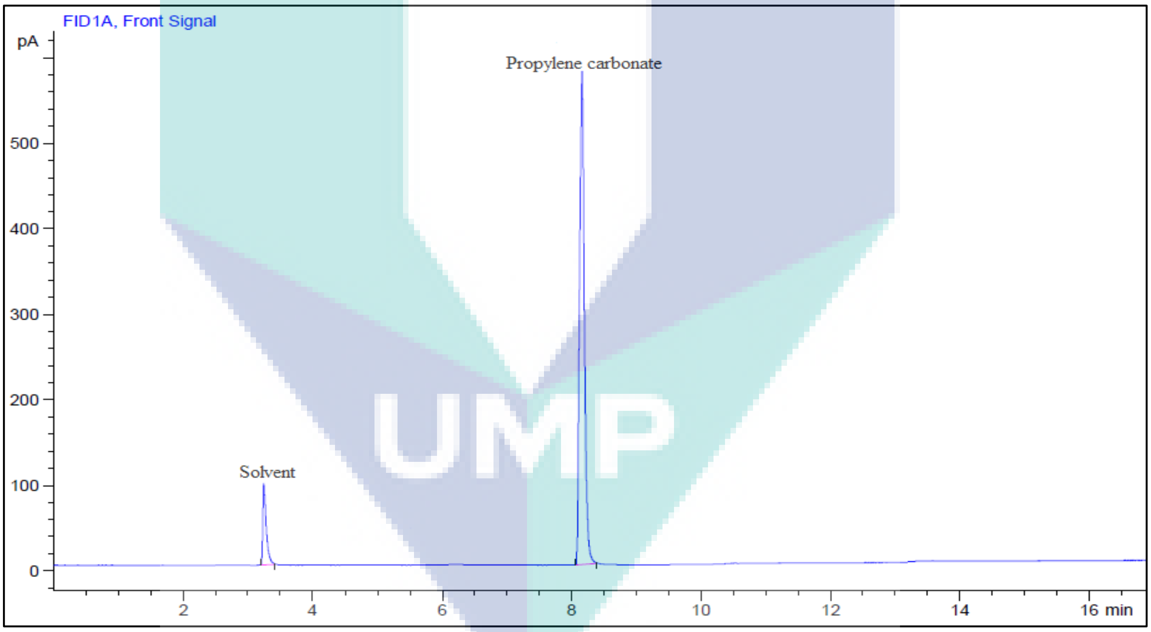
**Appendix C5:** GC-FID chromatogram of ethylene glycol, ethylene carbonate, 2-hydroxyethyl carbamate, oxazolidin-2-one and 3-(-2-hydroxyethyl) oxazolidin-2-one.



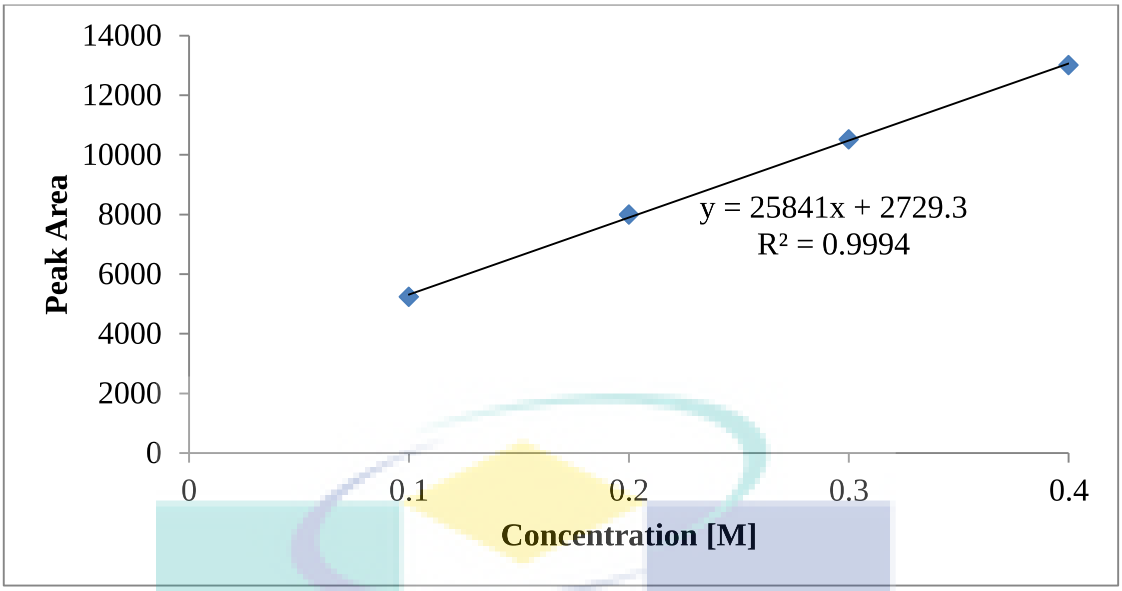
**Appendix C6:** GC-FID chromatogram of propylene glycol.



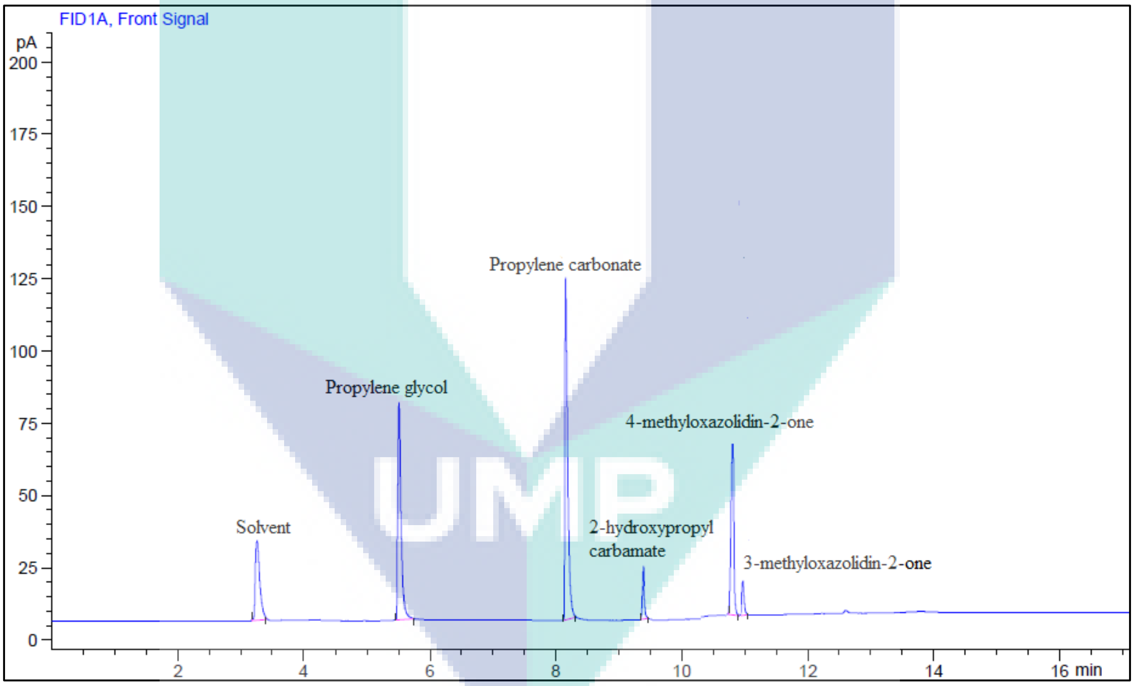
**Appendix C7:** Standard calibration curve of propylene glycol.



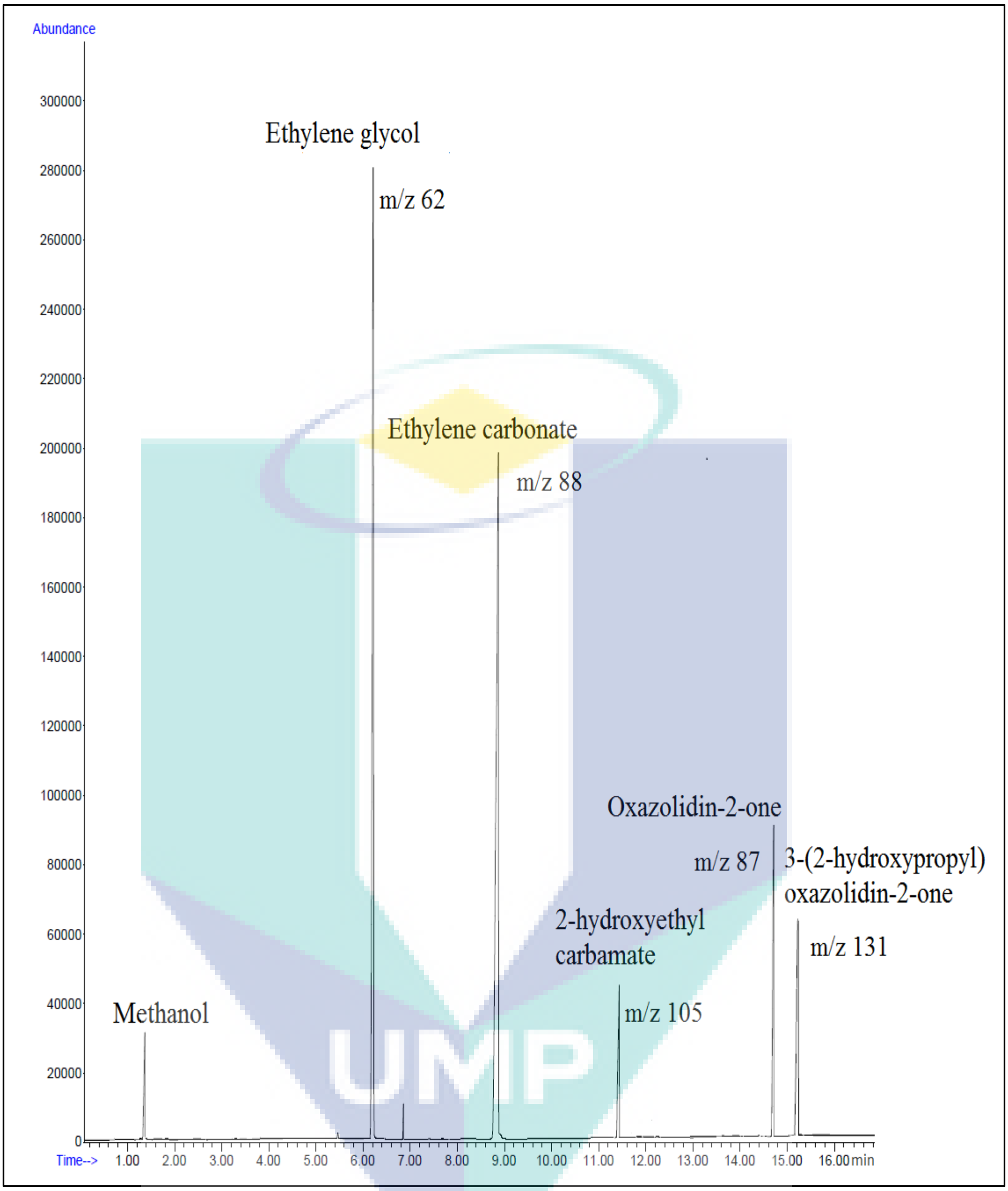
**Appendix C8:** GC-FID chromatogram of propylene carbonate.



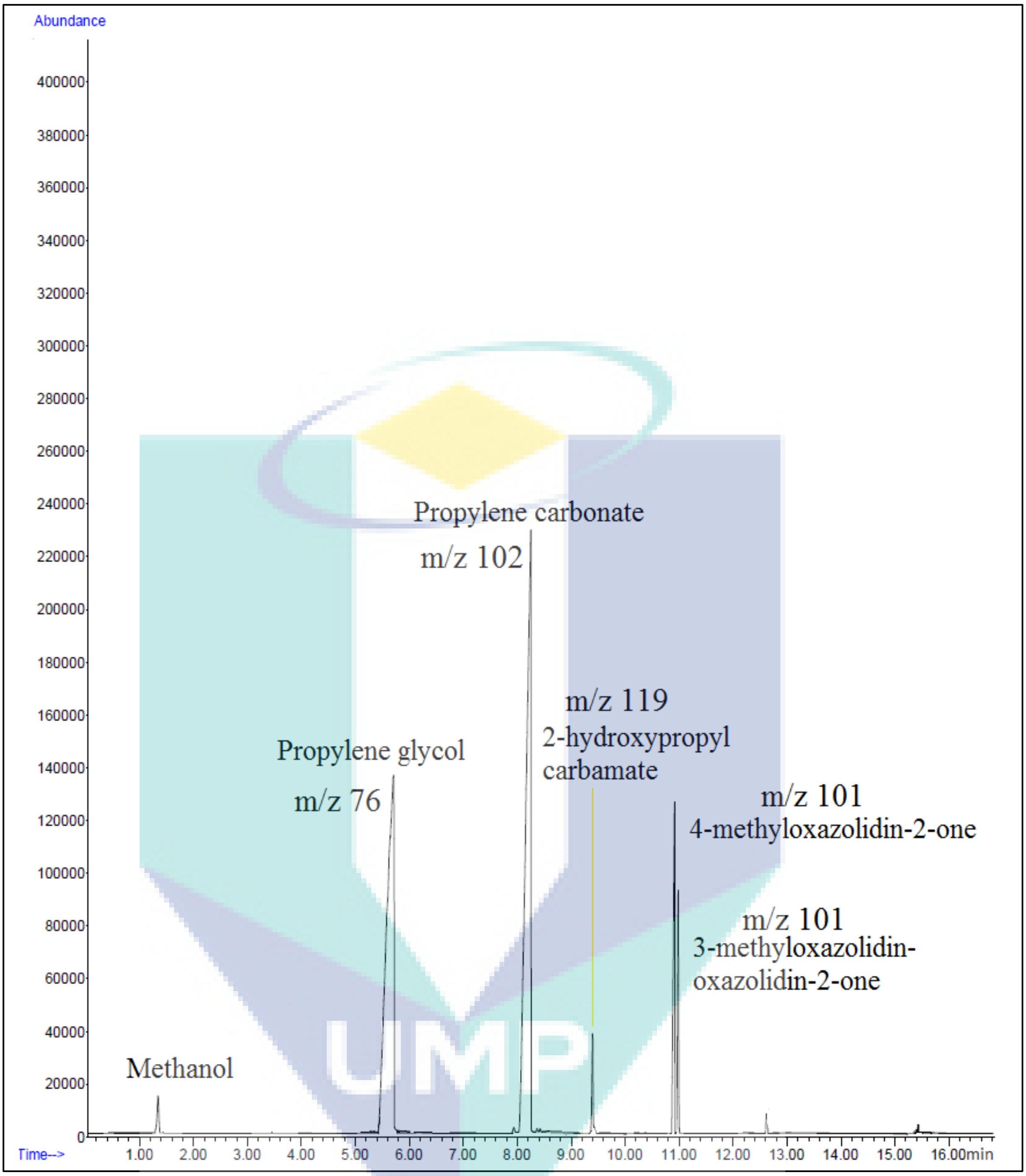
**Appendix C9:** Standard calibration curve of propylene glycol.



**Appendix C10:** GC-FID chromatogram of propylene glycol, propylene carbonate, 2-hydroxypropyl carbamate, 4-methyloxazolidin-2-one and 3-methyloxazolidin-oxazolidin-2-one.



**Appendix C11:** GC-MS chromatogram of ethylene glycol, ethylene carbonate, 2-hydroxyethyl carbamate, oxazolidin-2-one and 3-(-2-hydroxyethyl) oxazolidin-2-one.



**Appendix C12:** GC-MS chromatogram of propylene glycol, propylene carbonate, 2-hydroxypropyl carbamate, 4-methyloxazolidin-2-one and 3-methyloxazolidin-oxazolidin-2-one.

# APPENDIX D

## **Appendix D1:** List of Publications

| No. | Publications | Status |
|---|---|---|
| 1 | Indran, V.P., Syuhada Zuhaimi, N.A., Deraman, M.A., Maniam, G.P., Yusoff, M.M., Taufiq-Yap., Y.H. and Rahim, M.H.A. 2014. An accelerated route of glycerol carbonate formation from glycerol using waste boiler ash as catalyst. *RSC Advances*, *4*(48): 25257–25267. | Published online |
| 2 | Zuhaimi, N.A.S., Indran, V.P., Deraman, M.A., Mudrikah, N.F., Maniam, G.P., Taufiq-Yap., Y.H. and Rahim, M.H.A. 2015. Reusable gypsum based catalyst for synthesis of glycerol carbonate from glycerol and urea. *Applied Catalysis A: General. 502:* 312–319. | Published online |
| 3 | Saud, A.S.H., Indran V.P., Talib, N. and Rahim M.H.A. 2015. Low metal loading palladium mixed-oxides catalyst for the synthesis of glycerol carbonate. *Asian Journal of Applied Science. 4*(1): 181-189. | Published online |
| 4 | Indran, V.P., Saud, A.S.H., Maniam, G.P., Yusoff, M.M., Taufiq-Yap., Y.H. and Rahim M.H.A. 2016. Versatile Boiler Ash Containing Potassium Silicate for the Synthesis of Organic Carbonates. *RSC Advances*. 6, 34877-34884. | Published online |
| 5 | Indran, V.P., Maniam, G.P. and Rahim M.H.A. 2016. Effect of reaction conditions on the synthesis of glycerol carbonate catalysed by boiler ash derived from palm oil industry. *International Journal of Interdisciplinary and Multidisciplinary Studies.* | Accepted |
| 6 | Indran, V.P., Saud, A.S.H., Maniam, G.P., Yusoff, M.M., Taufiq-Yap., Y.H. and Rahim M.H.A. 2016. Direct Crude Glycerol Utilisation for the Synthesis of Glycerol Carbonate. *Waste and Biomass Valorization.* | Under review |

## **Appendix D2:** List of Patents

| No. | Patents |
|---|---|
| 1 | "A Method for Preparing Glycerol Carbonate". Patent Filed: PI 2013702147**.** |
| 2 | "A Method of Using Gypsum as Catalyst for Glycerol Carbonate Production". Patent Filled: PI2014002079 |

## **Appendix D3:** List of Conferences

| No. | Conferences |
|---|---|
| 1 | Malaysian Technical Universities Conference on Engineering and technology, (MUCET 2013). 3rd-4th December 2013. Boiler Ash Catalysed Synthesis of Glycerol Carbonate from Glycerol. Oral Presenter. |
| 2 | National Conference on Industry-Academia Initiatives in Biotechnology, CIA-BIOTECH 2013. 5th-7th December 2013. Synthesis of Glycerol Carbonate Fine Chemical from Bio-renewable Feedstock. Oral Presenter. |
| 3 | 9th International Materials Technology Conference and Exhibition, (IMTCE 2014). 13th-16th May 2014. Green Synthesis of Glycerol Carbonate from Glycerol Catalysed by Boiler Ash. Poster Presenter. |
| 4 | Malaysia International Conference on Oils and Fats, (SMILE2014). 20th-21st August 2014. Synthesis of Glycerol Carbonate using Catalyst Derived from Boiler Ash. Oral Presenter. |
| 5 | 5th International Conference for Young Chemist, (ICYC 2015). 5th-7th August 2015. Synthesis Of Cyclic Organic Carbonates Using Catalyst Containing $K_2SiO_3$ Derived From Waste Boiler Ash. Poster Presenter. |

## **Appendix D4:** List of Awards

| No. | Awards |
|---|---|
| 1 | 25th International Invention, Innovation & Technology Exhibition, (ITEX 2014). Silver Medal. (2014). |
| 2 | Best Poster Award (1st Prize) in 9th International Materials Technology Conference & Exhibition (IMTCE 2014). |
| 3 | Trans-Tasman Minute Thesis (3MT) Competition (2014) at University of Western Australia (UWA), Perth, Australia. (Semi Finalist). |
| 4 | Citrex Gold Medal Award for the invention/innovation of "Utilisation of Local Industrial Waste for the Production of Valuable Fine Chemical". (2014). |
| 5 | Citrex "Green Technology Award" for the invention/innovation of "Utilisation of Local Industrial Waste for the Production of Valuable Fine Chemical". (2014). |
| 6 | Citrex Silver Medal Award for the invention/innovation of Green Production of Organic Carbonate from Waste Materials. (2013) |
| 7 | BioInnovation Awards. Green Production of Organic carbonate from Waste Materials. (Bronze Award). (2013). |
| 8 | Pencipta 2015. Novel Fuel Additive Chemical from Oil Palm Sap. (Gold Award) (2015). |
| 9 | International MERIT Award. Novel Fuel Additives Chemical From Oil Palm Sap. INPEX in Pitsburgh, PA, USA. (2016) |