UTILIZATION OF SUGARCANE BAGASSE AS A CO-CATALYST WITH POTASSIUM IODIDE FOR CO_2 CONVERSION TO CYCLIC CARBONATE

By

MISS Kawisa CHAIPOJJANA

A Thesis Submitted in Partial Fulfillment of the Requirements
for Master of Engineering (CHEMICAL ENGINEERING)
Department of CHEMICAL ENGINEERING
Graduate School, Silpakorn University
Academic Year 2017

การใช้วัสดุชานอ้อยเพื่อเป็นตัวเร่งปฏิกิริยาร่วมกับโพแทสเซียมไอโอไดด์ ในการเปลี่ยนก๊าซคาร์บอนไดออกไซด์เป็นสารประกอบคาร์บอเนตแบบวง

โดย
นางสาวกวิศา ชัยพจนา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี แผน ก แบบ ก 2 ระดับปริญญามหาบัณฑิต
ภาควิชาวิศวกรรมเคมี
บัณฑิตวิทยาลัย มหาวิทยาลัยศิลปากร
ปีการศึกษา 2560

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Title	Utilization of sugarcane bagasse as a co-catalyst with potassium iodide for CO_2 conversion to cyclic carbonate
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Field of Study	(CHEMICAL ENGINEERING)
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58404202 : Major (CHEMICAL ENGINEERING)

Keyword : CO2 utilization; Cycloaddition reaction; Cyclic carbonate; Dewaxed sugarcane bagasse

MISS KAWISA CHAIPOJJANA : UTILIZATION OF SUGARCANE BAGASSE AS A CO-CATALYST WITH POTASSIUM IODIDE FOR CO_2 CONVERSION TO CYCLIC CARBONATE THESIS ADVISOR : ASSISTANT PROFESSOR WORAPON KIATKITIPONG, D.Eng.

In this research, the utilization of lignocellulose dewaxed sugarcane bagasse (D-SCB) as a new cooperative catalyst with potassium iodide (KI) in cycloaddition reaction of 1, 2-butylene oxide (BO) with CO_2 to formed 1,2-butylene carbonate (BC) was studied under free-solvent. The effects of reaction temperature, CO_2 pressure, reaction time, and amount of water (hydroxyl group) were investigated and the suitable conditions for cycloaddition reaction. Also, the efficiency of biomass structure after fractionation, lignin and cellulose, along with potassium iodide (KI) were also considered in cycloaddition reaction of 1, 2-butylene oxide (BO) with CO_2 to formed 1,2-butylene carbonate (BC). According to the results, this catalytic system exhibited excellent cycloaddition activities since the immense hydroxyl groups in dewaxed sugarcane bagasse are able to coordinate with oxygen atoms of epoxide and activate ring opening of epoxide through hydrogen bonding. The suitable operating conditions for cycloaddition reaction to achieve high 1, 2-butylene carbonate yield are 120 °C, 20 bar CO2 pressure, and reaction time 6 h.

ACKNOWLEDGEMENTS

First and foremost, the author wishes to express his sincere gratitude and appreciation to my advisor, Assistant Professsor Worapon Kiatkittipong, and co advisor, Dr. Mutsee Termtanun for providing guidance and valuable advice throughout this research and devotion to reise this thesis. In addition, the author would also be grateful to Professor Suttichai Assabumrungrat and Dr. Sunthon Piticharoenphun as the members of the thesis committee. The author would like to thank the financial supports from silpakorn University sopporting equipment and laboratory.

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CHAPTER I

INTRODUCTION

1.1 Motivation

Carbon dioxide, approximately 82% of the greenhouse gases emitted annually that causes global warming, is mainly produced from chemical industry, energy supply industry, power plant and especially transportation sector that use fossil fuels as resource[1].To manage the CO_2 emissions efficiently and alleviate the relevant adverse consequences, many researchers pay much attention to CO_2 capture and sequestration (CCS), and conversion to formulate a CO_2 recycle value chain as the most promising approach for suppressing CO_2 emissions. However, each technique has different advantages-disadvantages, for limitations of carbon capture and sequestration (CCS) which is expensive, requires high energy for separation and sequestration [2]. The process of CO_2 conversion to produce value added chemicals and fuels require harsh conditions since CO_2 has high kinetic and thermodynamic stability which challenges the conversion of CO_2 to chemicals and fuels. Hence, an efficient catalyst is necessary to reduce the activation energy of cycloaddition reaction of epoxides and CO_2.

CO_2 has been used in many applications since it has been considered as non-toxic, non-flammable, renewable, inexpensive, and an abundant carbon feedstock for the synthesis of valuable chemicals such as dimethyl carbonate[3] [4], methanol [5], urea [6], cyclic carbonate [7] [8] [9], formic acid [10] and etc. The synthesis of cyclic carbonates through cycloaddition of CO_2 with epoxides is considered as one of the most interesting process, further discussed in chapter 2 and 3.

Cyclic carbonates are valuable compounds, bearing some interesting properties including high boiling point, low toxicity and being odorless, used as polar aprotic solvents, electrolytes in lithium secondary batteries, fuel additives, precursors for the formation of polycarbonates, and intermediates in pharmaceuticals and fine chemicals

[11] [12] [13] [14]. The synthetic pathway of cyclic carbonates brings about aromatic polycarbonates. The utilization of CO_2 is the promising route in that it reduces greenhouse gas emissions and provides environmentally friendly alternative instead of phosgene, which is highly toxic and corrosive chemical. To develop the synthesis of cyclic carbonates, appropriated catalyst system is compulsory for the mild operating condition to minimize the overall expense for cyclic carbonate production.

Lots of homogeneous and heterogeneous catalysts have been explored for CO_2 cycloaddition to epoxides, further explained more details in Chapter 2. The common homogeneous catalysts are alkali metal salts, organophosphorus compounds, organic bases, and organometallic compounds [15] [16] [17] [18]. Though the homogeneous catalysts have high potential, the decomposition of the catalyst or formation of by-products due to complicated post-treatment, and the expense for further separation after the reaction seems to be the drawbacks. Therefore, heterogeneous catalysts have been widely developed in order to alleviate these problems, for example, polymeric nanoparticles [19], metal oxides [20] [21], molecular sieves [22], and supported catalysts (supported on silica, cross-linked polymer, and, supported on biopolymer) [23] [24] [25]. However, their applications are rather limited due to low activity, poor stability and reusability.

Alkali metal salts are the most promising catalyst for the cycloaddition because of inexpensive, abundance and nontoxic. However, the drawback of alkali metal salts is that their low activities [26] [27]. Therefore, they require addition of co-catalysts or solvent is necessary for catalytic efficiency improvement [28]. In recent studies, it has been found that hydroxyl/carboxyl group-containing catalytic systems could coordinate with the oxygen atom of epoxides and accelerate the cycloaddition of epoxides with CO_2, leading to extensive studies of catalytic systems possessing hydroxyl or carboxyl groups [29] [30].

In this work, lignocellulosic component in sugarcane bagasse (SCB) was then applied due to the electron-rich feature of hydroxyl groups as a new cooperative catalytic system with the presence of potassium iodide (KI) for cycloaddition reaction of epoxides and carbon dioxide to form cyclic carbonates under solvent-free conditions.

1.2 Objectives of research

The major aims of this research are to

1. Convert 1, 2-butylene oxide to 1,2-butylene carbonate using sugarcane bagasse (SCB) as co-catalyst with potassium iodide (KI) for the cycloaddition reaction

2. Find the suitable operating parameters such as reaction temperature, CO_2 pressure, and reaction time.

3. Determine the effect of hydroxyl quantity on the catalytic efficiency of sugarcane bagasse in the cycloaddition reaction and compare the catalytic activities using different components of biomass which are cellulose and lignin

1.3 Scope of research

This research is divided into 2 parts, as follow:

1. Using various operating conditions, for example, reaction temperature (40, 80, 120, 140, and 180 °C), CO_2 pressure(10, 15, 20, 25, and30 bar) and reaction time (30, 50, 120, 240, 360 and 480 minutes) to determine the suitable condition in

cycloaddition reaction of 1,2 butylene oxide (BO) using dewaxed sugarcane bagasse (D-SCB) as a co-catalyst with KI.

2. Operating the reaction with the different components of dewaxed sugarcane bagasse (D-SCB) to identify the influence of hydroxyl quantity on catalytic efficiency of SCB in cycloaddition reaction of 1, 2- butylene oxide.

CHAPTER II

LITERATURE REVIEWS

Many researchers have studied utilization carbon dioxide as raw material for synthesis fuels and chemicals show in **Figure 1**, for example methanol, cyclic carbonate via CO_2 hydrogenation, CO_2 cycloaddition with epoxide. However, there are many challenges from carbon dioxide molecule in that of its thermodynamically, kinetically stable, or active catalysts, which requires harsh conditions both temperature and pressure for double bond-breaking of carbon dioxide [31]. For cycloaddition reaction, the insertion of CO_2 in the structure of epoxide via ring-opening to form cyclic carbonate under mild conditions need high active catalyst system consisting of Brönsted acid and base.

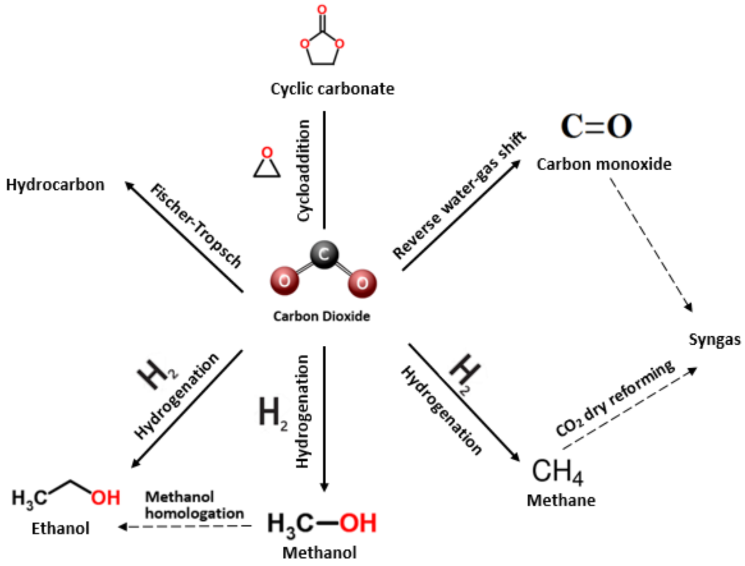

Figure 1: Schematic demonstration of fuel and chemicals production from carbon dioxide (CO_2)

2.1 Synthesis of cyclic carbonate via cycloaddition of carbon dioxide (CO_2) and epoxide

2.1.1 Catalytic system for cyclic carbonate synthesis

This section presents a review of the major developments in the part of both homogeneous and heterogeneous catalysts of cyclic carbonate synthesis. However, these catalysts normally suffer from catalytic instability, sufficient activity, air sensitivity, co-solvent or co-catalyst requirement and harsh operation condition [32] [33]. Hence, the development of highly efficient and environmentally benign catalysts with recycling performance for the reaction of epoxides with CO_2 is challenging.

2.1.1.1 Homogeneous catalysts

Inoue et al. [34] combined $ZnEt_2$, water, CO_2, and propylene oxide (PO) to yield a small quantity of polymeric material. However, this investigation achieved low catalytic activity and competitive formation of polycarbonates and undesired by-products. It was appeared that most polymer formation with the cyclohexene oxide (CHO)/CO_2 system yielding cyclic carbonate, whereas barely no conversion with PO/CO_2 as monomers. In this research, a wide range of homogeneous catalysts have been explored for the production of cyclic carbonates using CO_2. The most effective of these were found to be organometallic, salen complexes, alkali metal salts, metal complexes, quaternary onium salts, and ionic liquids.

Various homogeneous catalysts have been used in the production of cyclic carbonates, for example, metal complexes, salen complexes of aluminum [33] [34] [35], chromium [36], cobalt, and zinc [37]. Lu et al. [38] investigated bifunctional catalysts of tetradentate Schiff-base aluminium complexes (SalenAlCl) coupling with a quaternary ammonium or phosphonium salt for cycloaddition of supercritical carbon dioxide/ethylene oxide mixture leading to high reaction rate owing to rapid diffusion and high miscibility of ethylene oxide in supercritical carbon dioxide under employed condition. Substitution of SalenAlX on the aromatic rings has a negative influence on SalenAlX catalytic activity for the reaction. The catalytic activities of substituted aluminium-salen complexes exhibited in the following order: SalenAlCl > Salen(Cl)AlCl > Salen(NO_2)AlCl > Salen(t-Bu)AlCl, contrary to the order of size of the substituted groups. Therefore, existence of halides or a long oxyethylen chain in axial X-group benefits in the improvement of SalenAlX catalytic activity. However, with a quaternary salt as co-catalyst, these metal-salen complexes exhibit catalytic activities in the following order: SalenAlCl, SalenCrCl > SalenCo > SalenNi > SalenMg, SalenCu, SalenZn. Feng et al. [35] and Wang et al. [33] (slen)AlX with a quaternary ammonium salt (n-Bu4NY) in the absence of any solvent which effects on two features (1). electrophilicity of central Al^{3+} ion and the steric factor of substituent groups on the aromatic rings of (Salen)AlX (electrophile) and (2). nucleophilicity and leaving ability of the anion Y^- of n-Bu_4NY (nucleophile) on the bifunctional catalyst activity, arranged in the following order: n-Bu_4NI, n-Bu_4NBr > n-Bu_4NCl > n-Bu_4NCH_3COO > n-Bu_4NBF_4, n-Bu_4NClO_4, n-Bu_4NNO_3, n-Bu_4NOTs. Robert et al. [36] reported a novel highly active (salen)Cr(III)-based catalyst system for the synthesis of cyclic carbonate from the coupling of CO_2 and terminal epoxides under extremely mild conditions and in the presence of 4-dimethylamino)pyridine (DMAP) investigated with varying diamine backbones as catalysts of (salen)Cr(III) complexes. Among all catalysts, meso-phenyl salenCr(III) catalyst exhibited the highest catalytic activity and twice as much active as the racemic trans analogue. Furthermore, trans-cyclohexyl salen catalyst and the propylene salen catalyst are also slightly more active than the racemic trans analogue. Shen et al. studied various Metal-Salen complexes [39] in that the corresponding five-membered cyclic carbonate could be obtained in the excellent yield in the presence of binaphthyldiamino salen-type Cu(II), Zn(II), or Co(II) complexes with organic bases at 100 °C, especially Et_3N (triethylamine) and DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) are the superb organic bases under the same conditions. They reported that the reaction temperature, reaction time, and pressure of carbon dioxide are significant factors that influencing on the yields of cyclic carbonate, no any reaction taking place at an ambient temperature or under a CO_2 atmosphere (1.0 kg/cm^2). It was appeared that the applied catalysts in this research have high catalytic stability. Aluminum complexes of phthalocyanines or porphyrins are also highly active [40] [41].

In case of alkaline catalysts, Song et al. [15] demonstrated that hydroxyl containing **β**-cyclodextrin provides a significant catalytic efficiency when used as a co-catalyst with potassium iodide, donating hydroxyls on the cyclic oligosaccharide which would activate the epoxide whereas Han et al. previously researched crown-ether as a co-catalyst with potassium iodide [26]. With 2.5 mol% potassium iodide and 8 wt% **β**-cyclodextrin after 4 hours at 120 °C with 60 bar CO_2, the conversion of propylene oxide to propylene carbonate increased from 27% to 98%, whereas the chloride and bromide salts have inferior catalytic activities in comparison with the iodide salt [37] attributed to the increased ability of iodide as a leaving group. The enhanced activity observed when using **β**-cyclodextrin is due to hydrogen bond. Similarly, Han et al. [27] discovered the using of cellulose to enhance potassium iodide catalytic activity in synthesis of propylene carbonate from propylene oxide resulting in the conversion of 99% within 2 hours at 110 °C and 20 bar CO_2 and; providing high yields in a shorter reaction time and under comparatively mild conditions. Subsequently, a primary and secondary diols containing species were investigated as co-catalysts, especially cyclohexane-1, 2-diol, propylene glycol and ethylene glycol, contributing 96%, 96% and 92% conversions of propylene oxide into propylene carbonate, respectively. Nevertheless, conversions were reduced when using mono alcohols such as methanol (56%) and ethanol (48%). Park et al. [42] employed microwave chemistry as a green technology for the synthesis of cyclic carbonates using potassium iodide with formic acid as a co-catalyst to accomplishing high conversions within short reaction times. A conversion of 60% of propylene oxide to propylene carbonate was obtained within 15 minutes using 200 watts microwave reactor, 1.6 mol% of potassium iodide, 14.5 mol%

of formic acid and 9.6 bar CO_2. Increasing the microwave power exceeding 200 watts slightly reduced conversions, possibly due to a reduction of CO_2 solubility. The utilization of co-catalysts with long chain lengths, such as acetic and propionic acid also reduced conversions due to increase in steric effects and hydrogen bonding between acids. In this research, microwave synthesis offers significant energy savings along with relatively safety issue, simple and green co-catalyst available in large quantities. Above all the alkali metals, potassium iodide is the most superior based catalysts in nearly all cases.

Ionic Liquids (ILs) would be one of attractive catalysts for environment friendly reaction and separation processes because of their physicochemical properties. However, there were negative effects caused by their toxicity on environment and products when using ILs in practical applications. ILs are used in different form as cations and anions. Recently, Baiker et al. [43] have published a review on multiphase catalytic systems including ILs and CO_2. They demonstrated the significance of the combination of ILs and CO_2 for chemical and separation processes, dealing with physicochemical features of those multiphase reaction systems and catalytic reactions including using carbon dioxide as a reactant. The related applications of these compounds consist of solvents, reagents, fuel additives, and intermediates in the production of pharmaceuticals and fine chemicals [44] [45].

The first synthesis of cyclic carbonate using ionic liquids (ILs) of imidazolium and pyridinium salts at ambient temperature was reported by Peng and Deng [46]. It has been observed that cycloaddition of CO_2 to propylene oxide (PO) producing propylene carbonate (PC) is effectively catalyzed by [BMIm]BF_4. PO was quantitatively converted to PC with 2.5 MPa of CO_2 at 110°C for 6 h in the presence of 2.5 mol% [BMIm]BF_4. After the reaction, PC was distilled from the reaction mixture and the catalysts were four times recycled with only a minor loss in activities. The ionic liquid catalysts are recyclable for the cycloaddition of CO_2 to PO. They revealed that the type of cations and anions have influence on the activity of the ILs. The decrease of activity were in the orders of $[BMIm]^+ > [BPy]^+$ and of $BF^{4-} > Cl^- > PF^{6-}$. Later, quaternary ammonium salts catalysts were used to study for CO_2 fixation into cyclic carbonate. Caló et al. [47] reported that this reaction was effectively promoted by molten tetrabutylammonium bromide ($[Bu_4N]Br$) and/or tetrabutylammonium iodide ($[Bu_4N]I$) under atmospheric pressure of CO $_2$ at 120 or 60°C. Using these salts as solvents and catalysts, a less active substrate as styrene oxide and polymerization-sensitive epoxides (glycidyl methacrylate) were converted to the corresponding cyclic carbonates with the desirable yields. $[Bu_4N]I$ provided higher activity than $[Bu_4N]Br$ due to the difference in the nucleophilicity of the halide ions. The reaction rate depended greatly on the structure of the cation as well as the nucleophilicity of anion. It was appeared that these two salts possess efficient catalytic performance for the cyclic carbonate synthesis, significantly different in the activity when compared among [BMIm], N-methyl-pyridinium ([MPy]) and $[Bu_4N]$ iodides. It was also cleared that the ammonium salt was easily recyclable by vacuum distillation or extraction with ethyl acetate, in which the salt is insoluble. The presence of Lewis acidic compounds as co-catalysts greatly enhances the activity of ionic liquids (ILs) for the cyclic carbonate synthesis. Kim et al. [48] revealed that the catalytic activities of ionic liquids (ILs) such as [BMIm]Cl and [BMIm]Br for the reactions of CO_2 with ethylene oxide (EO) and propylene oxide (PO) can surprisingly be improved by the combination with zinc bromide ($ZnBr_2$), although $ZnBr_2$ is inactivity for the reactions. From the results, TOF value of 37 h^{-1} for PC production was obtained with [BMIm]Br alone at 100°C under CO_2 of 3.5 MPa, which increased to 1679 h^{-1} by the co-presence of $ZnBr_2$. They concluded that the high activities are attributed to the in situ formation of $[BMIm]_2ZnBr_2Cl_2$ and $[BMIm]_2ZnBr_4$, because these prepared tetrahalides showed similar activities to the corresponding catalyst systems of $[BMIm]Cl/ZnB_{r2}$ and $[BMIm]Br/ZnBr_2$. The catalytic activity of imidazolium zinc tetrahalide was greatly influenced by the bonding of halide groups with the zinc center. The activity was arranged in an order of $[ZnBr4]^{2-} > [ZnBr_2Cl2]^{2-} >> [ZnC_{l4}]^{2-}$, indicating the importance of the nucleophilicity of halide ligands. According to these results, they proposed that halide ions are dissociated from the zinc tetrahalide and subsequently attacks the carbon atom of epoxide. On the contrary, the alkyl group attached on the imidazolium cation would have a negligible effect on the activity. Moreover, it also can be inferred that the imidazolium zinc tetrahalide has high catalytic stability. Likewise, a similar catalyst system of [BMIm]Br/$ZnCl_2$ was reported by Li et al. [49]. NMR measurements of the catalyst in D_2O suggested the formation of a $ZnCl_2$–[BMIm] Br complex through the coordination of $ZnCl_2$ with the hydrogen atom on carbon of imidazolium rings. This catalyst system gave excellent yields for the cyclic carbonate synthesis with several types of epoxides at 100°C for 1 h under CO_2 of 1.5 MPa. They studied a series of metal halides together with [BMIm]Cl for the styrene carbonate (SC) synthesis from styrene oxide (SO), which is less reactive when compared with PO and EO [50]. It was discovered that the $ZnBr_2$ and [BMIm]Cl-catalyst system gives 93% yield with 100% selectivity to styrene carbonate at 80°C for 1hr, whereas, $ZnBr_2$ alone was inactive and [BMIm]Cl itself contributed to a little SC yield (6%). The type of metal cations had strong effect on the carbonate yield, arranged in the order of activity as followed, $Zn^{2+} > Fe^{3+} > Fe^{2+} > Mg^{2+} > Li^{+} > Na^{+}$, analogous to the order of Lewis acidity of the metal cations. Using ZnI_2, $ZnCl_2$ or ZnO instead of $ZnBr_2$ led to the decrease in the yield of styrene carbonate. It was obvious that both the type of anion ionic liquid (ILs) and the length of alkyl chain of the imidazolium cation had strong influence on the conversion and selectivity. Using [BMIm]BF_4 and [MIm]PF_6 rather than [BMIm]Cl provided low epoxide conversions. Moreover, the [BMIm]Cl/$ZnBr_2$ ratio also affected the carbonate yield by ratio at 2 and CO_2 pressure being optimum. After the reaction, the catalyst of [BMIm]Cl and $ZnBr_2$ can be separated by an extraction with ethyl acetate and recycle without significant loss in activity.

2.1.1.2 Heterogeneous catalysts

Heterogeneous catalysts are widely used in industries because of their advantages in the separation and recycling and their applicability for flow reaction systems. However, conventional heterogeneous catalysts are sometimes less active and selective when comparison to such homogeneous ones as metal complexes and organic bases including ionic liquids. The heterogeneous catalysts could be founded in form of those homogeneous immobilized on solids of metal oxides, or polymers. The immobilized catalysts have not only high activity and selectivity but also the advantageous in the catalyst separation, enabling more efficient and economical reaction processes.

Yano et al. [51] first reported the use of a metal oxide catalyst for CO_2 and epoxide-cycloaddition. They concluded that a commercial MgO could catalyze the reactions of CO_2 with propylene oxide (PO) and styrene oxide (SO) to achieve cyclic carbonates with 60 % and 41 % yields of styrene carbonate (SC) and propylene carbonate (PC), respectively at 135°C and 2 MPa of CO_2 for 12 h in a solvent of dimethylformamide (DMF). MgO calcination effects on MgO activation by improving yield rather than uncalcination. On the other hand, CO_2 pressure showed no impact on the carbonate yield within a range between 0.2 and 2.8 MPa. None organic solvent leads to more preferable reaction systems, already reported the CO_2 cycloaddition reactions under such conditions in some researches. Bhanage et al. [52] employed several metal oxide catalysts such as MgO, CaO, ZnO, Zr_2O, La_2O_3, CeO_2, and Al_2O_3 for conversion CO_2 and propylene oxide (PO) to propylene carbonate (PC). MgO is the superior among all examined metal oxides, with the 32 % yield, 92 % selectivity of PC, respectively, with dimethylformamide (DMF) solvent at 150°C and 8 MPa CO_2 for 15 hr. Though higher PC yield of 54 % was obtained with $La2O_3$, the PC selectivity was lower at approximately 75 %. Basic properties of these catalysts were investigated by temperature programmed desorption (TPD) of adsorbed CO_2. It was also reported that both moderately and strongly basic sites are active for the reaction, especially MgO, comprised of large amount of moderately basic sites, resulting in its high activity and selectivity. The reaction of CO_2 and styrene oxide (SO) to styrene carbonate (SC) was also examined with MgO catalyst, however, for this reaction, MgO induces 16% yield of product. As mentioned above, MgO renders a reasonable SC yield from CO_2 and SO at 135°C with the presence of DMF. In the meantime, poor SC yield at 150°C in the absence of DMF is according to the positive effects of DMF on the reaction. Yasuda et al. [53] carried out the PC synthesis with MgO, Mg–Al mixed oxide, or SmOCl in the presence and absence of DMF, confirming that the presence of DMF enhanced the PC yield twice as much with the catalyst independence. Similar results were also investigated for the cyclic carbonate synthesis using Nb_2O_3 and DMF and using titanosilicate and 4-(dimethylamino)pyridine (DMAP) [22] [54]. Mori et al. [55] discussed that a catalytic amount of DMAP combined with zinc-based hydroxyapatite (ZnHAP) implemented relatively high SC yield of 79 % at 100 and 0.5 MPa CO_2 for 20 hr. Since ZnHAP and DMAP are poorly active, there is an occurrence of the synergistic effect in the bifunctional catalyst systems consisting of inorganic metal compounds and organic bases.

Recently, carbon materials have received much attention as metal-free heterogeneous catalysts due to access availability from natural sources, ease of preparation and regeneration, excellent thermal and chemical stability, and high specific surface area. With high recovery potential, carbon materials offer advantages in terms of activity and regenerate ability over traditional metal-containing catalysts. There are many carbon materials, for example, graphene oxide (GO) and graphitic carbon nitride ($g\text{-}C_3N_4$) used in cycloaddition reactions. $g\text{-}C_3N_4$ is a polymeric carbon material mainly made up from C and N atoms connected in tris-triazine-based patterns, with H as the major impurity. Being rich in nitrogen species of different kinds, $g\text{-}C_3N_4$ is CO_2-phillic and can be used for CO_2 adsorption and activation. Ansari et al. [56] initially applied mesoporous carbons nitrides (MCN) prepared by a nano-casting method using mesoporous silica as template and melamine as precursor for CO_2

cycloaddition to PO. Though there was the use of a massive amount of dimethylformamide (DMF) as solvent, a rather low activity was recorded. Lan et al. [57] designed a simple and efficient method to prepare P-modified g-C_3N_4 (P-C_3N_4) with acid sites by thermolysis of a mixture of melamine and hexachlorotriphosphazene (HCCP) under metal-free conditions. At the initial, acid-base bifunctional P-C_3N_4 combined with Bu_4NBr was used as catalyst for the synthesis of cyclic carbonates by CO_2 cycloaddition to epoxides under mild conditions. It was observed that the catalytic activity of P-C_3N_4 increased with P content as a result from the formation of acid sites. P-C_3N_4-2 exhibited the outstanding activity with high PC yield of 94.6% at 90°C and 2 MPa in 4 hr. The excellent performance of Bu_4NBr/P-C_3N_4-2 was attributed to the synergetic effect of the acid sites and halide anions for ring opening of epoxide as well as to the basic sites for adsorption and activation of CO_2. Huang et al. [58] prepared amino- and hydroxyl-rich g-C_3N_4 by the hydrolysis of g-C_3N_4 in 60% H_2SO_4. The catalytic activity of g-C_3N_4 increased with the increase of H_2SO_4 treatment temperature from 40°C to 80°C. Further rising up the temperature to 100°C resulted in the dissolution of g-C_3N_4 in H_2SO_4 forming a clear solution. It was considered that enhanced catalytic activity resulted from enlarged specific surface area as well as the generation of amino and hydroxyl groups. Lan et al. [59] reported that graphene oxide (GO) exhibited excellent catalytic performance in the CO_2 cycloaddition with epoxides under mild conditions in the presence of Bu_4NBr. When using PO as a substrate, 96% yield of PC was affordable in 1 hr at 100°C and 2MPa CO_2, while PC yielded to 79% at ambient temperature and atmospheric pressure of CO_2 in 48 hr. The synergistic action of the hydroxyl group and nucleophilic anion was proved by FT-IR. In addition, the presence of a proper amount of H_2O remarkably enhanced the conversion of epoxide. Later, Saptal et al. [60] designed (3-aminopropyl)-trimethoxysilane functionalized graphene oxide (AP-GO) with acid-base cooperative catalytic functions. The presence of a hydrogen bond donating (HBDs) (acid) and amines (base), and the porous nature of AP-GO were essential factors for the promotion of the cycloaddition reaction. By combined with TBAI, AP-GO would serve as an efficient catalyst for the synthesis of cyclic carbonates at 100°C and atmospheric pressure, and yielding 94% of styrene oxide (SC) in 27 hr. Nevertheless, the recycle of homogeneous nucleophiles is complex.

2.1.2 Effect of operating conditions for cycloaddition reaction (reaction temperature, CO_2 pressure, and reaction time)

The catalytic activity of the catalyst system in cycloaddition of CO_2 and epoxides to cyclic carbonate is relatively sensitive to the reaction temperatures. Hexabutylguanidinium bromide/$ZnBr_2$ catalyst showed better activity with high turnover frequencies (TOF) after raising reaction temperature and the optimum temperature was equal to 130°C [32]. Comparable phenomenon was established by Xiao et al. [23] for the synthesis of propylene carbonate from chemical fixation of carbon dioxide with propylene oxide. However, the catalyst activity slightly increased when the reaction temperature up to 110°C. For styrene carbonate, Sun et al. [61] revealed that the optimum reaction temperature was at 80°C and the increase of temperature up to 90°C leads to the decrease in the styrene carbonate yield, related with the by-product formation and the complete decomposition of the oxidant during the high temperature affecting on the low yield of cyclic carbonate. The olefin epoxidation was verified to be parallel with the benzaldehyde (BA) formation by the breakage of the C–C bond. In addition, the cycloaddition of CO_2 and styrene to form styrene oxide (SO) was more facilitated than the epoxidation process, and the formation of styrene carbonate (SC) and benzaldehyde (BA) were then increased according with time. Besides, many researchers studied the production of commercial aliphatic polycarbonates from effective catalysts for copolymerization reaction.

CO_2 pressure also has an important role in cyclic carbonates synthesis via the coupling reaction of CO_2 and epoxides. The optimal catalytic activity for the reaction achieved at an operating pressure between 1.5 and 3.0 MPa, depending on the operating parameters and catalytic systems. Increasing or decreasing CO_2 pressure from the optimum value would decrease the catalytic activity, owing to the excessive CO_2 pressure reducing the speed of the epoxides interaction with the catalyst leading to low catalytic activity [23] [32] for example, the conversion and yield of styrene carbonate increased to 89% and 35% at 1 MPa CO_2, respectively. However, there was no significantly affected from CO_2 pressure within the range between 1 and 12 MPa on the conversion and yield. At 15 MPa, both conversion of styrene oxide and yield of styrene carbonate decreased according to the phase change in the reaction mixture, increasing in the volume during the reaction process, resulting in low concentration of substrate and reducing the styrene oxide conversion and yield of styrene carbonate [62].

From Table 1, we concluded catalytic system reaction conditions by comparison yield of synthesis cyclic carbonate, which both homogeneous and heterogeneous provided highly yield of cyclic carbonate but homogeneous has limiting for separation catalyst from product. Part this work although KI with biomass catalytic system give not high yield but has advantages management agricultural waste for apply improve reactivity with catalytic system.

Table 1: *Comparative of catalytic system and condition both homogeneous and heterogeneous with our catalytic system for cycloaddition of* CO_2 *and epoxide*

Catalytic system	Epoxide	Condition			Yield	Reference
		Temperature (°C)	Pressure (Bar)	Time (h)		
Homogeneous Catalyst						
IPr-CO_2	SO	120	20	24	97	Zhou et al. (2008) [63]
HEMIMB (Hydroxyl-functionalized ionic liquid)	PO	125	20	1	99	Sun et al (2008) [28]
KI/ triethanolamine (-OH 3 : 1 mol)	EO	90	10	3	98	Werner et al. (2014) [64]
Heterogeneous Catalyst						
MCM-41-Imi/Br (imidazole on MCM-41)	SO	100	30	4	97.7	Appaturi et al (2013) [65]
PS-HEIMI (Polymer-supported ionic liquid)	PO	120	25	4	98.01	Sun et al. (2009) [66]
KI/lecithin	PO	100	20	4	97.7	Song et al. (2012) [67]
Superbase/cellulose (DBU/cellulose)	PO	120	20	2	92.07	Sun et al. (2014) [68]
KI with Dewaxed SCB	**BO**	**120**	**20**	**6**	**73.4**	**This work**
KI with Dewaxed SCB and treated H_2SO_4	**BO**	**120**	**20**	**6**	**78.47**	**This work**
KI with Cellulose	**BO**	**120**	**20**	**6**	**53.96**	**This work**
KI with Dealkaline Lignin	**BO**	**120**	**120**	**6**	**87.80**	**This work**
KI with Organosolve Lignin	**BO**	**120**	**120**	**6**	**87.05**	**This work**

CHAPTER III

THEORY

3.1 Carbon Dioxide (CO_2)

3.1.1 Physical and Chemical Properties of Carbon Dioxide (CO_2)

Carbon dioxide (CO_2) is a colorless, odorless gas, non-toxic and non-flammable. The molecule is linear with a double bond between the carbon and oxygen atoms (O=C=O) can be occurs in nature and serves as source of carbon for photosynthesis of plants. It is a gas at standard temperature and pressure and not reactive under moderate conditions. At temperatures below -70°C can forms a solid substance and it may also transform into a liquid when it is dissolved in the water under constant pressure. CO_2 is very stable, consequently, a substantial input of energy, effective reaction conditions, and often active catalysts, are necessary for chemical conversion of CO_2 [69].

3.1.2 Chemicals Synthesized form Carbon Dioxide (CO_2)

Carbon dioxide can be used as reactant for several useful products and replaced other toxic carbon reactant such as carbon monoxide or phosgene [69]. Approximately 118 Mt of CO_2 are nowadays used as reactant for industrial chemical synthesis per year [70]. Consequently, developing highly efficient processes for lower energy input for CO_2 conversion is required. The cycloaddition reaction of CO_2 to epoxides represents a 100 % atom economical reaction, which is highly desirable for industry [71] and reduce using highly toxic phosgene. Other important products include urea, salicylic acid, cyclic carbonates, and polycarbonates, and formic acid [72].

3.2 Cyclic Alkylene Carbonate

Cyclic alkylene carbonates can be used as "safe" and environmentally friendly solvents due to biodegradable and non-toxic, substituting harsh products such as methylene chloride, acetone, aromatic solvents, and other highly volatile and hazardous solvents. It can also be employed as reactive intermediates replacing ethylene and propylene oxides and ethylene and propylene glycols in many reactions, which high flash points, low evaporation rates, low volatile organic compound (VOCs), and low toxicity. Additionally, they can be applied as versatile feedstock for the manufacturing of polymers [73] linear organic carbonates [74] or fine chemicals [75].

3.2.1 1, 2-Butylene carbonate (BC)

1, 2-Butylene carbonate, an alkylene carbonate, has been used as a long-term commercially solvent in many industrial applications such as cleaning or degreasing, dyeing, paint stripping, etc. It can be replaced the traditional methylene chloride in paint remover formulations because of combined properties of high flash points, high boiling points, low evaporation rate and low toxic.

3.3 cyclic carbonates synthesis via the cycloaddition of epoxides and CO_2

The synthesis of cyclic carbonates through cycloaddition of CO_2 with epoxides possessing an atom utilization ratio of 100% by epoxides are opened-ring and carbon dioxide inserted into epoxides [76] shows in **Figure 2.** The cycloaddition of epoxides and CO_2 is a typical gas–liquid multiphase catalytic process, involving the gas– liquid mixing/mass transfer in a reactor and the catalytic cycloaddition in the liquid feed. Therefore, a highly efficient reactor and catalyst should be required for further improving cyclic carbonates synthesis.

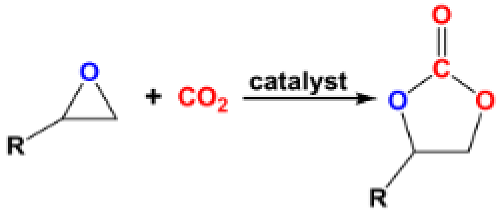

Figure 2: *Synthesis of cyclic carbonates from carbon dioxide and epoxides.*

3.4 Sugarcane Bagasse (SCB)

Sugarcane bagasse (SCB), lignocellulosic material of agricultural residues, is derived from the sugar industry and has many applications as biocompatible materials, chemicals, and fuels [77]. It consists of approximately 40% cellulose, 30% hemicellulose, and 20% lignin [41]. Hence, the electron-rich feature of hydroxyl and/or carbonyl groups in these components made used of lignocellulosic biomass (**β**-cyclodextrin [40] and cellulose [27], etc.) as catalytic system for the hydrogen bond donor (HBD) in cyclic carbonates synthesis via the cycloaddition of epoxides and CO_2.

3.4.1 Cellulose

Cellulose, approximately 40-45%, was a major component of wood. Cellulose is a linear homopolysaccharide containing of **β**-Glucose units linked by glycosidic linkages at C_1 and C_4 positions [78]. Properties of cellulose in hardwood and softwood were quite indifference. Nevertheless, it differs completely from starch that are repeating unit of glucose linking by **α**-1, 4 linkages. Microfibrils, composed of cellulose bundles are highly crystalline structures supplemented with highly degree of polymerization (DP). Therefore, cellulose fibers have high tensile strength, insoluble in most solvents and withstand hydrolysis.

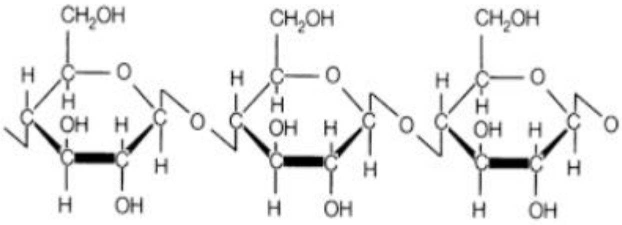

Figure 3: Structure of cellulose

3.4.2 Hemicellulose

Generally, lignocellulosic materials contain 20-30% hemicelluloses. Hemicelluloses were located between the microfibrils or inter laminar spaces 200. The sugar composition of hemicellulose was variable, generally consists of pentose (such as D-xylose and D-arabinose), hexose (such as D-glucose, D-mannose and D-galactose) and small amounts of sugar acid [78]. Hemicellulose was easier to degrade than cellulose because it contains less ordered (amorphous) regions and low degree of polymerization (DP). The principal component of hemicellulose from agricultural lignocellulosic materials was xylose [79].

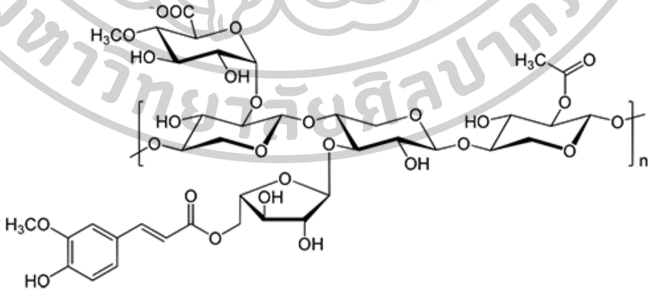

Figure 4: Structure of hemicellulose

3.4.3. Lignin

Lignin was a phenolic macromolecule that is primarily formed by the free-radical polymerization of p-hydroxyl cinnamyl alcohol unit with varying methoxyl content. Three of monomerric precursors were coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. The units of precursors are joined by C-O-C (ether) and C-C linkages in three dimension structure. The ether linkage was dominant and the rest is of the carbon to carbon type [78]. The major function of lignin was to give the plant structural support, impermeability and resistance against microbial attack and oxidative stress [79].

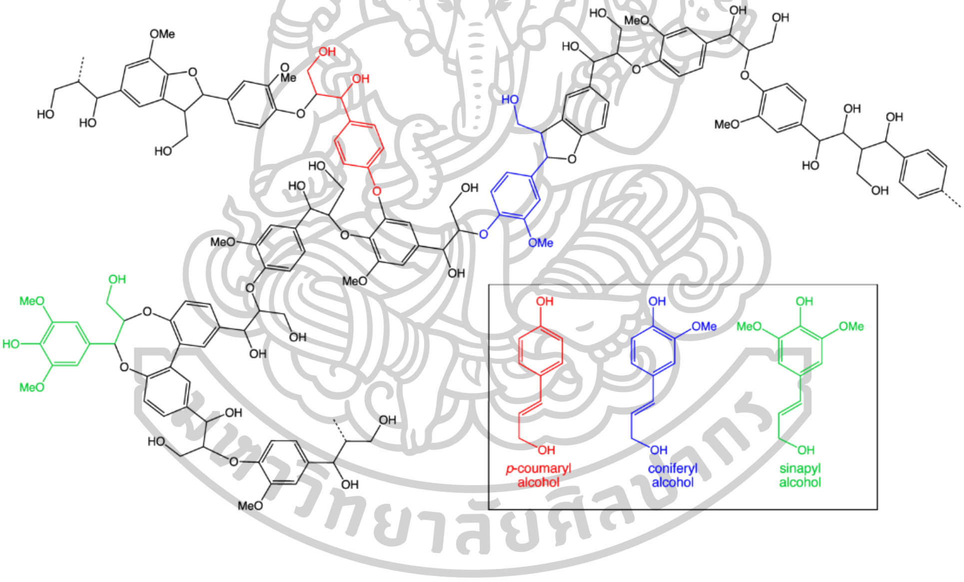

Figure 5: *Structure of lignin*

CHAPTER IV

Experimental

4.1 Materials and methods

4.1.1 Chemical reagents

The chemicals used in the research are shown in **Table 2**

Table 2: *The details of used chemicals*

Chemicals	Formula	Grade	Manufacture
Ethanol	C_2H_5OH	99.9 %	Qrec
Toluene	C_7H_8	99.9 %	Merck
1,2-Butylene Oxide	C_4H_8O	99.0 %	TCI
1,2-Butylene Carbonate	$C_5H_8O_3$	98.0 %	TCI
Potassium Iodide	KI	99.0 %	Ajax Finechem
Carbon dioxide	CO_2	99.5 %	Masser

4.1.2 Co-Catalyst preparation (Dewaxing of Sugarcane Bagasse (SCB))

Sugarcane bagasse (SCB) was dried in sunlight and then cut into small pieces (1-3 cm.). The cut sugarcane bagasse was grounded and dried in oven for 16 h at 60 °C. The dried powder was extracted with toluene/ethanol (2:1, v/v) in Soxhlet extractor for 6 h, following **Figure 6**. After the extraction was completed, dewaxed sugarcane bagasse (DSCB) was dried again in an oven for 16 hr. at 60 °C. The solvent mixture was then recovered by a reduced pressure distillation, while extract was concentrated, leading to brown crude wax. The DSCB was analyzed with Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric analysis (TGA)

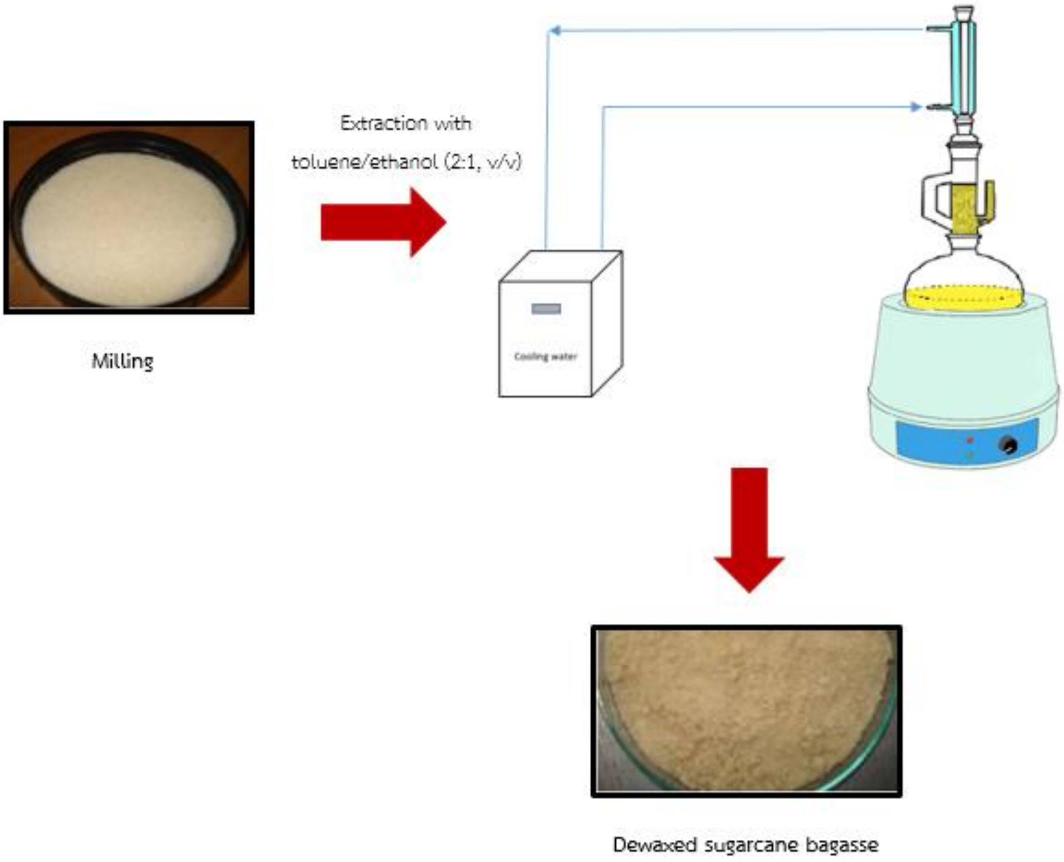

Figure 6: *Dewaxing of Sugarcane bagasse (SCB) using a Soxhlet extractor.*

4.2 Co-Catalyst characterization

4.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

This technique was used for structural characterization of the sugarcane bagasse (SCB). FT-IR spectra were obtained on an FT-IR spectrophotometer using a Potassium bromide (KBr) disk containing approximately 1% finely ground samples. Thirty-two scans were taken for each sample with a resolution of 2 cm^{-1} in transmission mode in the range of 4000-400 cm^{-1}.

4.2.2 Thermogravimetric analysis (TGA)

9-10 mg sample was performed thermal analysis using thermogravimetric analysis (TGA).The scans were run from room temperature to 1000 °C at a constant heating rate of 10 °C/min. The apparatus was continually flushed with air flow of 30mL/min.

4.3 Cycloaddition reaction of carbon dioxide (CO_2) and 1, 2-butylene oxide (BO)

In this part the cycloaddition reaction of carbon dioxide (CO_2) and 1, 2-butylene oxide (BO) using sugarcane bagasse (SCB) as a co-catalyst with potassium iodide (KI) were carried out under various operating conditions, for example, reaction temperature (40, 80, 120, 140 and 180 °C), CO_2 pressure (10, 15, 20, 25 and 30 Bar) and reaction time (30, 50, 120, 240, 360 and 480 minutes) to find out the suitable operating condition in the cycloaddition reaction.

Initially, the reaction was conducted in a 100 mL stainless steel autoclave equipped with a mechanical stirrer and automatic temperature control system. 1, 2-Butylene oxide (30 mmol), Dewaxed sugarcane bagasse (150 mg), and potassium iodide (0.75 mmol) were added into the reactor and purged with CO_2 several times after heat up to desired temperature. Later, the reactor was sealed and pressurized with 20 bar CO_2, and was stirred speed of 200 rpm in order to avoid mass transfer limitation. After completion of the reaction, the autoclave was cooled in a cooling bath, and the excess CO_2 was slowly vented. The reaction mixture was filtered to remove the catalyst. The catalyst was washed with ethanol twice times and dried in oven. The conversion of 1, 2- Butylene oxide (BO) and the selectivity of 1, 2 Butylene carbonate from the cycloaddition reaction were determined using gas chromatography flame ionized detector (GC-FID). The by-products were identified with gas chromatography mass spectroscopy (GC-MS). The products were further verified using ^1H and ^{13}C NMR spectra for confirm structure of product mixture.

Later, the cycloaddition reaction with the different components of sugarcane bagasse (SCB) from fractionation process, obtained as lignin and cellulose, was also performed to identify the influence of hydroxyl quantity on catalytic efficiency of sugarcane (SCB).

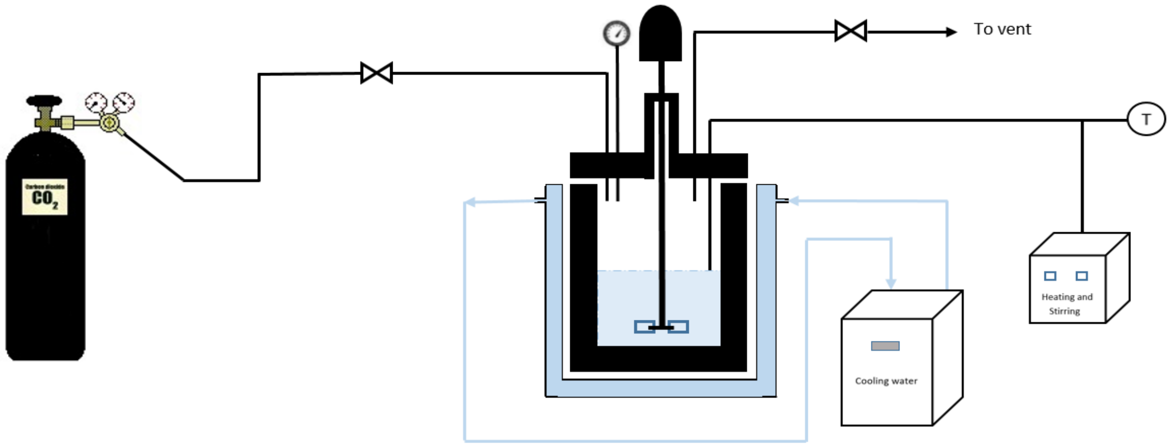

Figure 7: *Schematic of the experimental system.*

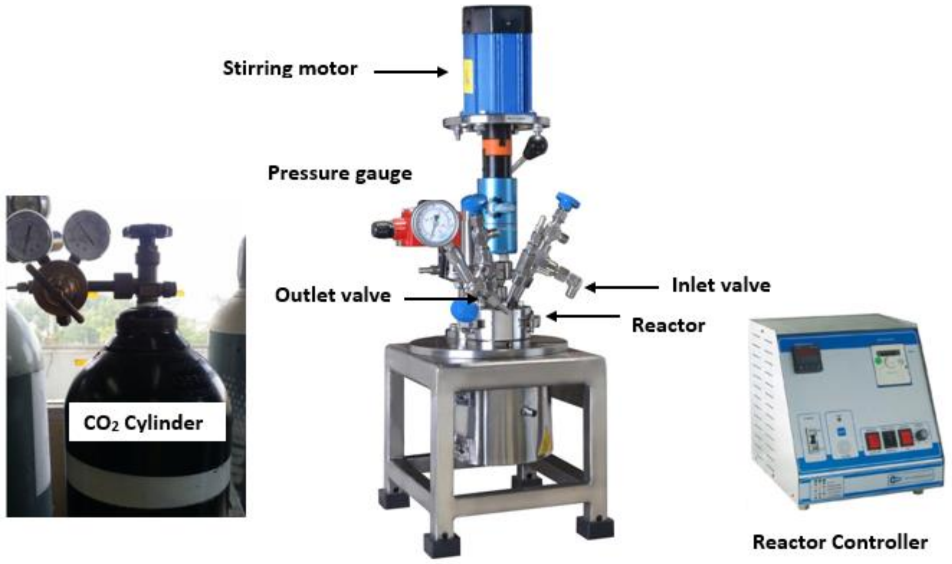

Figure 8: *Image of the experimental set-up for synthesis cyclic carbonate using high pressure reactor.*

4.3.1 Gas Chromatography with Flame Ionized Detector (GC-FID) analysis

Gas Chromatography (GC) were carried on a Shimadzu GC-14B Instruments equipped with capillary column (BP-210WAX, 30 m x 0.32 mm x 0.5 μm film thickness) using a flame ionization detector (FID). The product yield was determined using n-butanol as an internal standard (internal standard no reaction with product). The operation conditions of FID gas chromatograph for cycloaddition reaction are shown in the following **Table 3**.

Table 3: *Operating condition of analysis gas chromatograph*

Gas chromatograph	**Shimadzu GC-14B**
Detector	FID
Column	BP-210WAX (30 m x 0.32mm x 0.5 μm)
Carrier gas	N_2
Split/Splitless	40 mL/min
Purge flow rate	10 mL/min
Carrier pressure	40 kPa
Make up pressure	50 kPa
Injector temperature	270 °C
Detector temperature	300 °C
Column temperature	40 °C to 240 °C (heat rate 15 °C/min), then hold 20 min

4.3.1.1. Determination of Conversion of 1, 2-Butylene oxide (BO), Selectivity and Yield of 1, 2-Butylene carbonate (BC)

The conversion (X) of 1, 2-butylene oxide was calculated from the ratio of mol 1, 2-butylene oxide reacted to the mol of 1, 2-butylene oxide charged (Equation 4.1).

$$\text{Conversion (X)} = \frac{n_{AO}-n_{A}}{n_{AO}} \times 100 \qquad (4.1)$$

The yield (Y) was calculated from ratio of mol 1, 2-butylene carbonate to the mol of 1, 2-butylene oxide charged (Equation 4.2)

$$\text{Yield (Y)} = \frac{n_{BO}}{n_{AO}} \times 100 \qquad (4.2)$$

The selectivity (S) was calculated from the ratio of yield (Y) to conversion (X)

$$\text{Selectivity (Y)} = \frac{Y}{X} \times 100 \qquad (4.3)$$

When n_{AO} is the mol of 1, 2-butylene oxide (BO) charged into the reactor

n_{O} is the mol of 1, 2-butylene oxide (BO) after reaction

And n_{C} is the mol of 1, 2-butylene carbonate (BC) formed

4.3.2 Gas Chromatography with Mass Spectrometry (GC-MS) analysis

Gas Chromatography with Mass Spectrometry (GC-MS) were recorded on a Shimadzu GC-2010 with GCMS-QP2010 Plus mass spectrometer using Rtx-5MS capillary column (30 m x 0.25 mm x 0.5 μm film thickness), which helium as the carrier gas. The tested conditions were: initial temperature 40 °C, hold at initial temperature for 2 min then ramp rate 15 °C/min to 240 °C; hold at final temperature for 15 min.

4.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra measurement of the product mixture were carried out with a Bruker Avance 500 instrument at operation frequency of 100.61 MHz for ^{13}C NMR and 400.13 MHz for ^{1}H NMR, respectively.

CHAPTER V

RESULTS AND DISCUSSION

The results and discussion are divided into two sections: the effect operating conditions include reaction temperature, CO_2 pressure, reaction time, amount of addition water; on the cycloaddition activity and reusability of catalytic system. Moreover, the influence of the different components of dewaxed sugarcane bagasse on the yield and selectivity of product (1, 2-Butylene carbonate) was also compared.

The first section focused on co-catalyst characterization including Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric Analysis (TGA) and N_2 Physisorption analysis (BET)

5.1 Co-catalyst characterization

5.1.1 Fourier transform infrared spectroscopy (FT-IR)

The infrared technique was used to identify the chemical structure changes of the sugarcane bagasse biomass after the pretreated and fractionated to be cellulose and lignin. The main features of the FTIR spectra were attributed to the chemical bonds presenting on the main biomass component: cellulose, hemicellulose and lignin.

The infrared spectra verify FTIR spectra in the 4000 to 400 cm^{-1} range along **Figure 9**, that undewaxed sugarcane bagasse (A), dewaxed sugarcane bagasse (B), treated with H_2SO_4 sugarcane bagasse (C), cellulose (D), and lignin (E). The FTIR spectra were not significantly different among the undewaxed sugarcane bagasse (A), dewaxed sugarcane bagasse (B) and treated sugarcane bagasse with H_2SO_4 (C), which proved that no significant structure chemical changes of cellulose, hemicellulose, and lignin of the sample occurred during dewaxing treatment but used organic solvent functions in wax removal from the biomass surface and increasing the adsorption ability of biomass [80] [81].

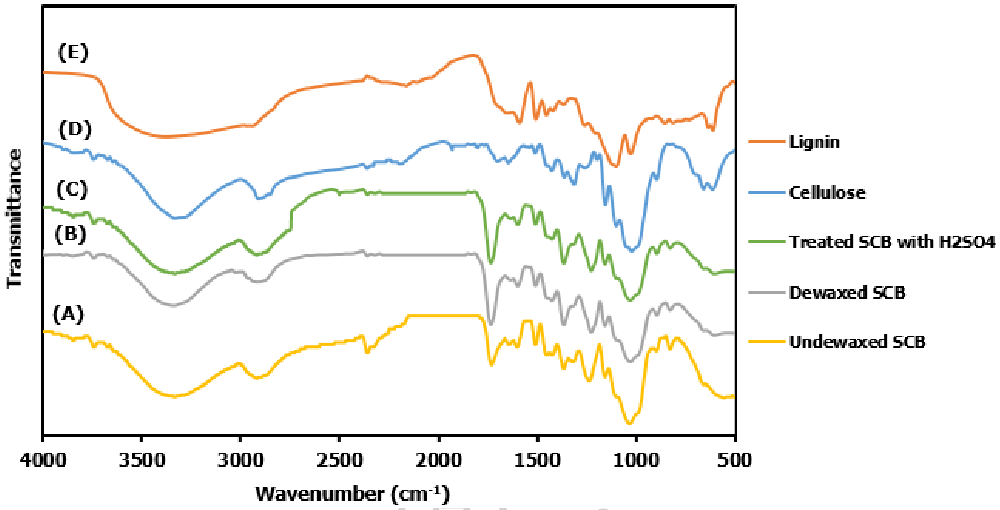

Figure 9: *Fourier transform infrared (FT-IR) spectra of: (A) Undewaxed SCB,(B) Dewaxed SCB, (C) Treated SCB with* H_2SO_4*, (D) Cellulose, and (E) Lignin*

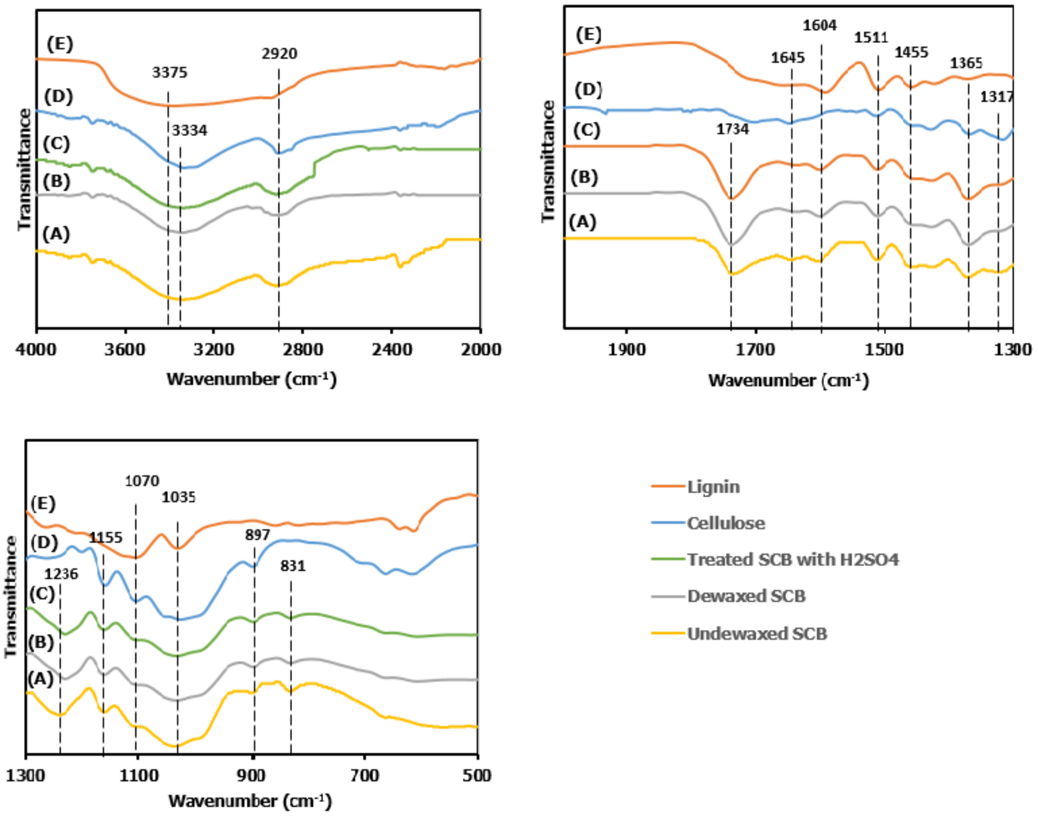

Figure 10: *FTIR spectra of the crushed in the range 4000 to 2000, 2000 to 1300, and 1300 to 500* cm^{-1}

According to **Figure 10**, it can be observed that there is a strong broad band at around 3334 cm^{-1}, which is assigned to different O–H stretching modes for all the biomass, but the peak of O-H bending shifted to higher frequency from 3334 cm^{-1} to 3375 cm^{-1} for lignin because the intramolecular hydrogen bond in a phenolic group in lignin (E) [82], and bands at around 2920 cm^{-1}, related to symmetric methyl and methylene stretching groups present in the spectra of all of the fiber components, found that most notably in the spectra for cellulose [83] [84], which after treated with H_2SO_4 the band not seem to change because that the major effect of treatment with dilute acid is hemicellulose removal of [85]. In the fingerprint region, the bands at 1511 cm^{-1} is assigned to C=C, stretching or bending vibrations of different groups present in lignin, which appear in all biomass (A, B, C, and E) except cellulose (D). The bands at 1734, 1317, 1236, 1070 and 1035 cm^{-1} are assigned to C=O, C–H, C–O–C and C–O deformation or stretching vibrations of different groups in carbohydrates [84]. A band around 1,455 cm^{-1} are reported to be a deformation of lignin CH_2 and CH_3, and 1,604, 1645 cm^{-1} is reported to be stretching of the C = C and C = O lignin aromatic ring. Moreover, the band 897 cm^{-1} is associated with β-glyosidic linkages of glucose ring in cellulose. **Table 4** summarized the results of the main functional groups in the biomass.

***Table 4:** Band component of the FTIR spectra of Undewaxed SCB, Dewaxed SCB, Treated SCB with H_2SO_4, Cellulose, and Lignin*

Band position (cm^{-1})	Functional group
3334/ 3375	O-H stretching vibration of cellulose and lignin
2920	C-H stretching vibration of cellulose
2361	CO_2 vibration (associated to CO_2 in the air)
1734	C=O stretching vibration of carbonyl in ester
1645, 1604, 1455	Aromatic ring stretching (benzene in lignin)
1511	C=C stretching vibration of aromatic (carbonyl, ketone in lignin)
1365	CH_2 bending vibration
1317, 1155	C-C, C-O stretching vibration
1236	C-O-C stretching vibration of pyranose skeletal
1070, 1035	C-O, C-H stretching vibration of guaiacyl unit in lignin
897	β-glyosidic linkages of glucose ring
831	C-H vibration of aromatic ring

Hydroxyl groups are crucial as active functional groups in cycloaddition for converted carbon dioxide and epoxide conversion to cyclic carbonate due to enhancing the ring-opening via hydrogen bond of hydroxyl with oxygen atom of epoxide molecule.

5.1.2 Thermogravimetric analysis (TGA)

TGA (A) and DTG (B) curve in **Figure 11** demonstrated thermal degradation of structural components of the sugarcane bagasse and after fractionated sugarcane bagasse into cellulose and lignin. The undewaxed SBC begin to decompose at the lower temperature because wax coat on surface wall cell are extractives, such as alkane, ester, fatty acids, and alcohol [81] consist the three steps for undewaxed SCB and the second weight loss after dewaxing and fractionating, respectively.

The first degradation step at 150°C - 235°C corresponds to a 15 %of wax consisted in undewaxed SBC, which was dewaxed from sugarcane bagasse. The second steps at about 220°C - 370°C is referred with overlapped weight loss step of hemicellulose and cellulose approximately 58 %, 65.3 %, 79.5%, 4.5 %, 18.51 % of undewaxed SCB, dewaxed SCB, cellulose, lignin (dealkaline), lignin (organosolve), respectively which was relating with previous discovery that [97] the deconvoluted of DTG curve for the main peak are cellulose decomposition, while the shoulder at lower temperatures to hemicellulose.

The last weight loss step occurred between 370°C – 500°C, is assigned to the lignin as decomposing component at 20.65 %, 19.54 %, 14.57 %, 83 % 81.1 % weight loss for the undewaxed SCB, dewaxed SCB, cellulose, lignin (dealkaline), lignin (organosolve), respectively and the residues are inorganic materials and carbon ash. These results were corresponding with Paresh et al. (2014) [86] for dealkaline lignin and William et al. (2018) [87] for organosolve lignin.

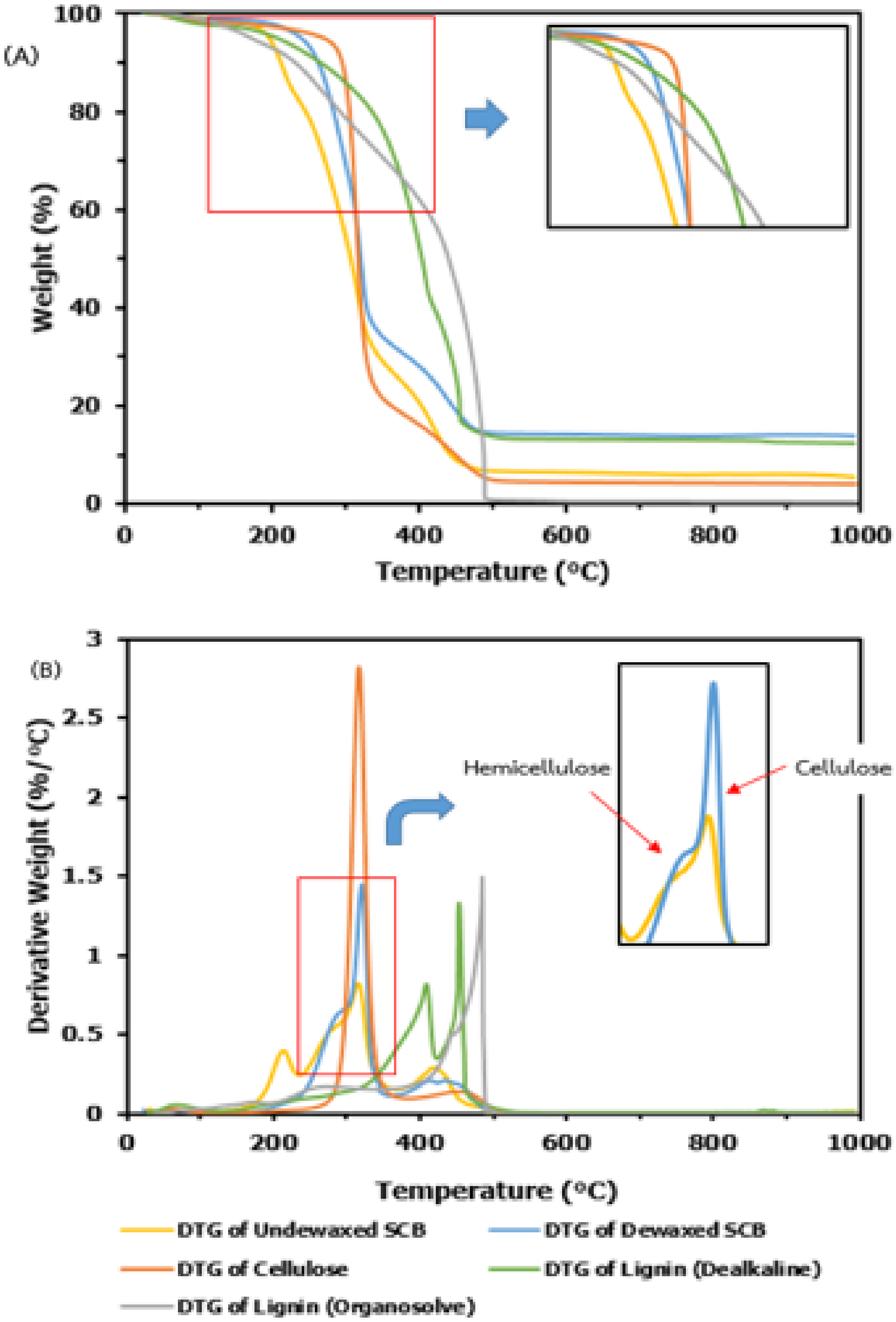

Figure 11: *(A) Thermogravimetric (TGA) and (B) Derivative Thermogravimetry (DTG) curve of: Undewaxed SCB, Dewaxed SCB, Cellulose, Lignin (Dealkaline), and Lignin (Organosolve) gated under air atmosphere 30mL/min, heating rate of 10 °C/min, and mass of 9-10 mg.*

5.1.3 N_2 Physisorption analysis (BET)

Table 5 shows specific surface areas (S_{BET}), volume pore (V_{BET}) and diameter using BET adsorption method. The highest BET values of undewaxed bagasse was 11.45 m^2/g, which corresponded to pore volume and pore diameter values. After dewaxing, treating, and fractioning, its surface area decreased and pore dimeter increased due to organic solvent disrupt the fiber shown in the table.

N_2 adsorption-desorption isotherms of undewaxed SCB and after dewaxing, treating, and fractioning are presented in **Figure 12.** It was clearly appeared that all the isotherm curve are corresponding to the type II model

Table 5: *Surface areas, pore volumes, and pore diameter of type of biomass by nitrogen physisorption.*

Type of biomass	S_{BET} (m^2/g)	Pore volume(cm^3/g)	Pore diameter (nm)
Undewaxed SCB	11.45	2.6315	7.4438
Dewaxed SCB	3.36	0.7717	20.3890
Dewaxed and treated with H_2SO_4 SCB	2.66	0.6111	23.3310
Cellulose	2.44	0.5601	15.5890
Lignin	1.40	0.3220	9.2215

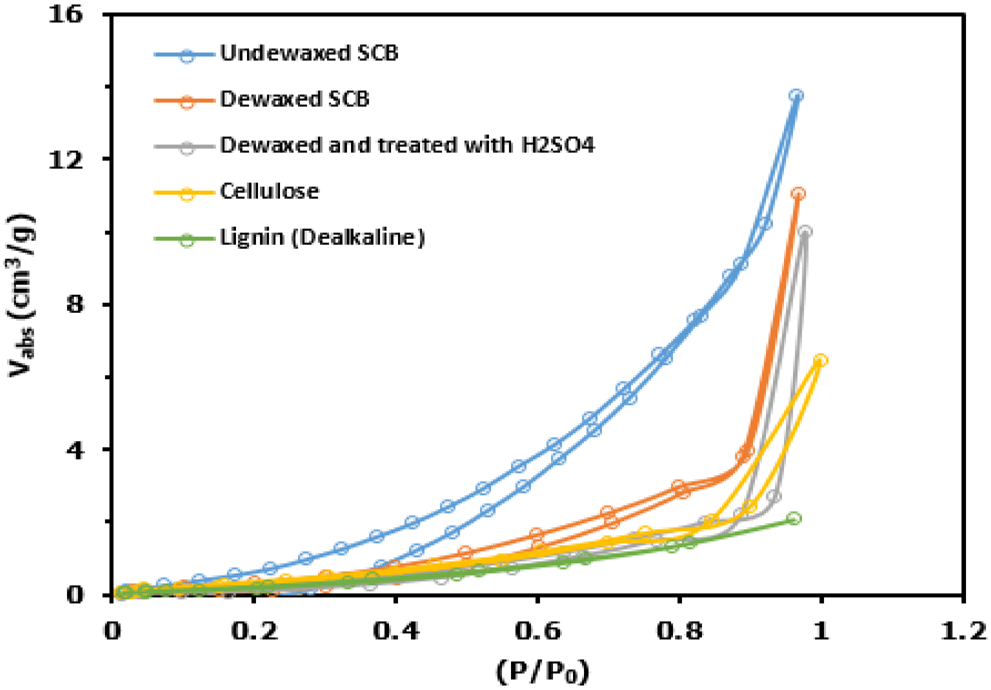

Figure 12: *N_2 adsorption-desorption isotherm of undewaxed SCB, dewaxed SCB, dewaxed and treated with H_2SO_4, cellulose, and dealkaline lignin*

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5.2 Operating conditions for synthesis 1, 2-butylene carbonate (BC) from 1, 2-butylene oxide (BO) and carbon dioxide (CO_2).

A challenge in the use of carbon dioxide as reactant in synthesis cyclic carbonate include dangers with high operating both temperature and pressure for activate bonding of carbon dioxide. In this section, the following results investigating the influence of reaction temperature, CO_2 pressure, reaction time, amount of water addition, and reusability of co-catalyst on cyclic carbonate performance are illustrated.

From **Figure 13**, shown that cycloaddition reaction required cooperation of potassium iodide catalyst and D-SCB co-catalyst wherewith obtained highly yield of BC. Moreover, very low yield BC when apply D-SCB or KI alone.

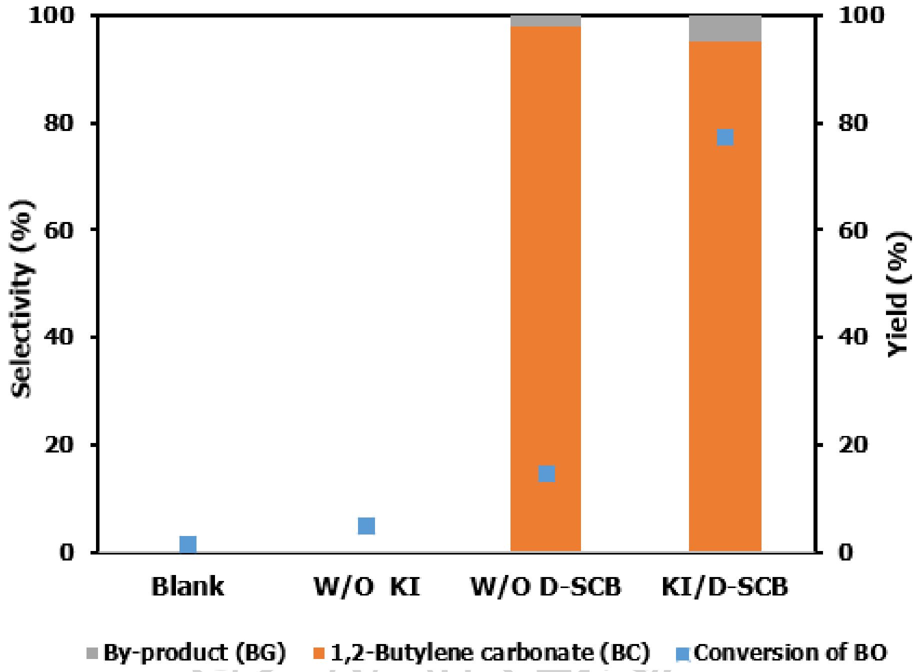


Figure 13: *Effect of catalyst (KI) and co-catalyst (D-SCB) on yield of 1, 2-butylene carbonate (BC). Experimental condition: reaction temperature of 120 °C,* CO_2 *pressure 20 bar, reaction time 6 h, stirring speed 200 rpm.*

5.2.1 Effect of reaction temperature

The reaction temperature is a major factor that effects on the formation rate of cyclic carbonate from epoxide and carbon dioxide in the catalytic system, which means the cyclic carbonate increasing along the enhancement of the reaction temperature. To investigate the effect of reaction temperature within the range of 40°C - 180°C on the yield and selectivity of BC exhibited in **Figure 14**, the experiments were carried out at 20 bar CO_2 pressure and 6 h reaction time. When the temperature increasing from 40°C to 120°C, the yield of BC dramatically increased from 4% to 73%, with the selectivity of BC stayed invariable at >93% and no significant change of the yield from 120°C to 140°C. However, further increase in the reaction temperature to

180 °C, BC yield a little decrease due to decomposition of 1,2-butylene carbonate at high temperature no significant change of BC selectivity [88].

Based on the experimental results, it can be concluded that 120 °C was the suitable reaction temperature. Hence, all the subsequent experiments for the BC synthesis were performed at the reaction temperature of 120 °C.

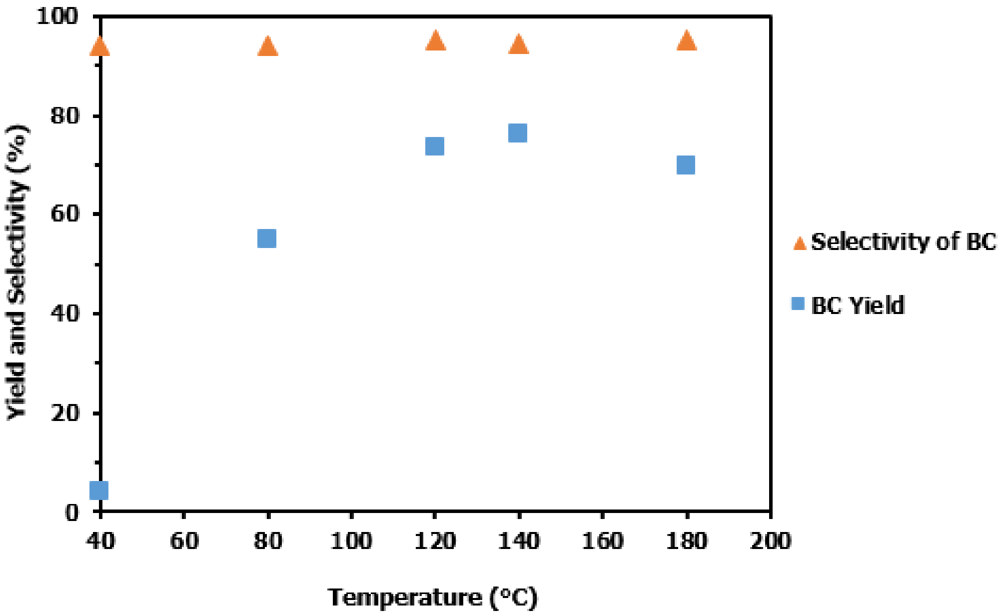


Figure 14: *Effect of reaction temperature on yield and seletivity of 1,2-butylene carbonate (BC) over KI/D-SCB. Experimental condition:* CO_2 *pressure 20 bar, reaction time 6 h, stirring speed 200 rpm.*

5.2.2 Effect of CO_2 Pressure

CO_2 pressure is one of the most significant factors to affecting the cycloaddition reaction with 1, 2 -butylene oxide, by the pressure required dependent on activity of catalyst used. The effect of initial CO_2 pressure was studied and the results are illustrated in **Figure 15**, cycloaddition reaction was carried out at CO_2 pressure 10, 15, 20, 25 and 30 bar to study its effect on BC selectivity and yield. All experiments were carried out at 120°C reaction temperature for 6 h. It can be seen from Figure 12 that when the CO_2 pressure increased from 5 bar to 20 bar, BC yield increases from 25% to 73% and selectivity stayed invariable at 93%. A possible explanation was that more CO_2 can be dissolved in BO as the increase of the initial reaction pressure [94]. However, when the initial of CO_2 pressure further increased from 20 to 30 bar led to the slight decrease of yield from 73% to 67%. High CO_2 pressure can effectively improve the absorption of CO_2 into the liquid of epoxide, contributing to a shift in the equilibrium towards the formation of BC yield. However, the cycloaddition reaction is vapor-liquid system, with the increase of CO_2 pressure, the concentration of BO decreased in liquid phase but increased in the vapor phase, leading to decreased of BC yield due to possibly hindering the interaction between epoxide and the catalyst [95] [96]. According Fujita et al. (2009) [89], multiphase reaction catalytic systems implicated with dense phase CO_2 and counter-phase whether it is a solvent, a substrate, or a catalyst show in **Figure 16**. When pressurizing CO_2 into liquid-phase , it will expand and dissolve in liquid phase as the rate enhanced follow at a CO_2 pressure but if CO_2 concentration excess, it will obstruct the interaction between reactant with catalyst.

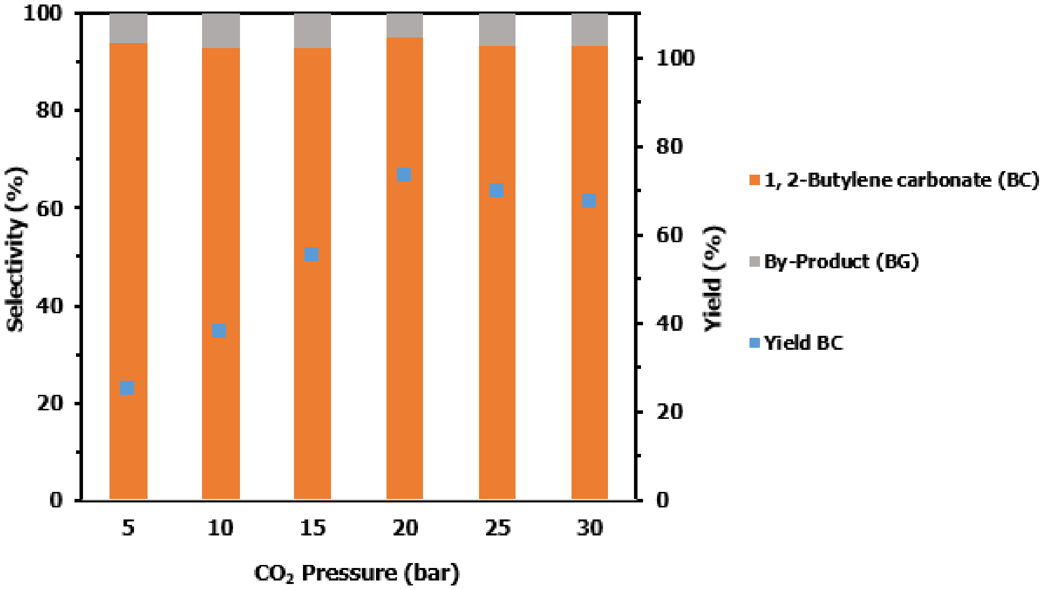
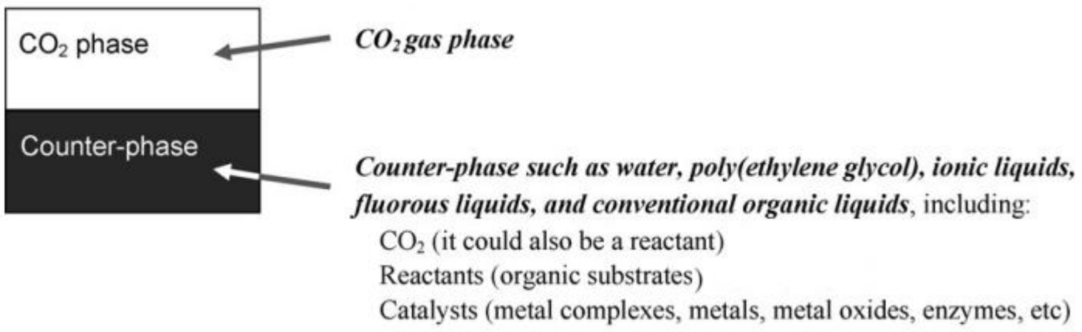


Figure 15: *Effect of CO_2 pressure on synthesis 1,2-butylene carbonate (BC) over KI/D-SCB. Experimental condition: reaction temperature of 120 °C,6 h. reaction time, stirring speed 200 rpm.*



Counter-phase such as water, poly(ethylene glycol), ionic liquids, fluorous liquids, and conventional organic liquids, including:
CO_2 (it could also be a reactant)
Reactants (organic substrates)
Catalysts (metal complexes, metals, metal oxides, enzymes, etc)

Figure 16: *Multiphase catalytic reaction system using dense phase CO_2 and various counter-phase [89].*

Hence, the suitable CO_2 pressure for operating this cycloaddition reaction is equal to 20 bar, which obtains 71 % yield of BC.

5.2.3 Effect of reaction time

Cycloaddition reaction of BO and CO_2 was studied at different reaction time to determine the optimum reaction time for synthesis of BC using KI/D-SCB catalytic system. The effect of time on catalytic activity was conducted at 120°C and 20 bar of CO_2 pressure. **Figure 17**, illustrates the effect of reaction time on the synthesis of BC. The rapidly reaction rate was in the initial stage, relating with an increase of BC yield from 32% to 68% when reaction time increase from 0.5 h to 4 h and the selectivity to BO is above 92% within the 0.5-8 h range. The further increase of reaction time from 4 h to 6 h resulted in a small increase in the BC yield and constantly at 8 h since for initial times, owing to highly epoxide concentration when prolonged reaction time generated cyclic carbonate product accumulation [90] [91].

It can be concluded that the reaction attains equilibrium at 6 h and the reaction time beyond 6 h would not be beneficial for this reactive system. As a conclusion, 6 h reaction time was suitable for this system.

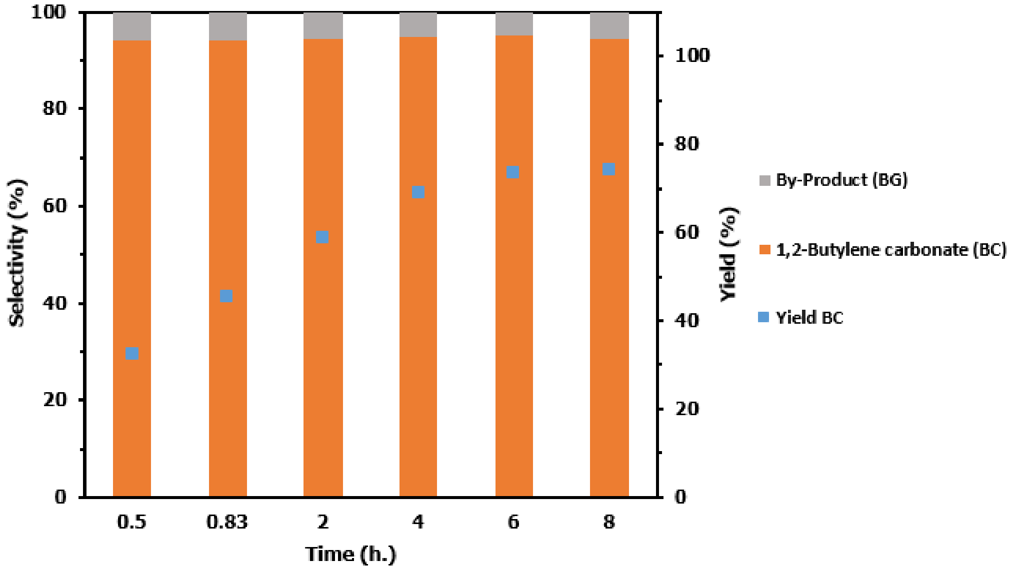


Figure 17: *Effect of reaction time on the yield of 1,2-butylene carbonate (BC) over KI/D-SCB. Experimental condition: reaction temperature of 120 °C, CO_2 pressure 20 bar, stirring speed 200 rpm.*

5.2.3.1 Kinetic study

The kinetic of the synthesis 1, 2-butylene carbonate (BO) over KI/D-SCB catalytic system was studied. The concentration of unreacted BO was calculated by plotting peak area ratio of BO/Butanol (as an internal standard). The order of cycloaddition reaction was estimated using following equation (1). First, it could be assumed that concentration of KI catalyst and D-SCB co-catalyst were constant during the reaction, while carbon dioxide was present in large excess, this can be simplified to equation (2).

$$\text{Rate} = k\,[\text{BO}]^{a}[\text{CO}_2]^{b}[\text{KI}]^{c}[\text{D-SCB}]^{d} \qquad (1)$$

$$\text{Rate} = k_{obs}\,[\text{BO}]^{a}\ \ ,k_{obs} = k\,[\text{CO}_2]^{b}[\text{KI}]^{c}[\text{D-SCB}]^{d} \qquad (2)$$

Where [BO] is the BO concentration, a is the order of the reaction, t is time, k_{obs} is the observed pseudo-first-order constant for BO conversion b, a, and d = 1

From equation (2) can be written as

$$\text{Rate} = -\frac{\mathbf{d[BO]}}{\mathbf{dt}} = k_{obs}\,[\text{BO}]^{a} \qquad (3)$$

Integrating equation (3) as function of time brings about the following equation:

$$\text{In}\,[\text{BO}] = -k_{obs}\,t + \ln\,[\text{BO}]_0\ ,\ [\text{BO}]_0 = \text{initial concentration of BO} \qquad (4)$$

Based on equation (4) graphs were plotted as In [BO]/[BO]0 versus time shown in **Figure 18**. After calculation the linear trend line has not as much R^2 value as in the second-order. Therefore order kinetic of cycloaddition of BO and CO_2 over KI/D-SCB is assumed to be not first-order, then the second-order that is more prefer to apply in the prediction of reaction kinetic along **Figure 19**.

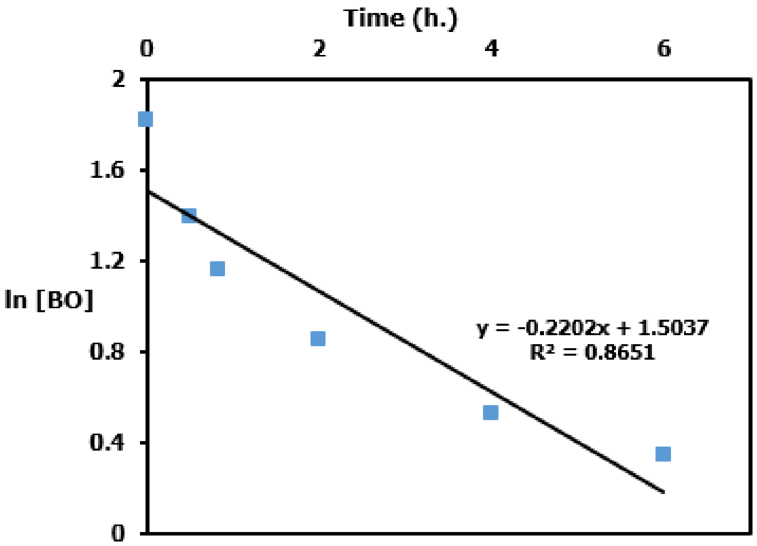


Figure 18: *First order plot ln [BO] versus time. Experimental condition: $[BO]_0$ = 30 mmol, KI = 0.75 mmol, D-SCB = 150 mg, reaction temperature of 120 °C, CO_2 pressure 20 bar, stirring speed 200 rpm.*

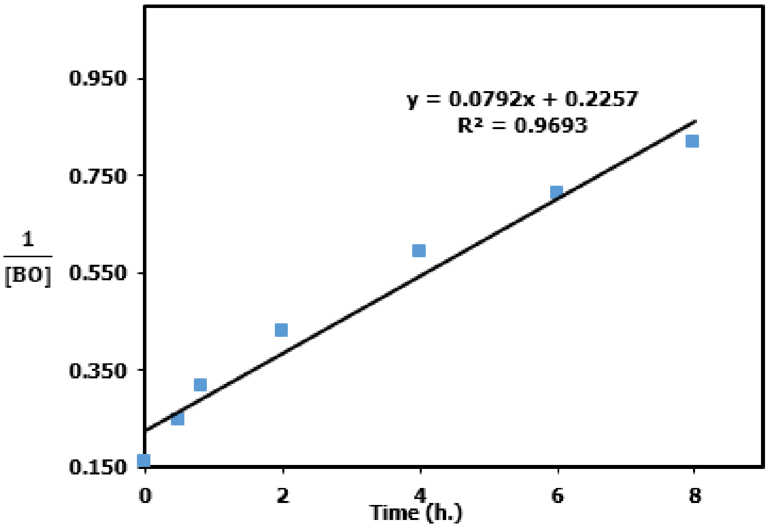


Figure 19: *Second order plot 1/[BO] versus time. Experimental condition: $[BO]_0$ = 30 mmol, KI = 0.75 mmol, D-SCB = 150 mg, reaction temperature of 120 °C, CO_2 pressure 20 bar, stirring speed 200 rpm.*

When consider **Figure 18 and 19** to predict the order of the reaction, it was observed that the trend line of second-order provides R^2 value nearby 1 over first order. The slope of graphs is rate constant (k_{obs}), which equals to 0.0792 M^{-1} h^{-1} of this reaction for the KI/D-SCB catalyst system.

5.2.4 Effect of water addition

Water played a significant role in the synthesis of PC, relating to the discovery by Zhang et al. (2009) [92] investigating the effect of addition water on ionic liquid and alkali halide catalysts activities by obtaining an increase of PO conversion and PC yield; The low ratio of H_2O/PO from 0 to 0.33 rapidly increased PO conversion and PC yield but selectivity little decrease. When high water ratio from 0 to 1.95, it provided constantly PO but PC yield and selectivity decreases quickly because the side reaction occurring to form 1, 2-propylene glycol (PG). For KI/D-SCB catalytic system in **Figure 20**, experiments were carried out in which the ratio of H_2O/BO was increased from 0 to 1. The result of BO conversion little enhanced from 77% to 90% after adding water into the reaction. On the other hand yield and selectivity of BC decreases because of the formation of 1, 2-butylene glycol (BG), which is by-product from the hydrolysis of 1, 2-butylene oxide (BO) with water shown in **Figure 21** [98]. For this catalytic system, using D-SCB as co-catalyst together with KI can provide high conversion and yield, unnecessary to add water because D-SCB is biopolymer containing hydroxyl/carbonyl group in structure, which can be accelerate ring-opening with the oxygen atom of epoxide via hydrogen bonding.

Therefore, the addition water without D-SCB was then carried out to study the conversion of BO and selectivity of by-product. An increase of little water leads to greatly increase of BO conversion because of –OH composition in water can be improve the activity for synthesis of BC. However, adding high amount of water enhances the side reaction, results in decrease of selectivity as shown in **Figure 22**.

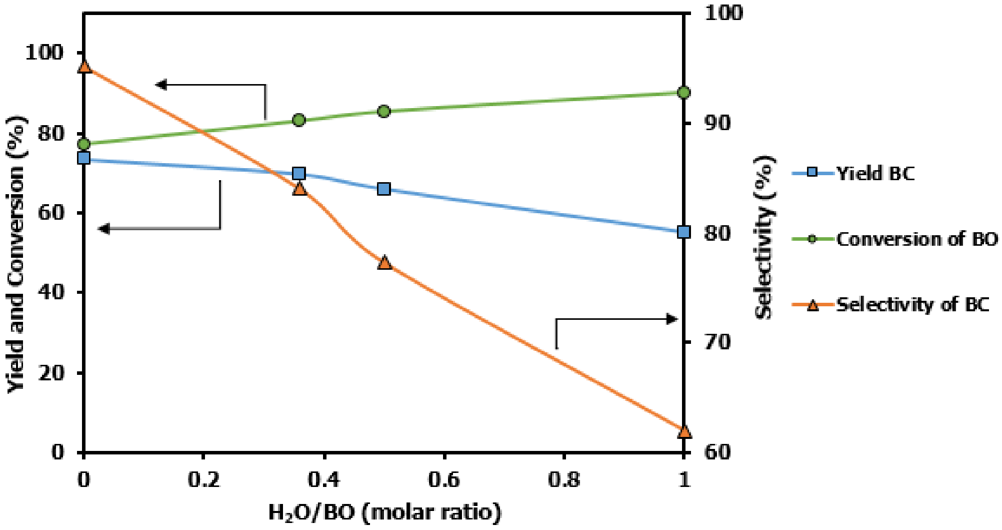


Figure 20: *Effect of water addition on synthesis of 1,2-butylene carbonate (BC) over KI/D-SCB. Experimental condition: reaction temperature of 120 °C, CO_2 pressure 20 bar, reaction time 6 h, stirring speed 200 rpm.*

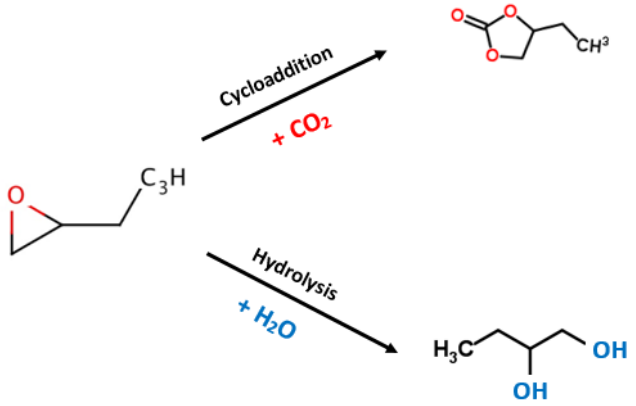


Figure 21: *Pathway of reaction of cycloaddition of CO_2 (main reaction) and hydrolysis of H_2O (side-reaction)*

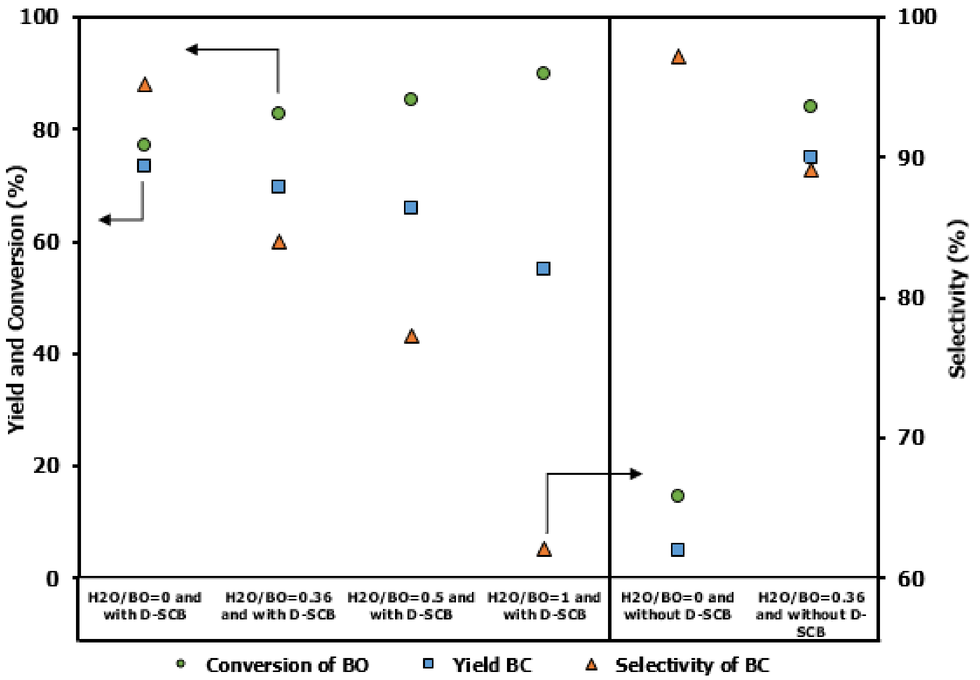


Figure 22: *Effect of water addition on synthesis of 1,2-butylene carbonate (BC) without D-SCB co-catalyst. Experimental condition: reaction temperature of 120 °C,* CO_2 *pressure 20 bar, reaction time 6 h, stirring speed 200 rpm.*

5.2.5 Effect of type of biomass

Biomass is a sustainable source of organic carbon in earth for the production of fuels and fine chemicals, which is the most abundant, bio-renewable resource and decrease CO_2 emissions in atmospheric pollution. Many researcher study lignocellulosic biomass for a renewable feedstock of production biofuels and biomaterials. From economic point of view, lignocellulosic biomass can be produced quickly and at lower cost than other agriculturally important biofuels feedstocks such as corn starch, soybeans and sugarcane [93].

In this research, D-SCB, a waste agricultural from sugar industrial, was applied as a new cooperative catalytic system. The influence of different components of dewaxed sugarcane bagasse (D-SCB), dewaxed SCB and treated H_2SO_4, such as cellulose, lignin (Dealkaline) and lignin (Organosolve) on reactivity of structure of the cycloaddition reaction were investigated. The reaction was then carried out at reaction temperature of 120 °C, 20 bar CO_2 pressure and 6 h reaction time. According to the results dealkaline lignin achieved the most BO conversion and BC yield with provided the BO conversion 92% and BC yield 87%. Though the organosolve lignin provided highly yield BC, it has non reusability due to organosolve lignin dissolve in organic, while after treated with H_2SO_4 BO conversion and BC yield slightly increased due to dilute acid pretreatment removes hemicellulose from sugarcane bagasse disrupting the cell wall with a loose matrix leads to large pore and easily contacting between biomass with reactant. The alphatic hydroxyl groups, cellulose acts as low reactivity co-catalyst when compared to the phenolic hydroxyl found in lignin structure. Therefore, dealkaline lignin is the best co-catalyst for this cycloaddition reaction [101].

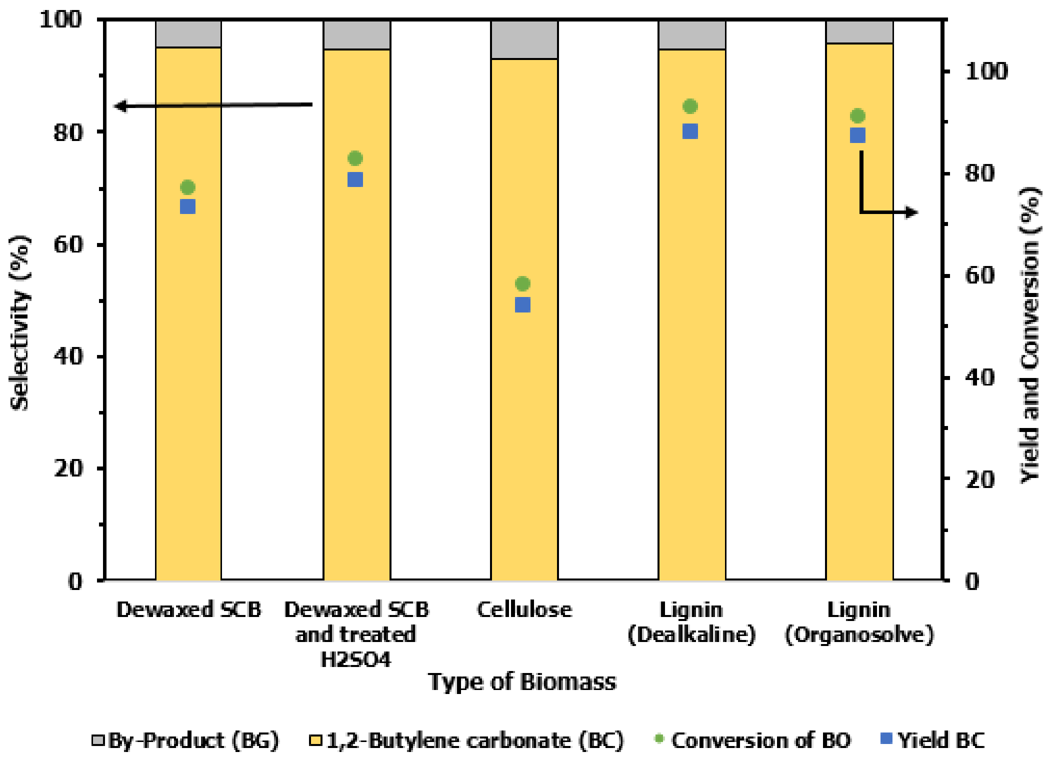


Figure 23: *Comparative of type of biomass for synthesis 1,2-butylene carbonate (BC) from 1,2-butylene oxide (BO) Experimental condition: reaction temperature of 120°C, CO_2 pressure 20 bar, reaction time 6 h, stirring speed 200 rpm.*

5.2.5.1 Determination hydroxyl content by phthalation substitution

As shown in **Table 5**, the substitution hydroxyl content (SHC) of phthalated dewaxed SCB, cellulose, and dealkaline lignin were 1.63, 0.23, and 1.80, respectively. Indicating the reactivity order of lignin was the highest when compare with cellulose and dewaxed SCB during the homogeneous esterification without any catalysts, which can be conclude that reactivity order of biomass followed dealkaline lignin > dewaxed SCB > cellulose because in structure of dealkaline lignin have rice phenolic hydroxyl per gram of biomass, which active more than aliphatic hydroxyl as result corresponded with Wang et al (2017) [94] and Liu et al (2017) [95]. Therewith, they studied reactivity order of phenolic hydroxyl too, it found that S-OH (Syringyl) > G-OH (Guaiacyl) > H-OH (p-Hydroxy phenyl).

Figure 24 present the reaction of phthalic anhydride with cellulose and dealkaline lignin, which was carried out in 5 g [Bmim]Cl ionic liquid with 0.25 g biomass under 80°C with agitation for 4 h to reach a solution. Phthalic anhydride was added to solution with the ratio of phthalic anhydride to cellulose or dealkaline lignin at 50 mmol/g. The reaction was performed at 80°C for 90 min with agitation, after that the mixture was slowly poured in to isopropanol, washed for remove unreacted anhydride and by-product, and then dried for 24 h.

The substitution hydroxyl contents (SHC) of the phthalated cellulose or dealkaline lignin were determined by the back-titration method with the excess sodium hydroxide (NaOH) 0.1 M and titrated with hydrochloric acid (HCl) 0.025 M. The titration was repeat three times and average. The substituted hydroxyl contents of biomass sample was calculated by using the according equation (5).

$$\mathrm{SHC} = \frac{C_{HCl} \times V_{HCl} \times C_{NaOH} \times V_{NaOH}}{2} \times \frac{100}{m} \qquad (5)$$

Where: SHC (mmol/g) is the substituted hydroxyl contents

m (g) is the weight of sample for analyzed

C_{HCl} (M) is the molarity of HCl standard solution

V_{HCl} (ML) is the consumed volume of HCl standard solution

C_{NaOH} (M) is the molarity of NaOH standard solution

V_{NaOH} (mL) is the consumed volume of NaOH standard solution

Table 6: The substituted hydroxyl content (SHC) of the biomass sample (D-SCB, Cellulose, and Dealkaline lignin)

	# 1	# 2	# 3	Substituted hydroxyl content (SHC) (mmol/g)
D-SCB	1.6480	1.6060	1.6242	**1.6260**
Cellulose	0.2409	0.2386	0.2159	**0.2318**
Dealkaline Lignin	1.7894	1.8145	1.7980	**1.8006**

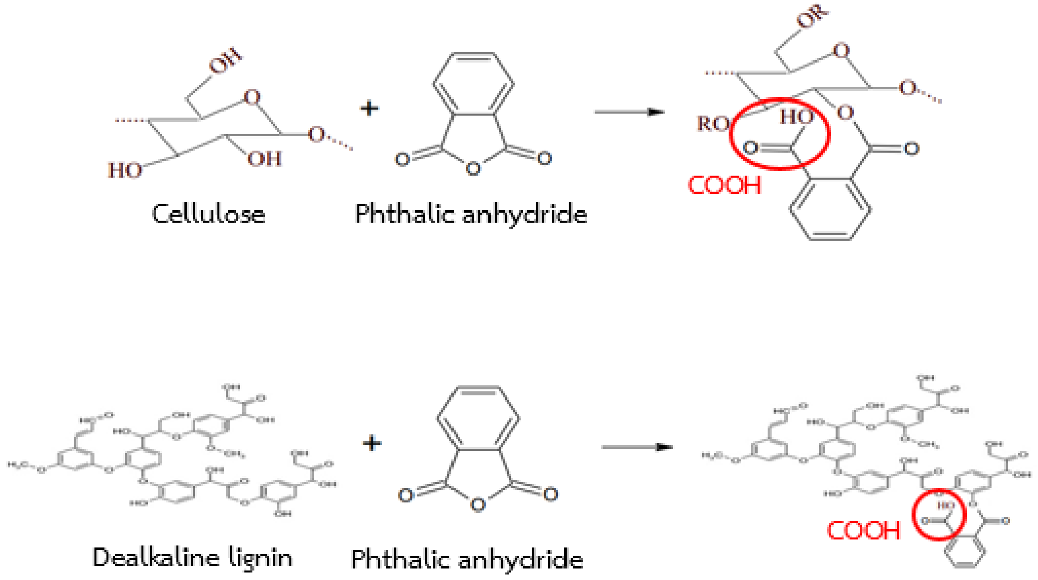


Figure 24: *The reaction route of phthalic anhydride with cellulose, dealkaline lignin*

5.2.6 Co-catalyst reusability and stability experiments

When comparing different component co-catalyst dewaxed SCB, dewaxed and treated SCB with H_2SO_4, cellulose, and dealkaline lignin, it was obvious that dealkaline lignin provides the most BC conversion and yield.

The reusability of the KI/dealkaline lignin catalytic system was examined under the suitable conditions for the cycloaddition reaction of BO and carbon dioxide. In each cycle, the catalytic system was recovered via simple filtration, and then used for the next cycle without any purification. The results are then shown in **Figure 25**. It can be assumed that the co-catalyst could be reusable for five times with the high yield, while the selectivity of the BC product remains constant. After the 5th cycle, the co-catalyst provided 81% BC yield and 97% selectivity, which demonstrates that dealkaline lignin has stability and reusability under suitable conditions. With this mild conditions, biomass still not decompose as: decomposition temperature occurred at 250 °C for cellulose and 350 °C for dealkaline lignin

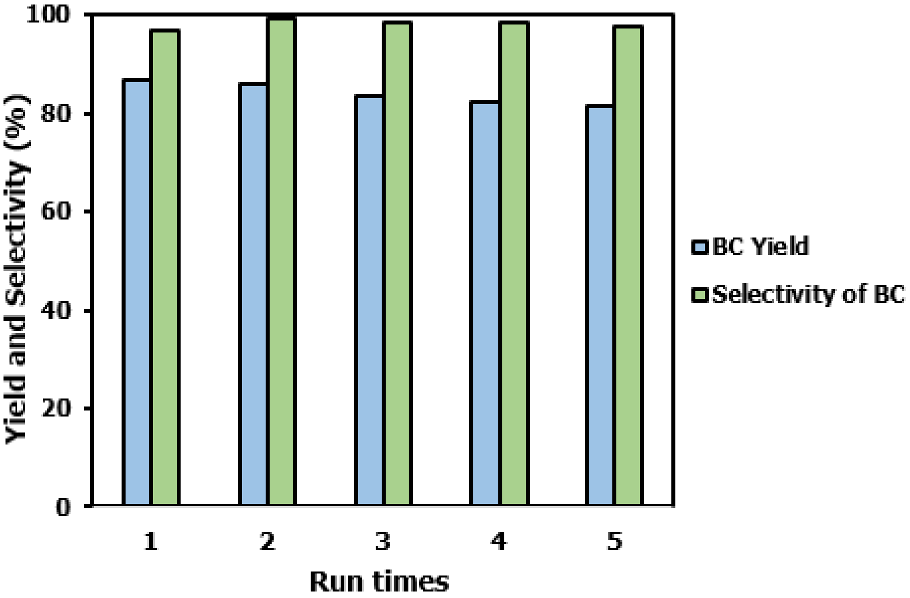


Figure 25: Co-catalyst recyclability for synthesis 1,2-butylene carbonate (BC) over KI/Lignin Experimental condition: reaction temperature of 120 °C, CO_2 pressure 20 bar, reaction time 6 h, stirring speed 200 rpm.

5.3 Characterization of the mixture products of 1,2-butylene carbonate (BC) and 1,2-butylene glycol (BG) from cycloaddition of 1,2-butylene oxide (BO) and carbon dioxide (CO_2)

The products were confirmed structural identification by nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra, respectively by using deuteron chloroform ($CDCl_3$) as solvent. The results of NMR spectra are shown in Figure 26-31

5.3.1 1,2-Butylene oxide (BO; Reactant)

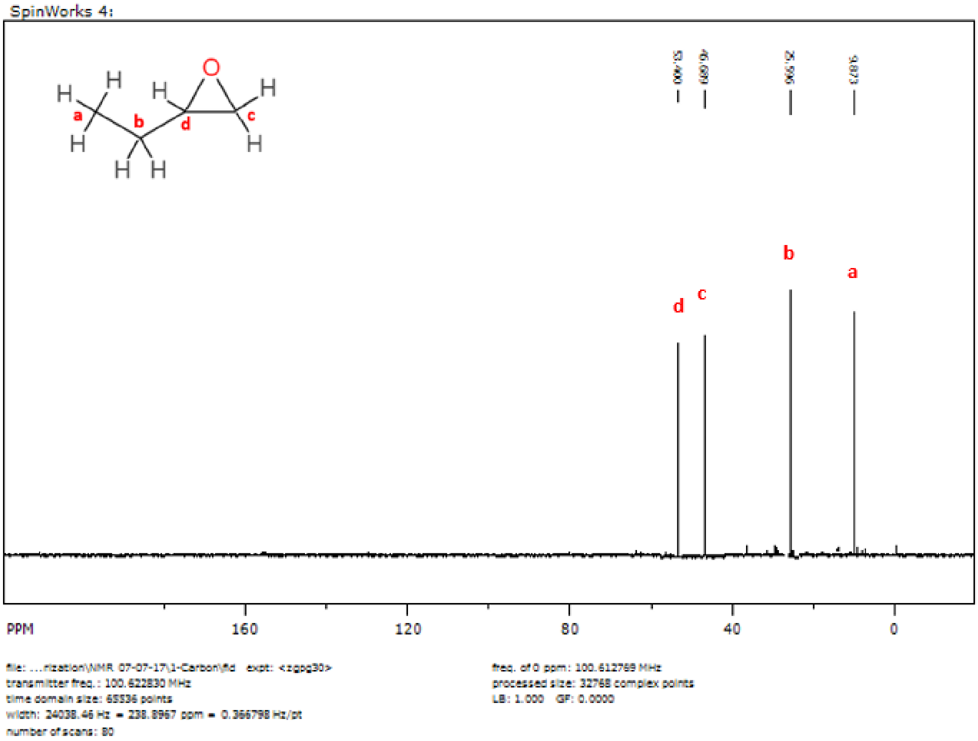
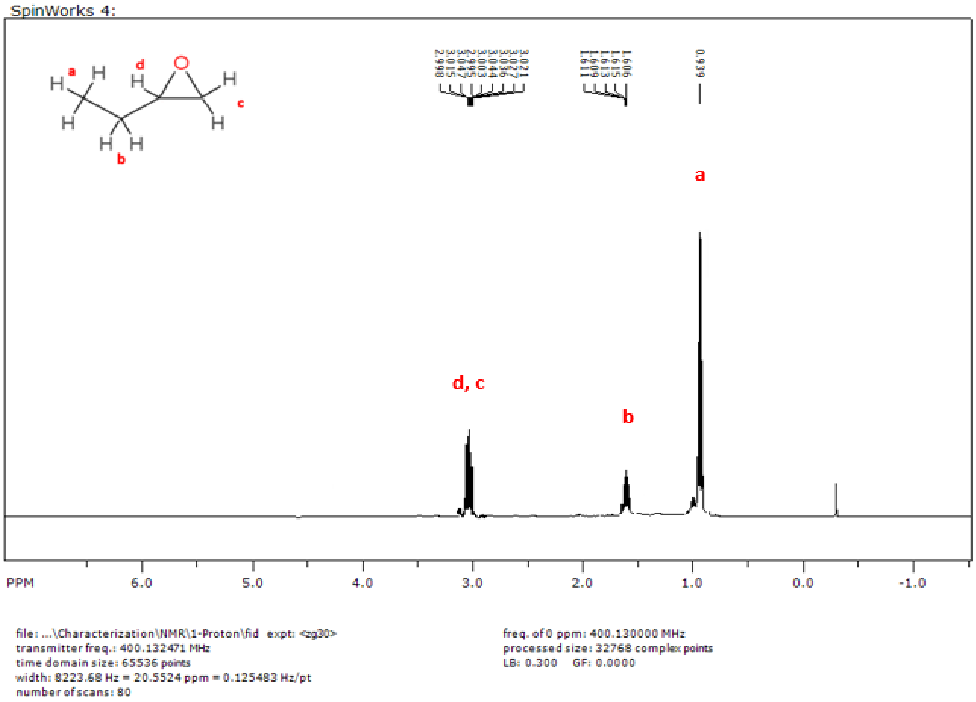


Figure 26: *^{13}C-NMR spectra of 1, 2-butylene oxide (100 MHz, $CDCl_3$): $\delta = 9.873$ (CH_3), 25.996 (CH_2), 46.689 (CH_2), 53.4 (CH) ppm*



file: ...\Characterization\NMR\1-Proton\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8223.68 Hz = 20.5524 ppm = 0.125483 Hz/pt
number of scans: 80

freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

Figure 27: *^{1}H-NMR spectra of 1, 2-butylene oxide (400 MHz, $CDCl_3$): δ = 0.939 (t, $^3J_{H,\,H}$ =7.5 Hz, 3H), 1.606-1.615 (m, 2H), 2.995-3.003 (dd, $^3J_{H,\,H}$ =7.7 Hz, $^2J_{H,\,H}$ =4.1), 3.01 (ddt, $J_{H,\,H}$ = 8.1 Hz, $^3J_{H,\,H}$ =7.7 Hz, $^2J_{H,\,H}$ = 5.4 Hz), 3.03 (m, 1H) ppm.*

5.3.2 1,2-Butylene carbonate (BC; Product)

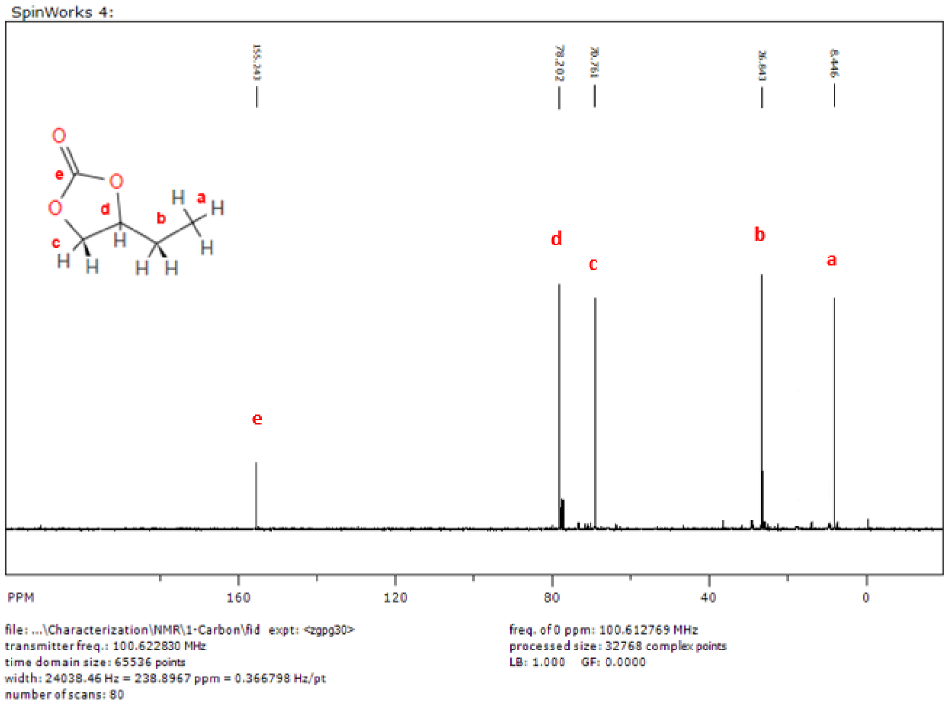
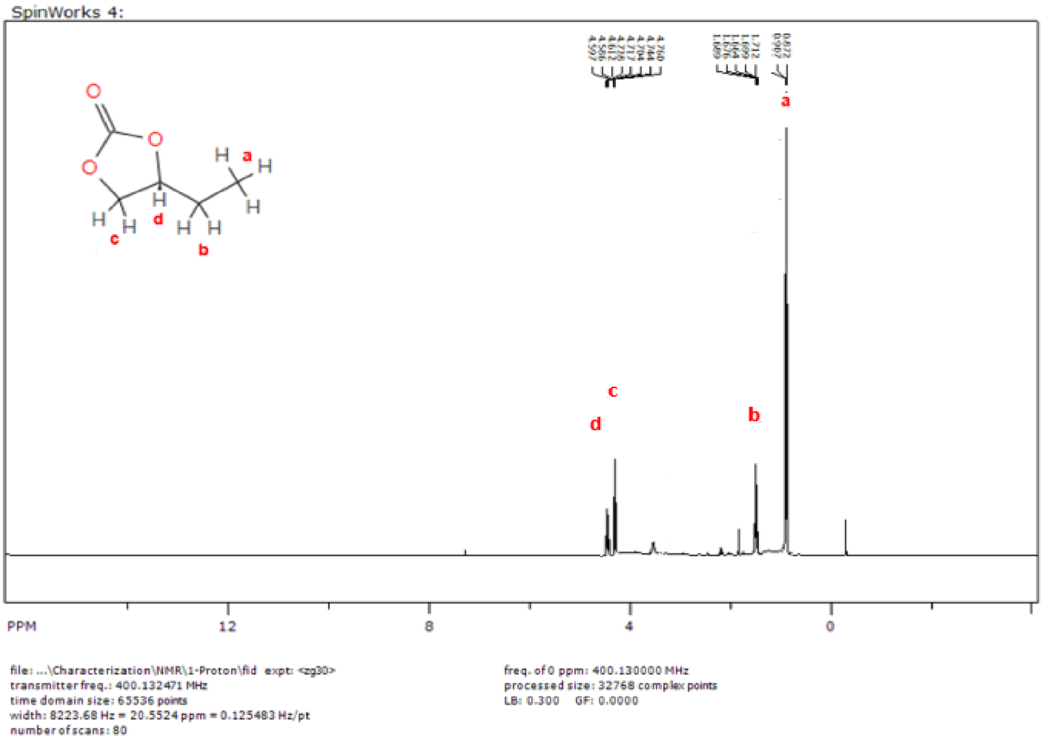


Figure 28: *^{13}C-NMR spectra of 1, 2-butylene carbonate (100 MHz, $CDCl_3$): δ = 8.446 (CH_3), 26.843 (CH_2), 70.761 (CH_2), 78.202 (CH), 155.243 (C=O) ppm*

From **Figure 28**, it was clear that the cycloaddition reaction of 1, 2-butylene oxide (BO) and carbon dioxide produce 1, 2-butylene carbonate (BC) from inserting of carbon dioxide in structure, corresponding with the appeared peak of C=O at the position of 155.243 ppm.



file: ...\Characterization\NMR\1-Proton\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8223.68 Hz = 20.5524 ppm = 0.125483 Hz/pt
number of scans: 80

freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

Figure 29: *^{1}H-NMR spectra of 1, 2-butylene carbonate (400 MHz, $CDCl_3$): δ = 0.872-0.907 (t, $^{3}J_{H,H}$ =7.6 Hz, 3H), 1.664 -1.712 (m, 2H), 4.599 (dd, $^{3}J_{H,H}$ = 7.8 Hz, $^{2}J_{H,H}$ = 7.9 Hz, 1H), 4.704 – 4.760 (m, 1H) ppm.*

5.3.3 1,2-Butylene carbonate (BC; Product) and 1,2-Butylene glycol (BG; By-Product)

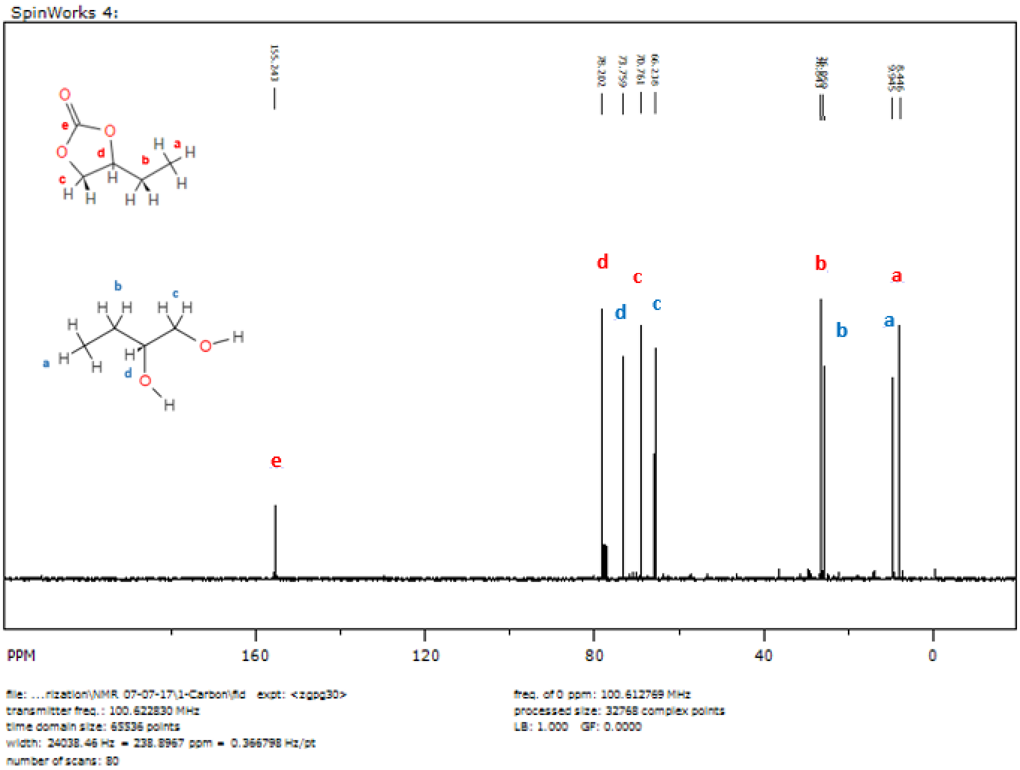


Figure 30: *^{13}C-NMR spectra of 1, 2-butylene carbonate (100 MHz, $CDCl_3$): δ = 8.446 (CH_3), 26.843 (CH_2), 70.761 (CH_2), 78.202 (CH), 155.243 (C=O) ppm and ^{13}C-NMR spectra of 1, 2-butylene glycol (100 MHz, $CDCl_3$): δ = 9.94 (CH_3), 26.06 (CH_2), 66.24 (CH_2), 73.76 (CH) ppm*

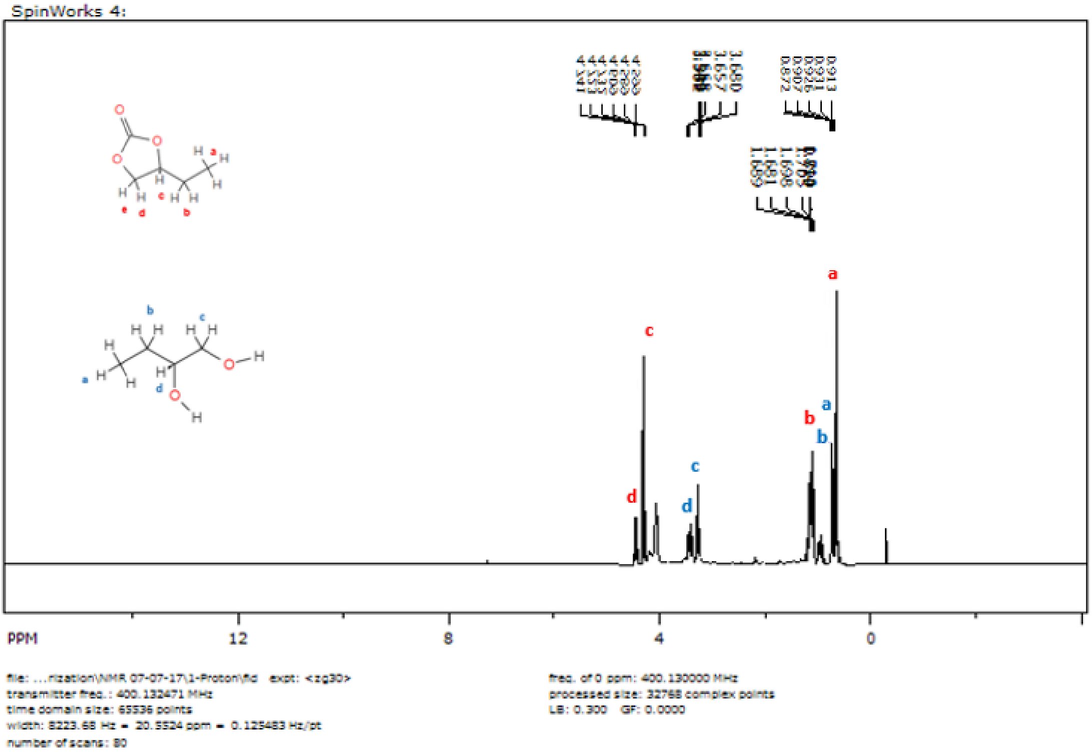


Figure 31: *^{1}H-NMR spectra of 1, 2-butylene carbonate (400 MHz, $CDCl_3$): δ = 0.872-0.907 (t, $^{3}J_{H,H}$ =7.6 Hz, 3H), 1.664 -1.712 (m, 2H), 4.599 (dd, $^{3}J_{H,H}$ = 7.8 Hz, $^{2}J_{H,H}$ = 7.9 Hz, 1H), 4.704 – 4.760 (m, 1H) ppm and ^{1}H-NMR spectra of 1, 2-butylene glycol (400 MHz, $CDCl_3$): δ = 0.926 (t, $^{3}J_{H,H}$ =7.6 Hz, 3H), 1.681-1.698 (m, 2H), 3.546-3.562 (dd, $^{3}J_{H,H}$ =8.4 Hz, $^{2}J_{H,H}$ =7.1 Hz, 1H), 3.657-3.680 (m, 1H) ppm*

5.4 Reaction mechanisms

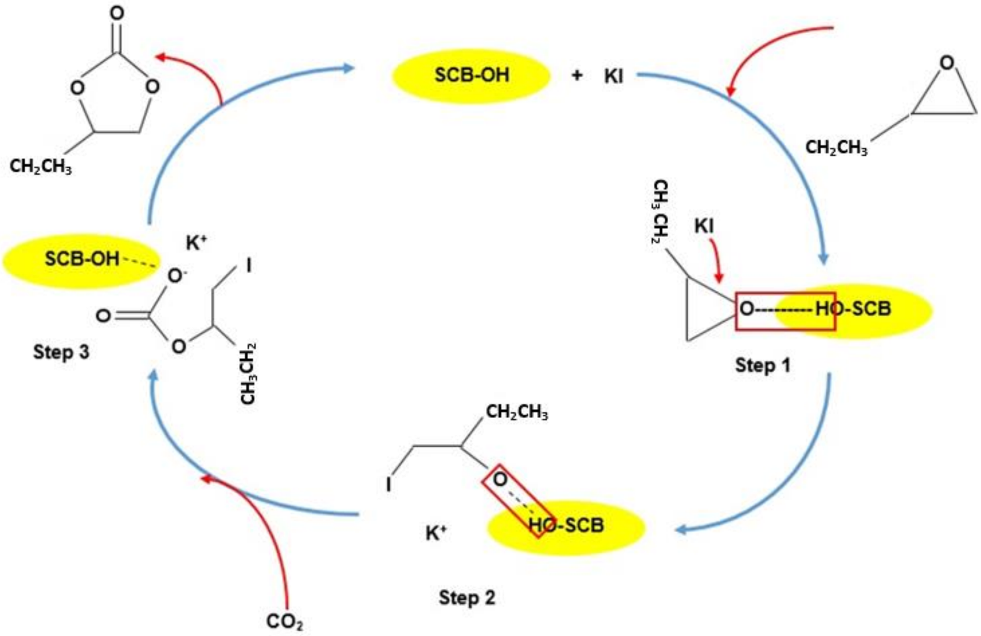


Figure 32: *Plausible mechanism for KI/D-SCB catalytic system of synthesis 1,2-butylene carbonate*

The mechanism for conversion of carbon dioxide with 1, 2-butylene oxide to produce 1, 2-butylene carbonate involve three major steps: epoxide ring-opening, carbon dioxide insertion and ring-closure to form the five membered cyclic carbonate shown in **Figure 32**.

Firstly, the hydroxyl groups in D-SCB activation of the epoxide by a hydrogen bond with an O atom together with nucleophilic attacks on the less hindered carbon atom of the epoxide in the activation of the ring of epoxide by I$^-$ anion of KI. Secondly, CO_2 insertion reaction appears into the complex. Thirdly, ring-closure forms the cyclic carbonate and regenerates catalyst.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

6.1.1 Cycloaddition reaction of 1, 2-butylene oxide (BO)

In this study, the utilization of lignocellulosic component for example dewaxed sugarcane bagasse (D-SCB), cellulose, and dealkaline lignin as a co-catalyst with potassium iodide (KI) on the cycloaddition reaction of 1, 2-butylene oxide (BO) and carbon dioxide to produce 1, 2-butylene carbonate (BC) was successful. The dealkaline lignin provided the most BC yield and conversion when compare with D-SCB with cellulose, it obtained BO conversion 92% and 87% BC yield, respectively. The rich hydroxyl groups in structure of biomass lead to coordinate with oxygen atoms of 1, 2-butylene oxide (BO) and activate opening-ring of epoxide through hydrogen bonding. Furtermore, the structure of hydroxyl groups has significantly effect on reactivity with epoxide. The phenolic hydroxyl structure in dealkaline lignin has much more reactive than the aliphatic hydroxyl in cellulose. The suitable operating conditions for this reaction to achieve high BC yield are as followed 120 °C reaction temperature, 20 bar CO_2 pressure, and 6 h reaction time. However, the amount of water addition leads to a little increase in conversion of BO according to adding hydroxyl groups, but rapidly decrease in selectivity and yield due to hydrolysis reaction of BO with water. In addition, the co-catalyst could be reused several times with high activity and selectivity.

6.2 Recommendations

From the results, lignocellulosic provides beneficial alternative for an ideal green process its rich in function groups of hydroxyl/carbonyl for activates reaction.

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