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Catalytic synthesis of diethyl carbonate via one-pot reaction from carbon dioxide, ethanol, and epoxide

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Abstract. Carbon dioxide is one of the responsible substances of the global warming effect. Gasoline consumption had increased significantly each year, it leads to the intense elevation of particulate matter and carbon dioxide compound in the atmosphere, which are the products of combustion of fuel. Carbon dioxide is possibly converted to high valued compound, diethyl carbonate (DEC) is one of the alternative compounds that is being employed as an additive for fuel to diminish the emission with increasing octane number of the fuel. The objective of this study was to research and develop a technology of direct synthesis of DEC from Carbon dioxide, ethanol, epoxide as dehydrating agent and KI/Sodium Ethoxide and KI/Zeolite catalysts. Operation condition in this experiment had an initial pressure of 35 bar and temperature of 170°C. Further, the effects of KI/Sodium Ethoxide and KI/Zeolite catalysts were examined to the performance of DEC synthesis. In addition, the influence of the type of dehydrating agent (epoxide), which was propylene oxide and butylene oxide was investigated as well. Subsequently, the products were analyzed using gas chromatography-mass spectrometry for qualitative analysis and gas chromatography for quantitative analysis. The results showed that DEC was successfully synthesis from carbon dioxide, and the optimum yield was obtained from the use of KI/Zeolite catalyst, propylene oxide as a dehydrating agent.

1. Introduction

Nowadays, human activities cause an increase in the concentration of CO₂ in the atmosphere. The increase in CO₂ concentration has an impact on increasing temperatures on earth because CO₂ is one of the greenhouse effects that have the most significant impact on global warming. Efforts to reduce CO₂ in the air have been widely studied earlier. This is because CO₂ is a renewable, non-flammable, non-toxic and widely available raw material. One of the studies that have been done is to use CO₂ as a raw material to produce another chemical compound that can be used extensively for solvents, additives, and others. One of them is the organic carbonate compound.[1]

Organic carbonate is an oxygenate compound that can be used as an additive in the fuel. So far ethanol has been widely used as an additive in gasoline to reduce gasoline consumption and increase octane numbers. One of organic compound that can be used as an additive in fuel is Diethyl Carbonate (DEC). As an additive for fuel, DEC has many advantages. First, DEC has lower vapor pressure and mixed power with water than ethanol. Second, this compound is also good to use as an octane booster because of its high octane number. Third, it has a higher heating value and oxygen content than ethanol. Therefore, the addition of DEC into a mixture of gasoline and ethanol can increase the



amount of ethanol added to the gasoline mixture by more than 15% by volume with vapor pressure and the effect of minimum water solubility[2]

According to various studies that have been conducted, DEC can be synthesized with various raw materials and methods. First, in Wang's research, DEC can be synthesized from urea reacted with ethanol [3]–[5]. Second, Zhang and Briggs synthesized DEC by reacting CO and ethanol [6]–[10]. Third, DEC can also be synthesized from DMC [11]. Fourth, DEC has also been synthesized from Ethyl Carbamate reacted with ethanol [12]–[15]. Fifth, Iida synthesized DEC by reacting ethylene carbonate with ethanol [16]. Sixth, Gasc synthesized DEC by reacting CO₂ and ethanol [16–21] and others.

According to various studies regarding the synthesis of DEC with CO₂ raw materials influenced by several things including dehydration agents, catalysts and operating conditions used. This has been proven by several researchers including, First, Wang Yanlou has done direct DEC synthesis with CO₂ raw materials using Propylene Oxide dehydration agent and KBr-KNO₃-CeO₂ catalyst at 150°C for 2 hours to produce DEC yield of 13% [22]. Second, Wang Liguó also conducted research for the synthesis of DEC through a coupling reaction with dehydration agent propylene oxide and PVEImBr / MgO catalyst at 170°C for 6 hours to produce DEC yield of 38.2%. Third, Wang Liguó has done DEC direct synthesis using ethylene oxide dehydration agent and KI / EtONa catalyst for 3 hours at 170°C to produce a DEC yield of 65.5%. Besides that, in Wang Liguó's research Propylene Oxide was used as a dehydration agent with a catalyst and the same reaction temperature for 4 hours to produce a DEC yield of 46%. In this study also carried out direct synthesis under different temperature conditions, namely 130°C. Where at this temperature DEC yields were obtained using the same dehydration agent namely Ethylene Oxide and the same catalyst at 13.5% [1].

Based on various existing studies, catalysts and epoxides have the potential to increase DEC production in synthesis. Dehydration agents are needed in this synthesis. The reaction of DEC synthesis is difficult to occur spontaneously. So it is necessary to add dehydration agents to direct the reaction to the formation of carbonate compounds [1]. Based on the studies described above, due to the lack of direct DEC synthesis research using Propylene Oxide and Butylene Oxide dehydration agents over KI / Molecular Sieve catalysts, Propylene Oxide and Butylene Oxide in this study were selected as dehydration agents to study further in direct DEC synthesis from CO₂ and ethanol.

2. Experiment Details

2.1. Materials

CO₂ (99.8%) was purchased from PT. Aneka Gas Industri Samator. Ethanol (99.5%), propylene oxide (99.5%), and butylene oxide (99%) were purchased from Sigma-Aldrich. Molecular Sieve 0,3 nm and sodium ethoxide were purchased from Merck. All the chemicals were analytical grade.

2.2. Synthesis Diethyl Carbonate

In this research, the reactor used is made from stainless steel with an inner volume of 34.57 mL equipped with a stirrer, heating jacket, electric heater, and a temperature controller to keep the reaction temperature constant. In this research, the reaction was conducted in a batch operation mode. In a standard procedure, epoxide and ethanol which have mole ratio 1:15 and a 0.2-gram total amount of catalyst were added into the reactor. The catalyst used in this research is KI/EtONa and KI/Zeolite which have a mass ratio for KI and EtONa or KI and Molecular Sieve as a zeolite 1:3. Total volume liquid used in this research is 60% of the total volume reactor. After that, CO₂ was introduced with an initial pressure of 35 bar at room temperature, and the reactor was completely sealed. The reactor was heated and stirred constantly at 170°C and 500 rpm during the reaction. After the reaction, the reactor was cooled to room temperature and the residual gas was depressurized slowly. Then, the composition of the resulting mixture was measured qualitatively by GC–MS (Agilent 6980-433 HP-5MS) and quantitatively by gas chromatography (Shimadzu) with a capillary column (Stabilwax 30m x 0.25mm x 0.25µm) equipped with a flame ionization detector (FID).

3. Results and Discussion

3.1. The One-Pot Synthesis of DEC

The one-pot reaction of DEC synthesis might be composed of cycloaddition reaction and subsequent transesterification reaction. As analyzed by the GC–MS method in this research, the main products of DEC synthesis from CO₂, ethanol, and propylene oxide were 1,2-propanediol (PG) and DEC. Whereas for the DEC synthesis from CO₂, ethanol and butylene oxide, the main products were butylene glycol (BG) and DEC. [22][19]

3.1.1 The One – Pot Synthesis of DEC over Catalyst.

As reviewed in many works of literature which have used a catalyst for DEC synthesis, DEC synthesis run in two steps of the reaction, the cycloaddition and transesterification reaction. Each reaction was also needed a suitable type of catalyst. Cycloaddition reaction occurs when carbon dioxide reacts with epoxide that forms a carbonate compound. This reaction requires a catalyst to occur. Wang said that several types of catalyst could be used, such as onium salts and metal halides. But KI is one of the best catalysts for industrial processes in terms of economy and resilience even though the activity is not too high at low temperatures [23]. According to the work that has done by Wang, KI plays an important role in the formation of intermediate products. KI plays a role in opening bonds to ethylene oxide [1].

In addition, DEC synthesis in this research can also be improved with EtONa catalyst. According to the experiment that has done by Wang, this EtONa catalyst will play a role in transesterification reactions. EtONa is a component with a high base level. In that experiment base catalyst has been proven to be an effective catalyst for the transesterification process [23]. But the disadvantage of this catalyst is that the price is quite expensive and the process of separation is difficult.

Not only EtONa but also molecular sieve catalyst can improve the synthesis of DEC. Molecular Sieve characteristics have a uniform pore size, high surface area and resistance to high temperature. Based on Zhang's research, it can be seen that the specific surface area of the catalyst increases after the addition of molecular sieve in the synthesis process. This can also be the reason for increasing DEC yield [24]. This catalyst is a heterogeneous substance, so it has a smaller amount of active site, but the advantage of this catalyst is cheaper than EtONa and the process of separation is not difficult.

The results of the comparison between KI/ EtONa and KI/Molecular Sieve in a synthesis of DEC from CO₂, ethanol and propylene oxide or butylene oxide can be seen in Figure 1 and figure 2.

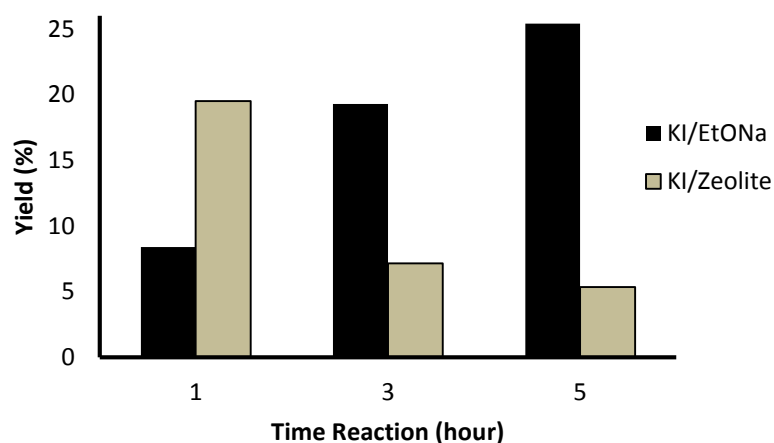


Figure 1. Effect of Catalyst to DEC yield for DEC Synthesis from CO₂, Ethanol and Propylene Oxide

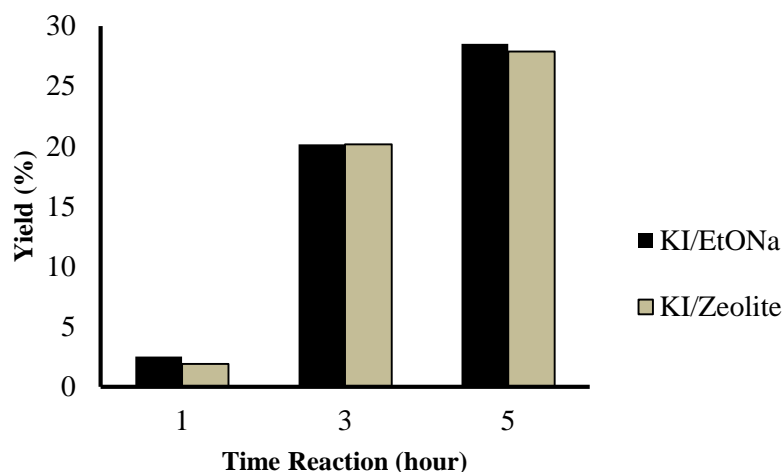
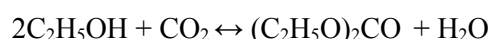


Figure 2. Effect of Catalyst to DEC yield for DEC Synthesis from CO₂, Ethanol and Butylene Oxide

Based on Figure 1 and figure 2, we know that the addition of catalyst can form DEC. Not only it Molecular Sieve have a potential for being a substituent for EtONa catalyst. Because figure 2 shows that the highest yield of DEC from synthesizing with butylene oxide over KI/EtONa catalyst is close to the highest yield of DEC from synthesizing over KI/Molecular Sieve catalyst. Figure 1 also shows that the Yield of DEC from synthesizing with propylene oxide over KI/Zeolite has the highest yield of DEC within one- hour time reaction. It faster than the highest yield of DEC synthesis over KI/EtONa catalyst which has 5 hours' time reaction. So, we can conclude that DEC synthesis over KI/Molecular Sieve catalyst is more optimal than KI/EtONa. Because we can get enough DEC yield and almost has the same value as using KI/EtONa catalyst only in one hour. So, we can save some things in this synthesis such as energy and economics. This is because molecular sieve is cheaper than sodium ethoxide.

3.1.2 Effect of Epoxide in DEC Synthesis.

Addition of epoxide also has a play role in this synthesis. Because epoxide is a dehydrating agent in this reaction. The dehydrating agent will decrease water from the reaction. Because from the reaction, DEC synthesis from CO₂ and ethanol will produce water as a by-product.



Because of it, Wang said that DEC synthesis reaction from CO₂ and ethanol is difficult to occur spontaneously even in a harsh condition caused by thermodynamic limitations. Therefore with the addition of dehydrating agent, it is expected that the reaction can shift towards carbonate formation[1]. Thus, the presence of water must be minimized because it can disrupt the equilibrium of the reaction process.

The dehydrating agent has used as one of the variables in Leino's research in 2011 [18] for DEC synthesis from CO₂ with butylene oxide as a dehydrating agent and without a dehydrating agent in 2015[21]. According to Leino's research, DEC yield obtained without the addition of dehydrating agent is lower than using butylene oxide as a dehydrating agent. Addition of dehydrating agent increased DEC yield 4 times higher than without the addition of dehydrating agent [18],[21]. Thus, the addition of epoxide is possible to suppress thermodynamic limitations and shift the equilibrium towards DEC synthesis.

In this research, propylene oxide and butylene oxide was used as a dehydrating agent in DEC synthesis. This experiment shows that addition of butylene oxide obtained DEC yield higher than propylene oxide. But, according to Herzberger research, the longer the chain of an alkylene oxide, the more reactivity will decrease. Primary hydroxyl group will show higher reactivity compared to the secondary hydroxyl group[25]. As we all know that the epoxide chain on propylene oxide is shorter

than butylene oxide. So propylene oxide should be more reactive than butylene oxide. This may occur because of the addition of catalyst which causes it to inhibit the reactivity of the epoxide chain.

4. Conclusion

In conclusion, an efficient approach to synthesize DEC directly from carbon dioxide, ethanol and epoxide was successively developed. According to the catalyst that has tested, there is some effect of the addition of each catalyst in DEC synthesis reaction. The addition of KI/Molecular Sieve in that reaction was found to be a substituent for KI/EtONa catalyst. Not only it, but the production of DEC can be maximized by the addition of epoxide. Epoxide involvement increases DEC formation because thermodynamic limitations are effectively overcome. For the first step, CO₂ and epoxide reacted to form alkylene carbonate via cycloaddition reaction. For the second step, the transesterification of alkylene carbonate with ethanol reacted to produce DEC and alkylene glycol. The optimum reaction mechanism for DEC synthesis is by reacting ethanol and CO₂ with the addition of propylene oxide as a dehydration agent and KI/Molecular Sieve catalyst with an operating temperature of 170°C, a reaction time of 1 hour and 35 bar CO₂ initial pressure. Compared with other current routes, this research has provided an easy and economical route to synthesize DEC directly from CO₂. This research also shows promising application on an industrial scale with respect to the merits of high efficiency, energy saving, and eco-friendly feature.

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