Use of metal mesh to assist the multi-phase reaction in a microreactor

P Charoenpong and V Pavarajarn

1 Center of Excellence in Particle and Material Processing Technology, Department of Chemical Engineering, Chulalongkorn University, Bangkok, Thailand

Varong.P@chula.ac.th

Abstract. Glycerol is a by-product from biodiesel production. Glycerol can be further converted to glycerol carbonate by several reaction routes. One of the feasible routes that have been generally reported is the reaction between glycerol and urea, while ammonia gas is generated as one of byproducts. The reaction generally requires a heterogeneous catalyst, which causes mass transfer problem. Most researchers have applied this reaction in batch, continuous-stirred tank, or fixed bed reactors, in which the external mass transfer resistance is still dominant. Due to many advantages of microreactor including high surface area-to-volume ratio, short diffusion distance, small mass and heat transfer resistances, applying the microreactor can solve the problems and enhance the reaction. Therefore, in this work, microreactor was utilized in the production of glycerol carbonate from glycerol and urea, which one side of microchannel wall was coated by commercial catalyst. In addition, Metal mesh sheet with pores is used to separate ammonia gas from the reaction. This research studies the effect of residence time, microchannel thickness, shear stress of reactants and a quantity of generated gas on a catalyst slipping, and also investigates the effect of metal mesh size on yield of glycerol carbonate from reaction in microreactor.

1. Introduction

Since energy from petroleum causes many disadvantages, renewable energy is expected to replace petroleum. One of the most important renewable energy is biodiesel. Biodiesel is typically made by chemically reacting lipids with an alcohol. From the reaction, glycerol is a byproduct. As more biodiesel is produced, the quantity of glycerol also increases. Glycerol carbonate is the one of many ways for adding value to glycerol. Glycerol carbonate is the substance that can be applied to many interesting things including solvent, cement, cosmetics, membrane in gas separation, surfactants and chemical intermediate leading to glycidol [1]. There are many routes for Glycerol carbonate production from glycerol; for example, urea, ethylene carbonate, dimethyl carbonate, carbon dioxide and carbon monoxide routes [2]. Urea route is preferred because it’s convenient and not expensive [3]. The accepted mechanism for the reaction of urea with glycerol involves two steps. Figure 1 shows pathway of glycerol carbonate reaction from glycerol and urea [4]. The reaction of glycerol carbonate from glycerol and urea prefers high temperature and low pressure [5]. Many researchers have studied this reaction with catalyst both of homogeneous and heterogeneous reactions. There are many catalysts that can be used in this reaction. Their yields could be found from 35% to 95%. The reaction’s temperature was always set in range 130 Celsius to 150 Celsius. Heterogeneous reaction is preferable because ease of separation, and zinc oxide is chosen for the reaction due to low cost and availability [6-12]. Decreasing in molar ratio of glycerol to urea can make higher in conversion but lower in selectivity. Moreover, removing ammonia from the reaction can affect yield of glycerol [8]. Synthesis in a microreactor system has higher efficiency when compared with industrial plant. Mass and heat...
transport are significantly fast. In addition, with less quantity of reactant, safety can be guaranteed in microscale experiment [13]. In this reaction, ammonia gas is generated as by product. For avoiding problems caused by gas phase occurring in microreactor, removing gas out of reaction is needed. Mesh contactor is used to be a tool for separating gas from reaction. With capillary action within mesh pores, only gas can get through the mesh when suitable condition is done [14].

Although much work has been done to date, there is not a research studying about glycerol carbonate production from glycerol and urea in the microreactor. Because the reaction is a multi-phase reaction, the purpose of this project is to use metal mesh to assist the multi-phase reaction in a microreactor.

![Figure 1. Pathway of glycerol carbonate from glycerol and urea [4]](image)

2. Materials and methods

2.1 Materials
Glycerol (99.5%), lab grade of zinc oxide and urea were purchased from Ajax Finechem and used without further purification. Metal Mesh was purchased from Ek Saeng Panich limited partnership.

2.2 Microreactor design
The microreactor in this research was made of 4 stainless steels, a mesh and 2 Teflon sheets. 2 stainless steels have 3x8 square meters of size and 3 millimeters of thickness, one of them was one-site coated with zinc oxide. Other stainless steels have 14x8 square meters of size and 10 millimeters of thickness. 2 big stainless steels were used to make the microreactor strength. A mesh was used to separate gas phase from liquid phase. It was placed between 2 Teflon sheets. The Teflon sheets were cut to make 2 space areas, rectangle shape with 5 millimeters in width and 2 millimeters in length, between two stainless steels. The assembly of microreactor is shown in figure 2. The space area from the one of Teflon sheets was the place where reactants do react with each other. Another was the place where nitrogen gas brought ammonia gas out of the reactor. A height of the microreactor was controlled by thickness of Teflon sheet. Moreover, residence time was controlled by flow rate of reactant and volume of the gap in the Teflon sheet.
2.3 Reaction procedure

A microreactor is a continuous reactor needed continuously feed flow rate of reactants to do react in the reactor. Generally, it is preferable to feed the reactant individually then let them mix with each other. To avoid incompletely mixing, glycerol and urea did mix before feeding to a microreactor. The glycerol was heated to 80 degree Celsius and stirred around 300 rpm before mixing with the urea for 1 hour. Then the solution was pull into a syringe pump feeding to the microreactor. The syringe pump was heated to 90 degree Celsius, controlled by temperature controller with PID control, during the reaction because reactant changes phase when its temperature lower than 40 degree Celsius. Zinc oxide was coated into the one side of microreactor by spinning coating process using ethanol as a solvent. The microreactor was heated until temperature reaching set point. Another PID controller was used to control reaction temperature. Before reactants were fed to the microreactor, nitrogen gas was fed to the microreactor with requiring flow rate. The product was collected after time reaching the steady state. Gas chromatography was used to analyze the quantity of glycerol and glycerol carbonate. Figure 3 shows an experiment procedure.
2.4 Characterization
Gas chromatography (GC) is used to analyze the quantity of glycerol and glycerol carbonate. Temperature program was set. A column is HP-INNOWAX and a detector is a flame ionization detector. Inductively coupled plasma (ICP) is used to analyze the quantity of zinc oxide in product for checking catalyst slipping.

2.5 Coating
Zinc oxide as a catalyst in the reaction was adhered to the stainless steel by coating process. Ethanol was used to be the solvent. After the reaction, some zinc oxide was slipping from the stainless steel called catalyst slipping. Moreover, the catalyst is slipped in a uniform layer.

3. Results and discussion
3.1 Effect of shear stress and generated gas on catalyst slipping
According to figure 4, reaction meant the glycerol carbonate reaction from glycerol and urea using zinc oxide as a catalyst while non-reaction meant the experiment which was not occurring any reaction. The result showed that shear stress is not affecting on the catalyst slipping. To investigate the relation between rate of reaction and catalyst slipping, reactant was diluted by dimethyl sulfoxide for decreasing rate of reaction. Decreasing in rate of reaction reduced generated gas from the reaction. As you seen in figure 4, catalyst slipping decreased when concentration of reactant decreased.

3.2 Effect of thickness
Figure 5 shows the effect of thickness on the conversion and selectivity. the reaction was carried out at 140 degree Celsius of temperature, 1 atm of pressure, 1:1 molar ratio of reactants and 18.9 minute of residence time. The increase in thickness of gap in microreactor caused the decreased conversion and selectivity. Actually, the increase in the thickness caused the limitation of mass transfer in the gap. So, glycerol carbonate reaction from glycerol and urea can neglect mass transfer limit when conducted in microreactor. Moreover, figure 5 demonstrates the effect of catalysis reaction and non-catalysis reaction. The results implied that there is catalyst adhered to the reactor after the reaction is complete and shows how important of catalyst in the reaction.
3.3 Effect of mesh number
From figure 6, the reaction was carried out at 140 degree Celsius of temperature, 1 atm of pressure, 1:1 molar ratio of reactants and 18.9 minute of residence time. The experiment with bigger in pore size of metal mesh gave the higher in the conversion. Conversely, the selectivity is lower. This result expressed that increasing in pore size of metal mesh made the surface tension weak. Ammonia gas can easily get through the mesh pore away out from the reactor. it means that reaction is shifted forward. As shown in figure 1, the direction of reaction should reach to the way which ammonia gas occurs when ammonia gas is brought out of microreactor. With higher in conversion but lower in selectivity, the experiment with big metal mesh number tends to produce byproducts such as glycridol and methyl carbamate.

![Figure 6](image6.png)

**Figure 6.** Relation between mesh number of metal mesh and conversion(left)/selectivity(right)

3.4 Effect of gas flow rate
In order to investigate the influence of gas flow rate, reaction was conducted at three different flow rate of nitrogen gas. 3, 6.82 and 9.6 milliliter per minute were chosen. Other reaction conditions were 140 degree Celsius of temperature, 1 atm of pressure, 1:1 molar ratio of reactants and 18.9 minute of residence time. The result is presented in figure 7. There is no obvious difference in conversion when flow rate of nitrogen gas changed, but selectivity is lower with higher in nitrogen gas flow rate. There are 2 reasons. Firstly, nitrogen gas has a higher chance to go through the metal mesh mixing or dissolving with the product. As seen in figure 1, higher in flow rate of nitrogen gas leads reaction to the direction where gas is generated such as a path to glycerol carbonate, glycridol and methyl carbamate.

![Figure 7](image7.png)

**Figure 7.** Relation between flow rate of nitrogen gas and conversion(left)/selectivity(right)

3.5 Effect of residence time
In order to evaluate the effect of residence time on the reaction. The reaction was carried out at different residence time of 6.3, 9.45 and 18.9 minutes. Figure 8 shows that the conversion of glycerol and the selectivity of glycerol carbonate increased when residence time increased. As seen in figure 1, there is an intermediate. Higher in residence time can make the change of intermediate to glycerol carbonate rise.
3.6 Effect of dilution
Changing in reactant concentration by adding dimethyl sulfoxide in the reactant caused 2 situations at the same time. Firstly, the rate of reaction is decreased. Secondly, Diffusivity of solution is increased. From figure 9, the range between non dilution to 1 per 1 dilution of reactant, diffusivity is dominate function. With high diffusivity, ammonia gas generated from the reaction can easily go through the liquid phase making higher in removal gas. In addition, excess in dilution making the reaction worse.

4. Conclusion
In glycerol carbonate reaction from glycerol and urea, microreactor is preferable for studying the reaction because mass transfer can be neglected. Generated gas causes catalyst slipping. Metal mesh is an important part to separate gas from liquid. flow rate of carrier gas, residence time and thickness are effect on the reaction.

References
A reference
[1] Sonnati MO, Amigoni S, de Givenchy EP, Darmanin T, Choulet O and Guittard F. Glycerol carbonate as a versatile building block for tomorrow: synthesis, reactivity, properties and applications. Green Chemistry. 2013;15(2):283-306.
[2] Reshma D and Reshma S, Manufacturing of Glycerol Carbonate in Aspen Plus. International Journal of Latest Technology in Engineering, Management & Applied Science (IJLTEMAS) 2018. VII(V): p. 39 - 61.
[3] Hammond C, Lopez-Sanchez JA, Ab Rahim MH, Dimitratos N, Jenkins RL, Carley AF, He Q, Kiely CJ, Knight DW and Hutchings GJ. Synthesis of glycerol carbonate from glycerol and urea with gold-based catalysts. Dalton transactions. 2011;40(15):3927-37.
[4] Kusumaningtyas RD, Prasatiawan H, Pratama BR, Prasetya D, Hisyam A. Esterification of Non-edible Oil Mixture in Reactive Distillation Column over Solid Acid Catalyst: Experimental and Simulation Study. Journal of Physical Science. 2018 May 2;29
[5] Li J and Wang T. Chemical equilibrium of glycerol carbonate synthesis from glycerol. The Journal of Chemical Thermodynamics. 2011 May 1;43(5):731-6.
[6] Aresta M, Dibenedetto A, Nocito F and Ferragina C. Valorization of bio-glycerol: New catalytic materials for the synthesis of glycerol carbonate via glycerolysis of urea. *Journal of Catalysis*. 2009 Nov 15;268(1):106-14.

[7] Fujita SI, Yamanishi Y and Arai M. Synthesis of glycerol carbonate from glycerol and urea using zinc-containing solid catalysts: A homogeneous reaction. *Journal of Catalysis*. 2013 Jan 1;297:137-41.

[8] Kondawar SE, Mane RB, Vasishta A, More SB, Dhengale SD and Rode CV. Carbonylation of glycerol with urea to glycerol carbonate over supported Zn catalysts. *Applied Petrochemical Research*. 2017 Apr 1;7(1):41-53.

[9] Munehisa O and Mitsuru U. Wakayama (JP). *PROCESS FOR THE PREPARATION OF GLYCEROL CARBONATE* U.S. Patent, Editor. 2002, Kao Corporation, Tokyo (JP).

[10] Turney TW, Patti A, Gates W, Shaheen U and Kulasegaram S. Formation of glycerol carbonate from glycerol and urea catalysed by metal monoglycerolates. *Green Chemistry*. 2013;15(7):1925-31.

[11] Wang D, Zhang X, Liu C and Cheng T. Synthesis of glycerol carbonate from glycerol and urea over lanthanum compounds. *Reaction Kinetics, Mechanisms and Catalysis*. 2015 Aug 1;115(2):597-609.

[12] Wang L, Ma Y, Wang Y, Liu S and Deng Y. Efficient synthesis of glycerol carbonate from glycerol and urea with lanthanum oxide as a solid base catalyst. *Catalysis Communications*. 2011 Sep 15;12(15):1458-62.

[13] Geyer K, Codee JD and Seeberger PH. Microreactors as tools for synthetic chemists—the chemists' round-bottomed flask of the 21st century. *Chemistry–A European Journal*. 2006 Nov 15;12(33):8434-42.

[14] R Prasomsup. Use of metal mesh to increase absorption efficiency of volatile organic compound in microchannel, in *Chemical Engineering*. 2016, Chulalongkorn University. p. 86.