

Reactive Extraction of 1,3-Propanediol from Model Mixture of Fermentation Broth Using Novel Carbon Based Catalyst

P. Boonnoun¹, C. Muangnapoh¹, P. Prasitchoke², V. Tantayakom², and A. Shotipruk^{1,*}

¹ Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Patumwan, Phayathai Road, Bangkok 10330, Thailand

² PTT Chemical Public Company Limited, 14 I I Road, Tambon Map Ta Phut, Amphoe Mueang Rayong, Rayong 21150, Thailand

* Corresponding author: artivan.sh@chula.ac.th

Abstract: This study deals with the development of a novel carbon based catalyst for use in reactive extraction, to separate 1,3-PDO from a model solution of the fermentation broth. The catalyst was synthesized by incomplete carbonization of naphthalene, in sulfuric acid at 523 K. The surface area and pore volume of the catalyst were found to be $1.1 \text{ m}^2 \text{ g}^{-1}$ and $0.07 \text{ cm}^3 \text{ g}^{-1}$, respectively. The acidity of the catalyst was 1.46 mmol/g. The test of the catalyst for the acetalization of acetaldehyde and 1,3-PDO in an aqueous solution indicated its applicability for such a reaction. The optimal quantity of the catalyst required for this reaction was 0.7 g/g 1,3-PDO, giving a conversion of approximately 92%, after 2 h of reaction at 35°C. In addition to acetalization reaction, a reactive extraction was also carried out, using ethyl-benzene as an extractant. At 40 g/L of initial 1, 3-PDO solution, a typical concentration of 1, 3-PDO was derived from the fermentation process, the conversion was found to be 78.92% after 60 min for a reactive extraction at 35°C. The results of this study thus confirm the potential application of the lower cost carbon-based catalyst to replace the expensive polymeric ion exchange resins, for 1,3-PDO reactive extraction.

Key words: 1,3-propanediol, fermentation broth, separation, solvent extraction.

1. Introduction

Bio-diesel is among the most promising alternatives for renewable energy that has recently attracted much interest, because it is a green energy and its properties are similar to those of petroleum diesel. Bio-diesel is typically produced by transesterification of plant oils or animal fats, whose processing results in the production of glycerol as a major by-product. Nowadays, a great number of large biodiesel plants are being built and operated actively, resulting in a large quantity of glycerol produced each year. Generally, glycerol can be used in the cosmetic industry or as animal feed. However, as the supply of glycerol increases, the price of glycerol becomes considerably lower. It is therefore of great interest to convert glycerol into other value-added products. One of the most interesting compounds that could be produced from glycerol, is 1,3-propanediol (1,3-PDO). 1,3-PDO is considered to be one of the major monomer components for the production of high performance polyester, such as polytrimethylene terephthalate (PTT), which can be used in various chemical and textile or fiber industries. The production of 1,3-PDO from glycerol could be achieved by the biological process of glycerol conversion to 1,3-PDO, using various types of microorganisms such as *Klebsiella pneumoniae*, *Citobacter freundii*, *Enterobacter agglomerans*, and *Clostridium butyricum*. Among these microorganisms, *Clostridium butyricum* produces the highest yield of 1,3-PDO.

Besides 1,3-PDO, some alcohols, acids, and other compounds are also produced, and the separation of 1,3-PDO from the aqueous system of fermentation broth therefore, becomes a big challenge. Several separation methods have been used for separation of 1,3-PDO from aqueous fermentation broth, such as distillation, liquid extraction, and pervaporation. Of these techniques, reactive extraction is an easy and energy-efficient process in which the reaction takes place simultaneously with the extraction. In this process, acetalization of 1,3-PDO and aldehydes was carried out, in order to convert 1,3-PDO to dioxane, which would then be extracted simultaneously, by an

organic solvent added to the system. Because of the high reactivity and extractability, the process requires a shorter operating time and a smaller amount of reactant and extractant, which could also be recovered and reused. Malinowski et al. (1999) [1] used a UNIFAC program to select an appropriate solvent for the extraction of dioxane. Three solvents that have a high mass partition coefficient were selected: toluene, o-xylene, and ethyl-benzene, whereas acetaldehyde was used as a reactant and Dowex ion exchange resin, as a catalyst. Of the extractants used in the experiment, toluene was found to be the most effective. The same group of researchers later investigated the effects of two types of ion exchange catalysts for the reactive extraction of 1,3-propanediol: Dowex and Amberlite ion exchange resins [2]. Dowex ion exchange resin was found to be a more effective catalyst. In addition, the authors reported the difficulty of using toluene as an extractant, since its boiling point was closer to dioxane. Thus, the choice of higher boiling extractants, such as o-xylene and ethyl benzene, would be more advantageous. Alternatively, Hao et al. (2005) [4] proposed a reactive extraction process using various aldehydes as both the reactants and the extractants. Since only one chemical was used both as the reactant and the extractant, the separation of the product from the reaction medium was much simpler, compared with the process that employed two different solvents. In all previous research on reactive extraction, either a homogeneous liquid acid or an ion exchange acid resin was used as a catalyst. Homogeneous acid catalysts are corrosive and cannot be reused. Furthermore, its use, particularly in an aqueous system such as this, leads to large amount of waste water. This problem can be solved by using solid acid catalysts, and those currently used are such as Dowex and Amberlite ion exchange polymeric resins. However, the high prices of these ion-exchange resins make the process uneconomical. Recently, a new class of sulfonated catalyst has been developed by incomplete carbonization of simple sugars. The advantages of this novel class of catalysts are low cost, simple preparation, high acid density and stability. The dense acidity causes higher activities for many acid-catalyzed reactions

such as Beckman reformation, esterification, and hydrolyzation. In fact, the activities for transesterification of fatty acids were found to be higher than many other solid acids used for this purpose. In addition to the sulfonic acids based on simple sugars, Gao et al (2007) [3] developed a novel sulfoaromatic hydrocarbon catalyst by incomplete carbonization of naphthalene in sulfuric acid and applied it for the acetalization of carbonyl compounds, in which different kinds of diols and carbonyl compounds were reacted. They reported a rather high reactivity and selectivity of the catalysts, for most of the reactions tested. In addition, the catalyst deactivation was found to be minimal and the catalysts could be recovered and reused expediently, without further treatment except filtration and drying. Although the reactions were tested in the organic phase, these results suggested a potential application of such catalysts for the reactive extraction of 1,3 PDO from the aqueous solution. This is when acetalization is carried out in an aqueous system simultaneously, with the extraction of the dioxane product into an organic solvent, and this is the aim of this work.

2. Experimental

2.1 Chemicals

1,3-propanediol (98% purity) was purchased from the Acros Organic Co, Singapore. Glycerol (99% purity) was supplied from Ajax Finechem. Acetaldehyde (99% purity), ethyl benzene (99% purity) were obtained from Aldrich (Sigma-Aldrich, Singapore). Sulfuric acid and naphthalene were purchased from Fluka and Merck, Singapore. 2-methyl-1,2-dioxane (2MD) and a sulfonated carbon-based catalyst were prepared, following the procedures subsequently described.

2.2 Preparation of 2-methyl-1,3-dioxane(2-MD)

For the quantification of the amount of 2-MD, the standard reference of 2-MD must be synthesized. To do this, a total of 45 g (0.57mol) of PDO and 25.1 g (0.57mol) of acetaldehyde were mixed in a 250-mL shaken flask, with the addition of 3.5 g of Dowex ion-exchange resin. A total of 12 g of $MgSO_4$ was then added, to absorb the water produced during the reaction, and after 4 h of shaking, 2 g of Na_2CO_3 was added to neutralize the sample. The ion-exchange resin, Na_2CO_3 and $MgSO_4$ were then separated from the reaction mixture by filtration, and the supernatant liquor was distilled. The distillate in the range of 100-140°C was collected. The distillate was analyzed with a HP 5890 gas chromatograph, equipped with TCD detector, and a 30-m HP-1 column (0.53 mm diameter, 0.88 mm film thickness) (Hewlett-Packard, USA), using helium as a carrier gas. The oven temperature was programmed from 70 to 200°C, while the injector and detector temperatures were set at 250 and 300°C, respectively.

2.3 Preparation of catalyst

Naphthalene (20 g) was heated in concentrated sulfuric acid (>96%, 200 mL) at 523 K, under a flow of N_2 . After heating for 15 h, excess sulfuric acid was removed from the dark brown tar, by vacuum distillation at 523 K for 5 h, which resulted in a black solid. The solid was then ground to a powder, and was washed repeatedly in boiling water, until impurities such as sulfate ions were no longer detected in the washing water.

2.4 Catalyst reactivity for acetalization of acetaldehyde and 1,3-PDO

A total 0.5 ml 1,3-PDO was added to the 15.7 ml of acetaldehyde solution (containing 3.7 ml acetaldehyde and 12 ml of water) in a 125-mL shaken flask, with a specified amount of added sulfonated carbon based catalysts. This is equivalent to having the reaction of 3.7 ml acetaldehyde and 12.5 ml of 40

g/L of 1,3 PDO solution). The reaction was mixed vigorously (150 rpm) at the controlled temperature, for up to 2 h. After the reaction, the catalyst was immediately separated from the reaction product, which was then kept in a refrigerator (4°C), until the analysis of 2-MD produced and the unreacted 1, 3 PDO. Following the above procedure, the effect of mass to volume ratio of the catalyst and 1,3-PDO solution on the conversion was determined for the range of 4 – 36 g catalyst/L of 1,3-PDO aqueous solution (40 g/L), which is equal to the mass ratio of catalyst to 1,3-PDO of 0.1-0.9 g/g. The suitable ratio was used for subsequent experiments.

2.5 Reactive extraction

To carry out the reactive extraction, a specified amount of catalyst (determined from a previous experiment) and the equal volumes (15.7 mL) of ethyl-benzene and acetaldehyde solution (containing 3.7 ml acetaldehyde and 12 ml of water) were first mixed in a 125-mL shake flask, and were brought to a desired reaction temperature. Then, a specified amount of 1,3-PDO was added, to the mixture and stirred vigorously (150 rpm) in a 125-mL shake flask. The reaction was catalyzed by a novel carbon based catalyst, and the reaction was allowed to take place for a specified reaction time (0-60 min) in a water bath at constant temperature.

2.6 Catalyst characterization

The total surface area, pore volume and pore size of catalysts were determined using a Micromeritics model ASAP 2020. The sample cell, which contained 0.5 g of the sample was placed in a Micromeritics model ASAP 2020. After the degassing step, N_2 physisorption was carried out to measure the surface area and pore volume of catalyst. The sulfur content of sulfonated carbon based catalysts was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), using 7500a ICP-MS (from Agilent, Japan).

2.7 GC analysis of 1,3-PDO and 2-MD

The analysis was performed on a HP5890 series II gas chromatography (Hewlett-Packard, USA) equipped with a thermal conductivity detector and a 30-m HP-1 column (0.53 mm diam, 0.88 μ m film thickness). Helium was used as a carrier gas. The injector and detector were set at 250 and 300°C, respectively, while the oven temperature was programmed from 70 to 200 °C.

3. Results and Discussion

3.1 Catalyst characterize

The physical properties of the novel carbon-based catalyst are shown in Table 1. The BET measurement shows that the catalyst has a low specific surface area with insignificant pore volume, while the acid site densities, calculated in the form of sulfonic acid site (estimated by elemental analysis), were found to be 1.46 mmol/g.

Table 1. Physical properties of the catalyst.

BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Sulfur content (mmol/g)
1.1	0.07	1.46

3.2 Catalyst reactivity for the acetalization of acetaldehyde and 1,3-PDO

The chromatograms of the reactants: 1,3-PDO and acetaldehyde in an aqueous solution are shown in Figure 1a and 1b, indicating that the retention times for 1,3-PDO and acetaldehyde were at about 7.5 minutes and 1.4 minutes, respectively. The

chromatogram of the product after the 2 hours of reaction shown in Figure 1c indicated the presence of 2-MD (retention time = 1.6 minutes) as well as unreacted acetaldehyde, which was originally present in excess. It may be seen from the same figure however, that only a small amount of the unreacted 1,3-PDO was found, indicating that the majority of 1,3-PDO was reacted with acetaldehyde to form 2-MD. Therefore, the conclusion can be drawn from this preliminary result that the novel carbon based catalyst was an effective catalyst for acetalization of 1,3-PDO and acetaldehyde in an aqueous solution. The suitable catalyst mass for acetalization was found to be 0.7 g per 1 g of 1,3-PDO. For this quantity of catalysts, the conversion of 2-MD was about 92%.

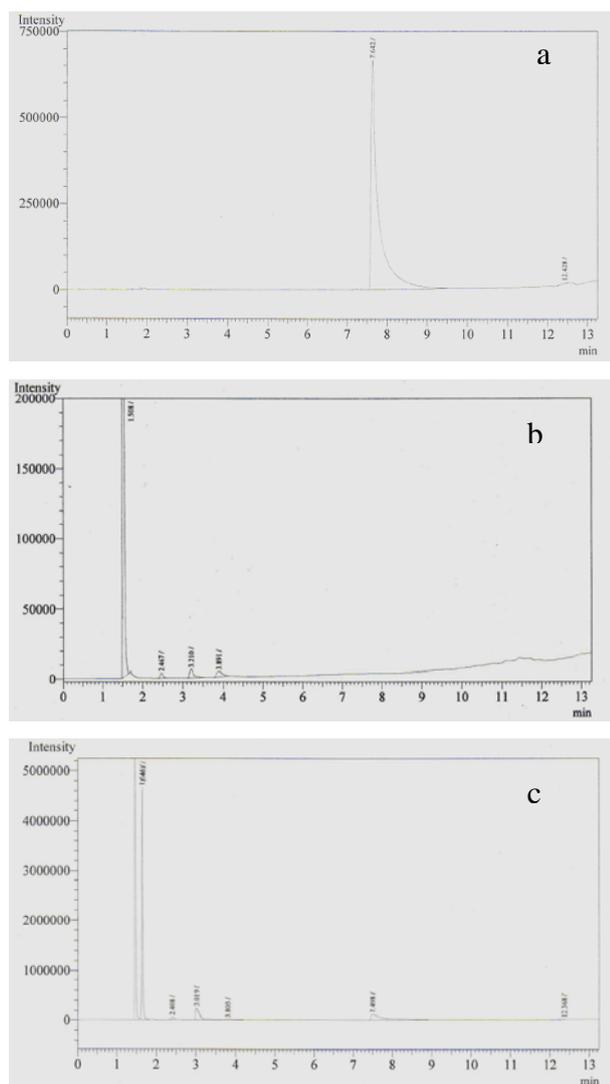


Figure 1. Chromatogram of reactants and product in aqueous solution (a = 1,3-PDO, b = acetaldehyde, c = product).

3.3 Reactive extraction

The chromatograms of the resulted aqueous phase and extract phase are shown in Figure 2a and 2b, respectively. The small amount of 1,3-PDO in the aqueous phase shows that it has been reacted with acetaldehyde and converted to 2-MD. The peak of 2-MD appeared, however, in both phases, but it has higher distribution in the ethyl-benzene extract phase. It should be noted here that acetaldehyde appeared in both aqueous and ethyl-benzene phases which means that its concentration in the

aqueous phase could be lowered by solubilization into ethyl-benzene. The lowered amount of acetaldehyde in the aqueous (reaction) phase could cause the lowering of reaction activity. Furthermore, its presence in the extract phase indicated a need for the separation of the solvent from the desired product (2-MD).

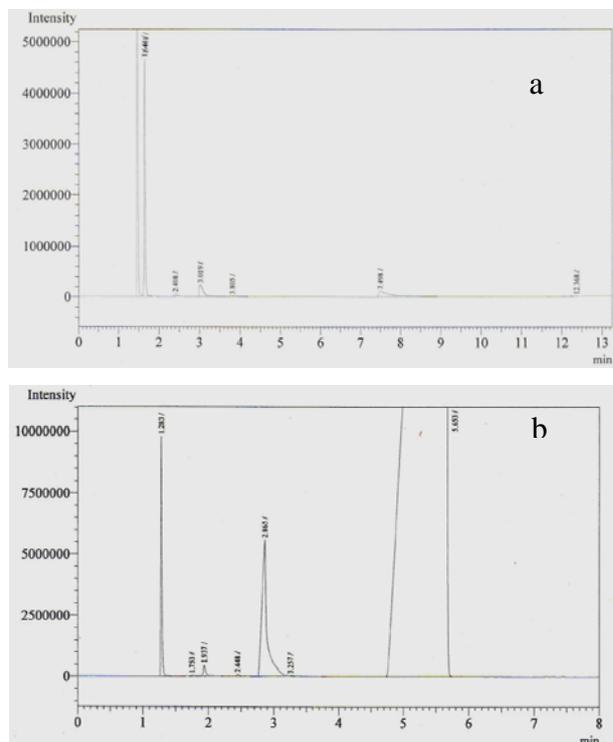


Figure 2. Chromatogram of sample in both phases (a = aqueous phase, b = solvent phase).

The concentration of 1,3-PDO in the aqueous phase and those of 2-MD in both phases are shown in Figure 3. From the figure, it can be observed that, as the reactive extraction proceeded, the concentration of 1,3-PDO decreased while those of 2-MD in both phases increased. Within the first 5 min. of reactive extraction, the 1,3-PDO concentration in the aqueous phase decreased sharply, giving a high initial rate of reaction. This was due to the initially high concentration of the reactants in the system. As the reaction proceeded, the reaction rate went down. The reaction conversion, calculated from the rate of 1,3-PDO decreased and was found to be 79% after 60 min. However, as seen from the constantly falling 1,3-PDO concentration, it would be expected that a higher conversion could be achieved, providing that a longer reactive extraction time is allowed.

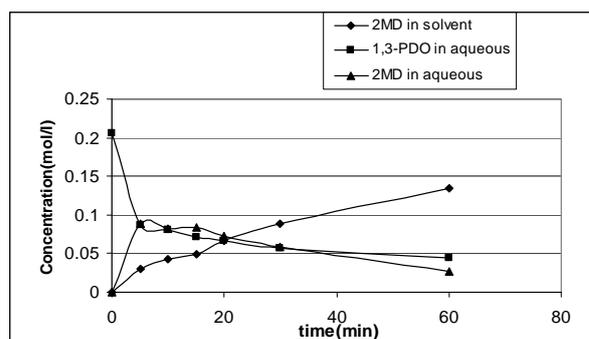


Figure 3. Reactive extraction at 35°C.

4. Conclusions

A small amount of the unreacted 1,3-PDO was found, indicating that the majority of 1,3-PDO was reacted with acetaldehyde to form 2-MD. Therefore, the conclusion can be drawn from this preliminary result that the novel carbon-based catalyst was an effective catalyst for acetalization of 1,3-PDO and acetaldehyde in an aqueous solution. The suitable catalyst mass for acetalization was found to be 0.7 g per 1 g of 1,3-PDO. For this catalyst quantity, the conversion of 2-MD was about 92%.

5. References

- [1] Malinowski J, Evaluation of liquid extraction potentials for downstream separation of 1,3-propanediol, *Biotechnology Techniques* 13 (1999) 127-130.
- [2] Malinowski J, Reactive extraction for downstream separation of 1,3-propanediol, *Biotechnology Progress* 16 (2000) 76-79.
- [3] Gao S, Liang XZ, Wang WJ, Cheng WP, Yang JG, High efficient acetalization of carbonyl compounds with diols catalyzed by novel carbon-based solid strong acid catalyst, *Chinese Science Bulletin* 52 (2007) 2892-2895.
- [4] Hao J, Liu H, Liu D, Novel route of reactive extraction to recover 1,3-propanediol from a dilute aqueous solution, *Ind. Eng. Chem. Res.* 44 (2005) 4380-4385.