รีแอกทีฟเอกแทรกชั่นของ 1,3-โพรเพนไดออลจากสารละลายผสมจำลองของน้ำหมัก

นาย ปณัฐพงศ์ บุญนวล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

REACTIVE EXTRACTION OF 1,3-PROPANEDIOL FROM MODEL MIXTURE OF FERMENTATION BROTH

Mr. Panatpong Boonnaul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2008

Thesis Title	REACTIVE EXTRACTION OF 1,3-PROPANEDIOL FROM MODEL MIXTURE OF FERMENTATION BROTH
By	Mr.Panatpong Boonaul
Field of Study	Chemical Engineering
Advisor	Assistant Professor Artiwan Shotipruk, Ph.D.
Co-Advisor	Associate Professor Chirakarn Muangnapoh, Dr. Ing.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……Dean of the Faculty of Engineering

(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

…….. Chairman

(Associate Professor Muenduen Phisalaphong, Ph.D.)

…….……. Advisor

(Assistant Professor Artiwan Shotipruk, Ph.D.)

…….……. Co-Advisor

(Associate Professor Chirakarn Muangnapoh, Dr. Ing.)

…….. Examiner

(Kasidit Nootong, Ph.D.)

…… External Examiner

(Phatthanon Prasitchoke, Ph.D.)

ปณัฐพงศ์ บุญนวล: รีแอกทีฟเอกแทรกชั่นของ 1,3-โพรเพนไดออลจากสารละลายผสมจำลองของน้ำหมัก (REACTIVE EXTRACTION OF 1,3-PROPANEDIOL FROM MODEL MIXTURE OF FERMENTATION BROTH) อ. ที่ปรึกษา : ผศ. ดร. อาทิวรรณ โชติพฤกษ์, อ. ที่ปรึกษาร่วม รศ.ดร. จิรกานต์ เมืองนาโพธิ์ 84 หน้า

งานวิจัยนี้ศึกษาการใช้ตัวเร่งปฏิกิริยาคาร์บอนแบบใหม่ เพื่อใช้ในการสกัดสาร1,3-โพรเพนไดออลจากสารละลายผสมจำลองของน้ำหมัก ที่ได้จากการหมักกลีเซอรอล ซึ่งเป็นของเหลือใช้จากกระบวนการผลิตไบโอดีเซล โดยวิธีเตรียมตัวเร่งเตรียมด้วยวิธีคาร์บอไนต์แบบไม่สมบูรณ์ที่อุณหภูมิ 573 เคลวิน โดยพื้นที่ผิวและปริมาตรของรูพรุนของตัวเร่งเท่ากับ 1.1 เมตร^{2} กรัม$^{-1}$ และ 0.07 เซนติเมตร^{3} กรัม$^{-1}$ ตามลำดับ ส่วนค่าความเป็นกรดของตัวเร่งที่วัดด้วยเครื่อง Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) มีค่าเท่ากับ 1.46 มิลลิโมลต่อกรัม และหมู่ซัลโฟนิกฟังก์ชันถูกหาโดย Nicolet Fourier Transfor Infared Spectroscopy (FTIR) นอกจากนี้ผลของ thermogravimetric analysis (TGA) ยังบอกด้วยว่าตัวเร่งชนิดนี้จะสลายตัวที่อุณหภูมิ200องศาเซลเซียสในการทดลองใช้ตัวเร่งตัวนี้กับปฏิกิริยาระหว่าง1,3-โพรเพนไดออลและอะซิตาดีไฮด์นั้นพบว่าปริมาณตัวเร่งที่เหมาะสมคือ 0.7 กรัมต่อ1กรัมของ 1,3-โพรเพนไดออล ซึ่งจะได้ร้อยละผลได้ของ1,3-โพรเพนไดออลประมาณ92%โดยทำปฏิกิริยาที่อุณหภูมิ 35 องศาเซลเซียสเป็นเวลา2ชั่วโมง ซึ่งเมื่อเปรียบเทียบกับตัวเร่งที่มีขายในท้องตลาดคือ Dowex 50-WX4-200 และ Ambelite IR120 พบว่า ปฏิกิริยาที่ใช้ ตัวเร่งปฏิกิริยาคาร์บอนแบบใหม่ นั้นใช้เวลามากกว่าตัวเร่งที่มีขายในท้องตลาดเนื่องจาก ตัวเร่งปฏิกิริยาคาร์บอนแบบใหม่ มีพื้นที่ผิวน้อย,ปริมาตรรูพรุนและค่าความเป็นกรดที่น้อยกว่า นอกจากนี้ยังได้ทำการทดลองใช้ตัวเร่งปฏิกิริยาคาร์บอนแบบใหม่ กับ กระบวนการรีแอกทีฟเอกแทรกชั่น โดยใช้เอทิล-เบนซินเป็นสารสกัด ซึ่งได้ศึกษาผลของอุณหภูมิ(15,20,25,30,35 องศาเซลเซียส)และความเข้มข้นเริ่มตัวของสาร1,3-โพรเพนไดออล(20,40,60,80,100กรัมต่อลิตร) ด้วย จากผลการทดลองพบว่า เมื่ออุณหภูมิเพิ่มขึ้นทำให้อัตราการเกิดเริ่มต้นและร้อยละผลได้เพิ่มขึ้นและผลของความเข้มข้นเริ่มต้นที่เพิ่มขึ้นก็ทำให้อัตราการเกิดเริ่มต้นเพิ่มขึ้นด้วย และที่ความเข้มข้นเริ่มต้นของ1,3-โพรเพนไดออลเท่ากับ 40 กรัมต่อลิตรซึ่งเป็นความเข้มข้นของน้ำหมักจริงพบว่าได้ร้อยละผลได้ 78.92%โดยทำที่อุณหภูมิ35องศสาเซลเซียส1ชั่วโมงซึ่งเมื่อเปรียบเทียบกับผลของการทำปฏิกิริยาเพียงอย่างเดียวโดยไม่ใส่สารสกัดพบว่าร้อยละผลได้เพิ่มขึ้นถึง20% นอกจากนี้ยังได้นำตัวเร่งนี้ไปทดสอบกับปฏิกิริยาไฮโดรไลซิสซึ่งเป็นปฏิกิริยาย้อนกลับของ1,3-โพรเพนไดออลก็พบว่าร้อยละผลได้สูงถึง 99% และสุดท้ายก็ได้ศึกษาผลของการเสื่อมสภาพหลังใช้ของตัวเร่งเปรียบเทียบกับตัวเร่งที่มีขายในท้องตลาดพบว่าตัวเร่งปฏิกิริยาคาร์บอนแบบใหม่ นั้นเสื่อมสภาพมากกว่าโดยร้อยละผลได้ลดลง 43% ซึ่งจากผลการทดลองพบว่าตัวเร่งปฏิกิริยาคาร์บอนแบบใหม่ นั้นมีข้อได้เปรียบในด้านของราคาที่ถูกกว่าตัวเร่งที่มีขายในท้องตลาดแต่อาจจะต้องปรับปรุงประสิทธิภาพให้ดีขึ้นทั้งในด้านของพื้นที่ผิวปริมาตรรูพรุนและค่าความเป็นกรดนั่นเอง

ภาควิชา..... วิศวกรรมเคมี.....ลายมือชื่อนิสิต……...

สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา……

ปีการศึกษา.....2551.....ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

5070578321 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : 1,3-PROPANEDIOL, REACTIVE EXTRACTION

PANATPONG BOONNAUL: REACTIVE EXTRACTION

OF 1,3-PROPANEDIOL FROM MODEL MIXTURE OF FERMENTATION BROTH. THESIS ADVISOR: ASST. PROF. ARTIWAN SHOTIPRUK, PhD., THESIS CO-ADVISOR ASSOC.PROF.CHIRAKARN MUANGNAPOH, DR.ING. 84 pages.

This study deals with the development of novel carbon based catalyst for use in reactive extraction to separate 1,3-PDO from a model solution of the fermentation broth, derived biologically from conversion of glycerol, the by-product of biodesel production. 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 $m^2 g^{-1}$ and 0.07 $cm^3 g^{-1}$, respectively. The acidity of the catalyst measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS was 1.46 mmol/g). The presence of sulfonic functional group was also confirmed by Nicolet Fourier Transfor Infared Spectroscopy (FTIR). In addition, the thermogravimetric analysis (TGA) results show that the catalyst was stable up to the temperature of 200°C. The test of the catalyst for the acetalization of acetaldehyde and 1,3-PDO in aqueous solution indicated its applicability for such reaction, and the optimal quantity of the catalyst required for this reaction was 0.7 g/ g 1,3-PDO, giving the conversion of approximately 92% after 2 h of reaction at 35°C. Compared with those of commercial ion-exchange catalysts (Dowex 50-WX4-200 and Ambelite IR120), the reaction in the presence of the novel carbon based catalyst took longer (2h) than that in presence of the commercial catalysts (about 1 h). The inferiority in the reactivity of the carbon based catalyst was possibly due to the lower acidity and lower surface area (1.1 vs. 300 for Dowex 50-WX4-200 and 1000 m^2/g for Ambelite IR120) and pore volume (0.07 vs 1.2 for both Dowex 50-WX4-200 and Ambelite IR120). In addition to acetalization reaction, reactive extraction was also carried out using ethyl-benzene as an extractant and the effects of temperature (15, 20, 25, 30, 35 °C) and initial 1,3-PDO (20, 40, 60, 80, 100 g/l) concentrations were determined. The initial reaction rate and the reaction conversion were found to increase as the temperature increased. On the other hand, as the initial 1,3-PDO increased, the initial reaction rate increased, but the conversion (after 60 min) decreased. At 40 g/L of initial 1, 3-PDO solution, a typical concentration of 1, 3-PDO derived from the fermentation process, the conversion was found to be 78.92% after 60 min for reactive extraction at 35°C. Compared with the conversion achieved by acetalization alone (without the presence of the extract phase), the conversion of reactive extraction was 20% higher for the same reaction condition. In addition, in this study,the novel catalyst was proven to be suitable for the reverse hydrolysis reaction to convert 2-MD to the desirable 1,3-PDO with the conversion expected to be higher than 99%. Finally, the results on multiple acetalization in aqueous solution in the presence of the catalyst indicated that the possibility of reusing, however the reactivity of the catalysts decreased about 43% Although the reactivity and the reusability of the carbon based catalyst was found to be inferior to the commercial Dowex 50-WX4-200 and Ambelite IR120, experimental results suggested a possibility of improving the carbon based catalysts properties further, possibly by improving the porosity, surface area, and acidity through optimal process conditions. 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.

Department : …Chemical Engineering... Student's Signature .....

Field of Study :..Chemical Engineering... Advisor's Signature .....

Academic Year :…….....2008……. Co-advisor's Signature .....

ACKNOWLEDGEMENTS

I would like to express my earnest gratitude to my advisor, Asst. Prof. Artiwan Shotipruk, Ph.D and my co-advisor Assoc. Prof. Chirakarn Muangnapoh, Dr.Ing for their encouragement, support, guidance, and unfailing faith all the way through my thesis work and study.

Thanks to all of my thesis committee, Assoc. Prof. Muenduen Phisalaphong, Ph.D., Kasidit Nootong, Ph.D. and Phatthanon Prasitchoke, Ph.D. for their kind advices and recommendations which are invaluable for improving my work.

Many thanks are also addressed to Mrs. Sunee Pakprapan (Scientific and Technological Research Equipment Centre, Chulalongkorn University) for her kind assistance in commencing Gas Chromatography (GC)

Sincere thanks are given to all members of the Biochemical Engineering Research Laboratory and all my friends and staffs in the Department of Chemical Engineering, Chulalongkorn University for their assistance, support, and warm collaborations.

Finally, I would like to express my highest gratitude to my parents for their affectionate support, blessings, inspiration, and love which guide me all the way throughout my life and study.

CONTENTS

PAGE

ABSTRACT (THAI) iv
ABSTRACT (ENGLISH) v
ACKNOWLEDGEMENTS vi
CONTENTS vii
LIST OF TABLES x
LIST OF FIGURES xi

CHAPTER

I INTRODUCTION 1
1.1 Rationale 1
1.2 Objective 4
1.3 Working scopes 4
1.4 Expected benefits 5

II BACKGROUND AND LITERATURE REVIEW 6
2.1 1,3-Propanediol and its applications 6
2.2 Chemical process for 1,3-Propanediol 6
2.3 Microbial formation of 1,3-Propanediol 7
2.4 Compositions of fermentation products 8
2.5 Downstream of 1,3-Propanediol 12
2.6 Reactive extraction 15
2.6.1 Reaction of 1,3-PDO to dioxane 24
2.6.2 Extraction of dioxane 24
2.6.3 Hydrolysis reaction 25
2.7 Catalysts for acetalization reaction 26

CHAPTER **PAGE**

III MATERIAL AND METHODS 29
3.1 Materials 29
3.2 Preparation of 2-methyl-1,3-dioxane(2-MD) 29
3.3 Preparation of catalyst.....30
3.4 Catalyst reactivity for acetalization of 1,3-PDO and acetaldehyde 30
3.5 Reactive extraction.....31
3.6 Hydrolysis of 2-MD to obtain 1,3-PDO 32
3.7 Catalyst characterization.....32
3.8 GC analysis of 1,3-PDO and 2-MD.....33

IV RESULTS AND DISCUSSION 34
4.1 Catalyst characterization.....34
4.2 Catalyst reactivity for acetalization of 1,3-PDO and acetaldehyde in aqueous solution.....36
4.2.1 Preliminary results of catalyst reactivity.....36
4.2.2 Determination of suitable catalyst to 1,3-PDO mass ratio for acetalization 38
4.2.3 Comparison of catalyst reactivity 39
4.3 Reactive extraction of 2-MD 40
4.3.1 Preliminary results of reactive extraction 41
4.3.2 Effect of temperature 43
4.3.3 Effect of initial concentration of 1,3-PDO.....46
4.4 Evaluation of catalyst deactivation 49
4.5 Hydrolysis reaction 50

V CONCLUSIONS AND RECOMMENDATIONS.....52
5.1 Conclusions …….....52
5.2 Recommendation ……. 53

CHAPTER **PAGE**

REFERENCES.....54
APPENDICES.....56
.....
APPENDIX A: Experimental data for analysis.....57
APPENDIX B: Experimental data.....62
APPENDIX C: List of publication.....68
VITA.....84

LIST OF TABLES

TABLE **PAGE**

2.1 By-products of fermentation 9
.....
2.2 Properties of 1,3-PDO and by-product 10
.....
2.3 Review of reactive extraction for separation of 1,3-PDO.....16
2.4 Review of reactive extraction for separation of 1,3-PDO.....18
2.5 Review of reactive extraction for separation of 1,3-PDO.....20
2.6 Review of reactive extraction for separation of 1,3-PDO.....22
2.7 Acetalization of carbonyl compounds with 1,2-ethanediol 27
2.8 Acetalization of carbonyl compounds with 1,4-butanediol 28
3.1 Studied variation of thesis.....32
4.1 Physical properties of catalyst 35
4.2 %conversion of 1,3-PDO with varied reactive extraction temperature 46
4.3 %conversion of 1,3-PDO with varied 1,3-PDO initial concentration 49
.....

LIST OF FIGURES

FIGURE **PAGE**

2.1 Metabolic pathway of glycerol metabolism.....7
2.2 Scheme of the acetalization of PDO 24
2.3 Schematic of diagram reactive extraction process.....26
2.4 Acetalization of diol under heterogeneous condition 27
3.1 Apparatus setup for catalyst preparation instrument 30
4.1 FTIR spectra of sulfonated carbon based catalyst 35
4.2 TGA analysis of sulfonated carbon based catalyst 36
4.3 Chromatogram of reactants and product in aqueous solution.....37
4.4 Effect of catalysts mass in the aqueous solution.....39
4.5 Compare catalyst with the commercials catalysts 40
4.6 Chromatogram of sample in both phases.....42
4.7 Effect of temperature on reactive extraction at initial concentration 40 g/L 45
4.8 Effect of initial 1,3-PDO concentration on reactive extraction at 35°C 48
4.9 Conversions of multiple reactions for various solid catalysts 50
4.10 Chromatogram of 1,3-PDO after hydrolysis reaction.....51

CHAPTER I
INTRODUCTION

1.1 Rationale

The high demand of energy and the depletion of the world supply of crude oil and natural gas have currently caused the fuel price to soar greatly, necessitating the development of alternative energy such as wind energy, solar energy, ocean energy, and bio-energy. Biodiesel is among the most promising alternatives for renewable energy that has recently gained much interest because it is a green energy and its properties are closed to those of petroleum diesel. Biodiesel is typically produced by transesterification of plant oils or animal fats, whose process 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 cosmetic industry or as animal feeds, 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 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 biological process of glycerol conversion to 1,3-PDO using various types of microorganism such as *Klebsiella pneumoniae, Citobacter frundii, Enterobacter agglomerans,*and *Clostridium butyricum.* Among these microorganisms, *Clostridium butyricum* leads to the highest yield of 1,3-PDO.

Beside 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 a challenge. Various separation processes have been investigated to purify 1,3-PDO. Ames (2002) studied evaporation and distillation

processes for the separation of 1,3-PDO from the aqueous fermentation broth. However, this process needs a large amount of energy. Malinowski (1999) proposed to extract 1,3-PDO from dilute aqueous solutions by liquid-liquid extraction with organic solvents. However this purification process requires handling of large quantities of organic solvents as its 1,3-PDO extraction efficiency is generally too low. Cho et al. (2006) proposed the use of phase separation with ethyl acetate to concentrate 1,3-PDO from fermentation broth, after which chromatography through silica gel column was employed to separate 1,3-propanediol from the mixture of 1,3-PDO and 1,2-PDO. Their study showed that the overall purity and yield of 1,3-PDO were high. But in this study, they only reported the results from the chromatography step. Although the results in phase separation were not the focus of their study, it was later shown by Boonsongsawat (2007) that for the 1,3-PDO extraction from the fermentation broth by ethyl acetate, the distribution of 1,3-PDO into ethyl acetate extraction solvent appeared to be rather low. In addition to phase separation, adsorption process with ion-exchange resins have been investigated, but the non-ionic properties of 1,3-PDO make the process unsuitable. Luerruk (2008) studied adsorption process for the recovery of 1,3-PDO using polymeric neutral resins such as the highly hydrophobic Amberlite XAD-16 and the functionalized more hydrophilic XAD-7. The results show that XAD-7 was an effective adsorbent for the recovery of 1,3-PDO compared with XAD-16 and other adsorbents previously investigated. However, there are still some problems with adsorption process such as the requirement of long operating time, rather low adsorbent capacity, and the need of an additional separation agent such as ethanol. Alternatively, Li et al. (2001) used a zeolite membrane for the separation of 1,3-PDO from glycerol and glucose by means of pervaporation. However a drawback of this process includes the low flux and selectivity.

Alternatively, reactive extraction is an easy and energy efficient process in which the reaction takes place simultaneously with 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 shorter operating time and smaller amount of reactant and extractant, which

could also be recovered and reused. Malinowski et al. (2000) used UNIFAC program to select an appropriate solvent for extraction of dioxane. Three solvents that have 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 researcher later investigated the effect of two types of ion exchange catalysts for reactive extraction of 1,3-propanediol: Dowex and Amberlite ion exchange resins [Malinowski et al. 2002]. Dowex ion exchange resin was found to be 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) proposed a reactive extraction process with use of the 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 researches on reactive extraction, either a homogeneous liquid acid or ion exchange acid resin was used as catalyst. Homogeneous acid catalysts are corrosive and cannot be reused. Furthermore, its use, particularly in aqueous system such as this, leads to large amount of waste water. This problem can be solved with use of solid acid catalysts, and those currently used are such as Dowex and Amberite ion exchange polymeric resions. 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 [Takagaki, 2006]. The advantages of this novel class of catalysts are the low cost, simple preparation, high acid density and stability. The dense acidity endues its 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 [Takagaki, 2006]. . In addition to the sulfonic acids based of the simple sugars, Gao et al (2007) 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 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 organic phase, these results suggested potential application of such catalysts for the reactive extraction of 1,3 PDO from the aqueous solution, in which acetalization is carried out in an aqueous system simultaneously with the extraction of the dioxane product into an organic solvent.

1.2 Objectives

Investigate the possibility of applying the low cost sulfonated carbon based catalyst for reactive extraction of 1,3-PDO from aqueous solution.

1.3 Working scope

1.3.1 Synthesize the novel carbon based catalyst by incomplete carbonization of naphthalene in sulfuric acid at a specified condition.

1.3.2 Characterize the synthesized catalyst.

- internal surface area and pore volume by BET analysis.
- concentration of acid sites by elemental analysis using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and titrations with KOH following ASTM D6751 metod.
- thermal characterisitics by thermogravimetric analaysis (TGA)

1.3.3 Test the novel carbon based catalyst for the acetalization of acetaldehyde and 1,3-PDO in aqueous solution and determine the suitable quantity of novel carbon based catalyst required for this reaction.

1.3.4 Compare the reactivity of the catalyst and compare it with those of commercial ion-exchange catalysts (dowex and amberlite)

1.3.5 Conduct reactive extraction of 1,3-PDO in aqueous solution by using ethyl-benzene as extractant and determine the effects of temperature and initial 1,3-PDO concentrations on the reactive extraction.

- Range of temperature studied: 15, 20, 25, 30, 35 °C
- Range of initial1,3-PDO concentration studied: 20, 40, 60, 80, 100 g/l

1.3.6 Test the possibility of recovering 1,3-PDO from the process by hydrosis of the extracted dioxane using the novel synthesized catalyst.

1.3.7 Test the deactivation of the catalyst by carrying out multiple acetalization in aqueous solution and compare the results with those of commercial ion-exchange resins.

1.4 Expected benefits

The results of this study suggested the possibility of using new low cost carbon based catalysts for the reactive extraction of 1,3-propanediol derived from biological process.

CHAPTER II
BACKGROUND & LITERATURE REVIEWS

2.1 1,3-propanediol and its applications

1,3-Propanediol (1,3-PDO) is one of the major monomer components for the production of high performance polyester such as polytrimethylene terephthalate (PTT). In addition, 1,3-PDO, has been necessarily used as a chemical intermediate in the productions of polyester, polyether, and polyurethane. 1,3-PDO production could be achieved by a chemical process, by the hydration and hydrogenation of acetaldehyde. However the high production cost of 1,3-propanediol by this method would limit the application range of 1,3-PDO, only to the productions of some organic solvents or polymers [Malinowski, 2000]. Until recently, the emergence of several new large biodiesel plants has led to a large amount of glycerol byproducts, which bring much interest to the research community to focus on the conversion of 1,3-PDO from the becoming-low cost-glycerol. The production of 1,3-PDO from glycerol could be achieved by an entirely different process, via biological conversion of glycerol by certain strain of bacteria [Zeng et al., 2002]. The chemical and biological processes for the production of 1,3-PDO are described as follow.

2.2 Chemical process for 1,3-propanediol

The chemical process for 1,3-PDO production starts from acrolein, which is obtained by catalytic oxidation of propylene. Acrolein is hydrated at moderate temperature and pressure to 3-hydroxypropionaldehyde which, in a second reaction, is hydrogenated to 1,3-PDO over rubidium catalyst under high pressure (90 bar). As an alternative to this process, the production of 1,3-PDO can be achieved by the oxidation of ethylene to produce ethylene oxide, which is then transformed with synthesis gas in a hydroformylation process to 3-hydroxypropanal. However for this reaction, very high pressure (150 bar) is required [Zeng et al., 2002].

2.3 Microbial formation of 1,3-propanediol

The bioconversion of glycerol has been known for almost 120 years and has been demonstrated for several bacterial strains, e.g., *Lactobacillus brevis* and *buchnerii*, *Bacillus wellchii*, *Citrobacter freundii*, *Klebsiella pneumoniae*, *Clostridium pastteurianum*, and *Clostridium butyricum*. The biosynthesis of 1,3-PDO under anaerobiosis take place via the following biochemical reaction: one portion of glycerol is oxidized to dihydroxyacetone by an NAD-dependent glycerol dehydrogenase, whereas the rest of the glycerol is dehydrated to 3-hydroxypropionaldehyde by a vitamin B12-dependent dehydratase. The production of the dehydration reaction, 3-hydroxypropionaldehyde (3-HPA), is reduced in 1.3-PDO by an NAD-dependent oxidoreductase as shown in Fig. 1. In this case, the final acceptor of the electrons is the 3-HPA [Zeng et al., 2002].

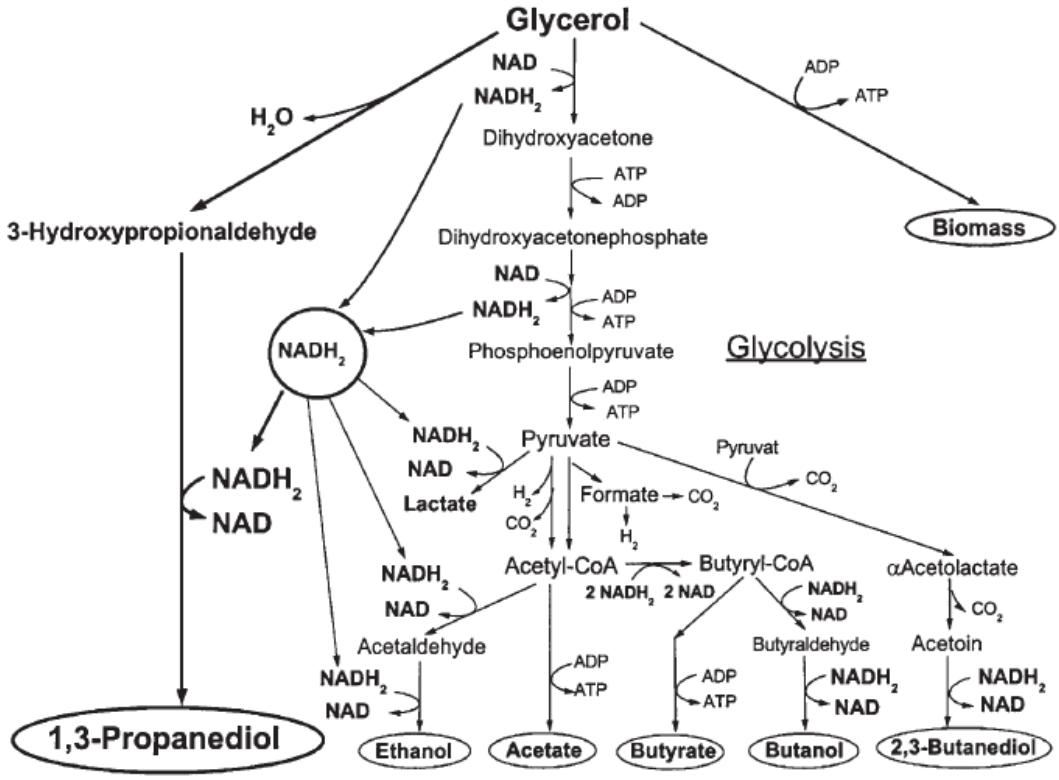


Figure 2.1 Metabolic pathways of glycerol metabolism

The yield of 1,3-PDO depends on the combination and stoichiometry of the reductive and oxidative pathways. It has been shown that the combination of 1,3-PDO generation with acetic acid as the sole by-product of the oxidative pathway results in the maximum yield of 1,3-PDO. For this combination, the fermentation equations can be written as:

$$CH_2OH\text{-}CHOH\text{-}CH_2OH + H2O \text{ ---- > } CH_3COOH + CO_2 + H_2 + 4[H]$$
$$2CH_20H\text{-}CHOH\text{-}CH_2OH + 4H \text{ ---- > } 2CH_2OH\text{-}CH_2\text{-}CH_2OH + 2H20$$

$$3CH_2OH\text{-}CHOH\text{-}CH_2OH \text{ ---- > } CH_3COOH + CO_2 + H_2 + 2CH_20H\text{-}CH_2\text{-}CH_2OH + H_2O$$

Unpurified glycerol, particular from biodiesel plants, has been shown to be an excellent fermentation substrate for 1,3-PDO production (Zeng et al., 2002). Barbirato et al., (1998) compared the production of 1,3-PDO from industrial glycerol sources and demonstrated the feasibility of the microbial fermentation technology. Among the microorganisms (*Klebsiella pneumoniae, Citobacter frundii, Enterobacter agglomerans, Clostridium butyricum)* studied, *Clostridium butyricum* leads to the largest production yield of 1,3-PDO. With this culture, two major acids (butyrate and acetate) and gaseous products, CO_2 and H_2 are produced. Moreover, Reimann et al. (1997) suggested that the productivity of 1,3-PDO from glycerol by *Clostridium butyricum* could be further improved by a factor of four in a continuous fermentation with cell recycling, compared with the continuous culture without cell recycling.

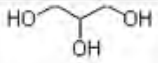
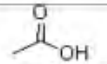
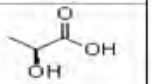
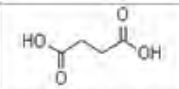
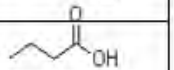
2.4 Compositions of Fermentation Products

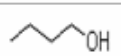
For extraction and purification of the 1,3-PDO from fermentation broths, the compositions of 1,3-PDO, unconverted glycerol, and other by-products, that are present in the broth, and their properties are the key data for determining the appropriate method and suitable conditions. The by-products resulted from the fermentation processes with different bacterial strains are listed in Table 2.1, and the general characteristics of 1,3-PDO and these by-products are summarized in Table 2.2.

Table 2.1 By-products of fermentation (Zeng et al., 2002)

Microorganisms	**By-product of 1,3-propanediol fermentation**	
Klebsiella Pneumoniae	Acetic acid, Ethanol, Lactic acid, Succinic acid, and 2,3-Butanediol	CO_2, H_2
Citrobacter freundii	Acetic acid, Ethanol, Lactic acid, Succinic acid, and 2,3-Butanediol	CO_2, H_2
Enterobacter agglomerans	Acetic acid, Ethanol, Lactic acid, Succinic acid, and 2,3-Butanediol	CO_2, H_2
Clostridium butyricum	Acetic acid, Butyric acid	CO_2, H_2
Clostridium pasteurianum	Acetic acid, Butanol	CO_2, H_2
Clostridium acetobutylicum	Acetic acid, Butyric acid	CO_2, H_2

Table 2.2 Properties of 1,3-PDO and by-products

Name	Synonyms	Molecular Formula	Molecular Weight	Melting point (°C)	Boiling point (°C)	Density (g/cm3)	Solubility in water	Structure
1,3-propanediol	1,3 propylene glycol	$C_3H_8O_2$	76.09	-32 °C	214 °C	1.052	100g/l	
Glycerol	Propane-1,2,3-triol	$C_3H_8O_3$	92.09	18°C	290°C	1.216	>500 g/l	
Acetic acid	Ethanoic acid	$C_2H_4O_2$	60.05	16 °C	117 °C	1.048	miscible	
Ethanol	Ethyl Alcohol	C_2H_6O	46.0688	-114.1 °C	78.3 °C	0.789	slightly soluble	
Lactic acid	2-Hydroxy propanoic acid	C3H6O3	90.07	53 °C	122 °C	1.05	miscible	
Succinic acid	Butanedioic acid	$C_4H_6O_4$	118.08	185 °C	235 °C	1.552	80g/l	
2,3-butanediol	2,3-Butylene glycol	$C_4H_{10}O_2$	90.12	19 °C	180 °C	1.01	miscible	
Butyric acid	n-Butyric acid	$C_4H_8O_2$	88.1	-7 °C	162°C	0.96	miscible	

Name	Synonyms	Molecular Formula	Molecular Weight	Melting point (°C)	Boiling point (°C)	Density (g/cm3)	Solubility in water	Structure
Butanol	n-Butyl alcohol	$C_4H_{10}O$	74.12	-89.5 °C	117.6 °C	0.81	80 g/l	
Carbon dioxide	-	CO_2	44.01	-57 °C	-78 °C	1.98	-	-
Hydrogen	-	H_2	2	-259.14°C	-252.87°C	0.089	-	-

2.5 Downstream of 1,3-propanediol

The downstream purification of 1,3-PDO can be proceeded with various methods. The conventional process is by evaporation and distillation, which give high yield and purity for recovery 1,3-PDO (Ames, 2002). However these processes could be difficult due to characteristics of 1,3-propanediol such as strong hydrophilic and low volatility in aqueous solutions, and thus the processes are neither economical nor suitable. Alternatively, liquid-liquid extraction of aqueous 1,3-PDO was investigated by Malinowski (1999) who reported that aldehydes were the most suitable solvents, giving the highest distribution coefficient and selectivity. However, the distribution of 1,3-PDO in such solvent was found to be insufficient to make simple extraction feasible. Recently, Kim et al. (2006) studied the isolation and purification method for producing 1,3-PDO with high purity and high yield from synthetic mixture containing 1,3-PDO, 1,2-PDO, glycerol, glucose. Their method consisted of phase separation to remove glucose and glycerol from the mixture and which was then followed by chromatographic purification of 1,3-PDO from its mixture with 1,2-PDO using a silica resin packed column. The elution condition was attained by using ethyl acetate/methanol (98/2, v/v) as a mobile phase in an isocratic mode. Their study showed that the over all purity and yield of 1,3-propanediol were 98% and 82% in the purification process, respectively. The purity of 1,3-PDO obtained was high, however, the high yield reported in their study was based on the amount of 1,3-PDO originally loaded onto the column without considering the extraction efficiency obtained from the first liquid-liquid extraction with ethyl acetate. This extraction efficiency was indeed expected to be quite low, according to the low value of distribution coefficient for such system reported by Boonsongsawat et al., 2007.

Alternatively, Corbin et al. (2003) proposed a separation process of 1,3- PDO from a biological mixture of 1,3- PDO and glycerol using a molecular sieve. The zeolite H-ZSM-5 (Si/Al=140) was used for batch 1,3- PDO removal from the cell-free fermentation. Ethanol/water mixture was used as an eluent. The yield of 1,3- PDO was increased by increasing the concentration of ethanol, which indicated the desirability of performing the elution of 1,3- PDO by an ethanol-rich mixture. The total recovery of 1,3- PDO product was found to be as high as 94.7%. But the preparation of the molecular sieve required rather complicated procedures. Roturier et

al. (2002) proposed the purification of 1,3- PDO from fermentation medium by chromatography using a strong acidic cation exchange resin of the polystyrene sulfonic acid type crosslinked with divinylbenzene, consisting of lanthanum, lead, zinc, iron, and aluminum with water as eluent. The maximum yield, which in the first fraction of elution was 31.9% using lanthanum resin and 47% using lead resin. The reason for low yield was due to the lack of ionic properties of 1,3-PDO. At the same time, Hilaly et al. (2002) studied a method of recovering 1,3-PDO from fermentation broth by ion exchange resins and utilized simulated moving bed technology, which is a convenient and efficient method of chromatographic separation of fermentation broth. In this method, ionic components were rejected due to ionic repulsion. The non-ionic components entered the pores of the stationary phase and, therefore, eluted from the column later than other ionic components. The purity of 88.1% and the recovery of 1,3-propanediol was 86.7% were achieved in a column containing 100 ml of a cation exchange resin (CS11GC350). The SMB experiments were carried out wherein 12 column, were loaded with 300 ml of cation resin (CS11GC350). The purity of 89.4% and the recovery of 99.5% were achieved. Despite the high purity and yield, SMB technology was too complicated to be applied in large scale. Although the recovery of 1,3-PDO was achieved with the above adsorbents, the capacity of the adsorbents for 1,3-PDO were quite low. Luerruk W. (2008) investigated the use of polymeric neutral resins such as the highly hydrophobic Amberlite XAD-16 and the functionalized more hydrophilic XAD-7 as alternative adsorbents. The results of a single component adsorption equilibrium indicated the capacity (q) of 1,3-PDO adsorption of 835.96 and 584.61 mg of 1,3-PDO /g dry resin for XAD-7 and XAD-16 respectively and this was achieved at 160 g/L 1,3-PDO initial concentration. Although the non-ionic polymeric resin like XAD-7 was shown to be an effective adsorbent for the recovery 1,3-propanediol, long operating time was required for adsorption of 1,3-PDO with XAD-7 polymeric neutral resins compared with other separation methods.

As an alternative process for the separation of 1,3-PDO from fermentation broth, Li et al. (2001) investigated the recovery of 1,3-PDO by pervaporation, using 6 types of zeolite membrane (silicalite-1, ZSM-5, ZSM-11, ZSM-5+11, modenite, X-type, and Y-type) to recover 1,3-PDO from glycerol and glucose. The results show that for the ZSM-5 and X-type, 1,3-PDO/glycerol selectivity decreased as the

temperature increased, and X-type gave the highest total and 1,3-PDO fluxes. In the same year, Li et al. investigated the use of ZSM-5 membrane for 1,3-PDO recovery in binary, ternary, and quaternary mixtures. The results were same as the recent study, in which 1,3-PDO/glycerol selectivity decreased when temperature was increased. They explained that the glycerol flux was higher than 1,3-PDO flux because glycerol could pass through the membrane through both zeolite and non-zeolite pores, while 1,3-PDO could pass only through the zeolite pores. The author also studied the quaternary solution and fermentation broth by used X-type zeolite membrane. The results show that total flux increased when temperature increased, as the membrane's pore size was larger than molecules of water, glycerol and 1,3-PDO. In addition, the concentration of 1,3-PDO in permeate increased when temperature was increased, because water could pass through the membrane faster than other compounds. Moreover, the results obtained with the actual fermentation broth followed the same trend with the model feed. In addition, Li et al. (2002) studied the recovery 1,3-PDO in ternary solution by using X-type membrane which was supported by difference materials. They found that the X-type membrane that was supported by γ-Al_2O_3 showed the most superior performance. Although pervaporation is an energy efficient process and need no an additional separation agent such as ethanol, this process still has some problems such as high membrane cost and low 1,3-PDO flux.

Alternative to all methods above mentioned, reactive extraction has been quite considerably investigated. It is a separation method which combines reaction and extraction together. This reaction was performed to convert 1,3-PDO to dioxane, which has higher solubility in organic solvent than 1,3-PDO, thus making it more effective procedure for the recovery 1,3-PDO than liquid-liquid extraction. After extraction the dioxane was then converted back to 1,3-PDO by simple hydrolysis. The reactive extraction process is therefore a simple method and energy efficient as it is operated at rather low temperature.

2.6 Reactive Extraction

The reactive extraction process is an interesting energy efficient process. For the recovery 1,3-PDO from aqueous solution by this method, Malinowski et al. (2000) first used UNIFAC program to determine the appropriate solvent for the extraction of dioxane, converted from 1,3-PDO. Three solvents that have high mass partition coefficient and were the least environment pollutant were toluene, o-xylene, and ethyl-benzene. For their reaction, they used acetaldehyde as a reactant and Dowex ion exchange as catalyst. Of the solvents used in the experiment, their results showed that toluene was the best extractant, which gave as high as 75% recovery. In addition, 98-99 % conversion (shown in table 2.3) could be obtained in all experiments. The same group of researcher later investigated the effect of two types of ion exchange catalysts for reactive extraction of 1,3-PDO: Dowex and Amberlite ion exchange resins (Malinowski et al. 2002). Dowex ion exchange resin was found to be more effective catalyst. In addition, the authors reported the difficulty of using toluene as the extractant as its boiling point was closer to dioxane. Thus the choice of higher boiling extractant, o-xylene or ethyl benzene would be advantageous (show in table 2.4). Fang et al. (2006) conducted a similar reactive extraction procedure employing o-xylene as an extractant and acetaldehyde as a reactant, using HD-8 ion exchange resins as catalyst. and investigated the kinetic model for the reactive extraction of 1,3-PDO. They concluded that the process of 1,3-PDO reactive extraction could be reasonably described by the first-order kinetic model, and the overall conversion of 1,3-PDO was found to be greater than 98% (Table 2.5).

Alternatively, Hao et al. (2005) proposed a reactive extraction process with use of the same chemical as both the reactant and the extractant. Propionaldehyde, Butyradehyde and Isobutyradehyde were investigated in this research, with use of liquid catalyst (HCl) for the reaction. They reported that Isobutyradehyde showed the most superior performance for the recovery of dioxane (Table 2.6). On the other hand, isobutyradehyde reacted with 1,3-PDO which produced 2-Isopropyl-1,3-dioxane, which has high boiling point (about 140°C), thus making it more difficult to be isolated than using acetaldehyde.

Table 2.3 Review of reactive extraction for separation of 1,3-PDO.

topic	Reactive Extraction for Downstream Separation of 1,3-Propanediol
author	Janusz J. Malinowski*, 2000
objective	Investigations of extractive reaction approach for the separation of 1,3-PD from a dilute, aqueous solution.
feed material	aqueous solution
solvent	toluene, o-xylene, and ethyl benzene
reactant	acetaldehyde
ratio	1,3-propanediol—39.95 or 59.60 g/L, acetaldehyde—235 or 352 g/L, catalyst—20, 50 or 100 g/L PDO solution : solvent = 50 ml : 50 ml (PDO solution contain an aqueous solution of 1,3-propanediol and acetaldehyde)
condition	Reactive extraction condition is 31.5 or 40 °C.
method	1. Equal volumes (50 mL) of a reaction mixture containing an aqueous solution of 1,3-propanediol and acetaldehyde together with a cation-exchange resin as a catalyst, and an appropriate organic extractant.
	2. Stirred vigorously in the one-step glass reactor–extractor.
	3. The tubes were placed in a shaker at 20 °C and 140 rpm.
	4. Analysis of 2-methyl-1,3-dioxane in both, aqueous and organic phases.
analysis	HP 5890 gas chromatograph equipped with TCD detector and a 30-m HP-1 column.
result	Toluene was the best extraction performance.
yield	91-92%

Table 2.4 Review of reactive extraction for separation of 1,3-PDO.

topic	The Effective Approach for Recovery of Methyl-substituted 1,3-dioxane from Aqueous Media
author	Janusz J. Malinowski1,* and Andrew J. Daugulis2 ,2002
objective	The application of solvent extraction for the recovery of 2-methyl-1,3-dioxane from the aqueous solution is discussed.
feed material	aqueous solution
solvent	toluene, o-xylene, and ethyl benzene
reactant	acetaldehyde
ratio	1,3-propanediol—39.95 or 59.60 g/L, acetaldehyde—235 or 352 g/L, catalyst—20, 50 or 100 g/L PDO solution : solvent = 50 ml : 50 ml (PDO solution contain an aqueous solution of 1,3-propanediol and acetaldehyde)
condition	Reactive extraction condition is room temperature
method	1. Equal volumes (50 mL) of a reaction mixture containing an aqueous solution of 1,3-propanediol and acetaldehyde together with a cation-exchange resin as a catalyst, and an appropriate organic extractant.
	2. Stirred vigorously in the one-step glass reactor–extractor.
	3. The tubes were placed in a shaker at 20 °C and 140 rpm.
	4. Analysis of 2-methyl-1,3-dioxane in both, aqueous and organic phases.
analysis	HP 5890 gas chromatograph equipped with TCD detector and a 30-m HP-1 column.

result	Toulene, despite the best extraction performance, has the boiling point (110.68C) too close to that of 2-methyl-1,3-dioxane (118C), thus the choice of a higher boiling extractant, o-xylene or ethyl benzene would be advantageous.
yield	-
recovery	75%
conversion	98-99%

Table 2.5 Review of reactive extraction for separation of 1,3-PDO

topic	Novel Route of Reactive Extraction To Recover 1,3-Propanediol from a Dilute Aqueous Solution
author	Jian Hao, Hongjuan Liu, and Dehua Liu* 2005
objective	A novel reactive extraction route is presented: propionaldehyde, butyraldehyde, or isobutyraldehyde were used to react with PDO to form substituted 1,3-dioxanes, which were extracted to an organic phase that exceeded the aldehyde formed.
feed material	aqueous solution
solvent	Propionaldehyde,butyraldehyde,Isobutyraldehyde
reactant	Propionaldehyde,butyraldehyde,Isobutyraldehyde
ratio	PDO : solvent = 0.5 ml : 0.5 ml (PDO concentration = 60 g/L)
condition	Reactive extraction condition is 20°C
	Hydrolysis temp must higher than solvent,but lower than water
methods	1. 60 g/L PDO aqueous solution was adjusted to pH) 1.22 ,1.53, and 1.90.
	2. A total of 0.5 mL of the PDO solutions and 0.5 mL of aldehydes were added to 1.5-mL tubes.
	3. The tubes were placed in a shaker at 20 °C and 140 rpm.
	4. Samples were taken, and the changes of PDO and acetals at the two phases were analyzed.
	5. A total of 10 mL of the extractant that was obtained from reactive extraction of propionaldehyde acetalization was placed in the distillation equipment.

yield	-
recovery	65%, 85%, 87%
conversion	-

Table 2.6 Review of reactive extraction for separation of 1,3-PDO.

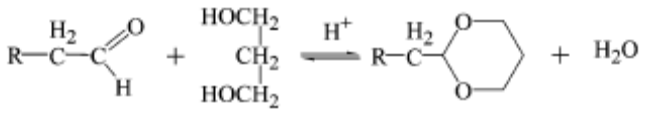
topic	Study on Reactive Extraction Kinetics of 1,3-Propanediol in Dilute Aqueous Solutions.
author	Yun-Jin Fang and Peng Zhou, 2006
objective	Study the reactive extraction kinetics of the reaction 1,3-PD with acetaldehydes in a dilute aqueous solution.
feed material	aqueous solution
solvent	o-xylene
reactant	acetaldehyde
ratio	2.09 g of 1,3-PDO : 100 ml of acetaldehyde solution (acetaldehyde concentration 30%) : 100 ml of o-xylene
condition	Reactive extraction condition is 293-343K Speed of agitation 423 r/min.
method	1. The reaction of 1,3-PD with acetaldehyde was completed in a 500 ml jacketed reactor with a motor stirrer.
	2. 100 ml acetaldehyde solution (acetaldehyde concentration 30%), 100 ml o-xylene and HD-8 ion-exchange resin of 40 g/L were first charged into the reactor with a agitating speed of 723 r/min, and preheated to the desired temperature by recycled hot water.
	3. 2.09 g 1,3-PD was introduced directly into the reactor.
	4. Samples of the two-phase mixture were analyzed on a gas chromatograph at a fixed time interval.

analysis	7890F series gas chromatograph (GC) a 15m SE-54 column.
result	1.The reactive extraction is a weakly exothermal reaction with the experimental and the calculated reaction heat being a good agreement.
	2. pseudohomogeneous kinetic model based on experimental data was established. The kinetics was found to be first-order in the concentrations of the reactants and the products.
	3. The comparison of experimental values and calculated values of 1,3-PDO reactive extraction rate can be seen that most relative deviation are less than 15%
yield	-
recovery	80.6%
conversion	98%

The reactive extraction process for recover 1,3-PDO can be provided three steps. 1) Reaction step is the step which 1,3-PDO reacted with reactant and is converted to dioxane. 2) Extraction step is the step which dioxane is removed from aqueous phase to the extractant phase. 3) Hydrolysis reaction is the step in which dioxane reacted with water and is converted back to 1,3-PDO.

2.6.1 Reaction of 1,3-PDO to dioxane

The reaction of 1,3-PDO and aldehyde to dioxane that is generally called acetalization reaction. After the reaction is completed, water is obtained as a by-product as shown in figure 2.2.



Aldehyde 1,3-PDO Dioxane water

Figure 2.2 Scheme of the acetalization of PDO.

Typically, the acetalization reaction sequence would also include the steps of stirring the mixture, aging the mixture at a modestly elevated temperature, e.g., about 30° C. to about 65° C. (to achieve an acceptable level of conversion to Dioxane). Moreover, the reaction is acid catalyzed. The catalyst can be a solid catalyst or liquid catalyst. The liquid catalyst (Homogeneous catalyst) is difficult to isolate from sample and therefore the solid catalyst (Heterogeneous catalyst) is more interesting. From the literature reviews, all of solid catalysts employed for this reaction are of the ion exchange resins. These catalysts are however quite expensive.

2.6.2 Extraction of Dioxane

Choices of extraction solvents need to be carefully evaluated when optimizing the design and operation of the extraction. The selection of alternative solvents can be performed empirically, theoretically or experimentally. Empirical methods generally involve comparison of one or more properties of solvents to classify them and to

assess the solvent capacity. These methods can only identify possible alternative solvent classes, but the selection of a specific solvent is not possible. Theoretical screening methods are based on a thermodynamic description of the investigated system. Here, solvent selection is based on the solute distribution ratio, selectivity, and mutual solvent solubility of liquid-liquid system, which can be calculated using various thermodynamic models. The Unifac model is usually initially applied for the prediction of distribution and mutual solubility data.

From the literature reviews, extractants used was consisted of toluene, o-xylene, ethyl-benzene, propionaldehyde, butyradehyde, and isobutyradehyde. However, toluene has the boiling point too close to dioxane, thus making it difficult to be isolated from dioxane. Moreover, isobutyradehyde reacted with 1,3-propanediol to produce 2-Isopropyl-1,3-dioxane which has high boiling point (about 140°C), and thus making it more difficult to isolated compared with acetaldehyde. Based on the literature reviews, two extractants of our interest would be o-xylene and ethyl-benzene. Since the efficiency of o-xylene was found to be comparable to ethyl-benzene, but has higher price higher, ethyl-benzene would be advantageous and would be chosen for the investigation in this study.

2.6.3 Hydrolysis reaction

Hydrolysis reaction needs be carried out to convert dioxane back to 1,3-PDO. In this step, dioxane will react with water at high temperature with use of strong acid catalyst as in the acetalization reaction.

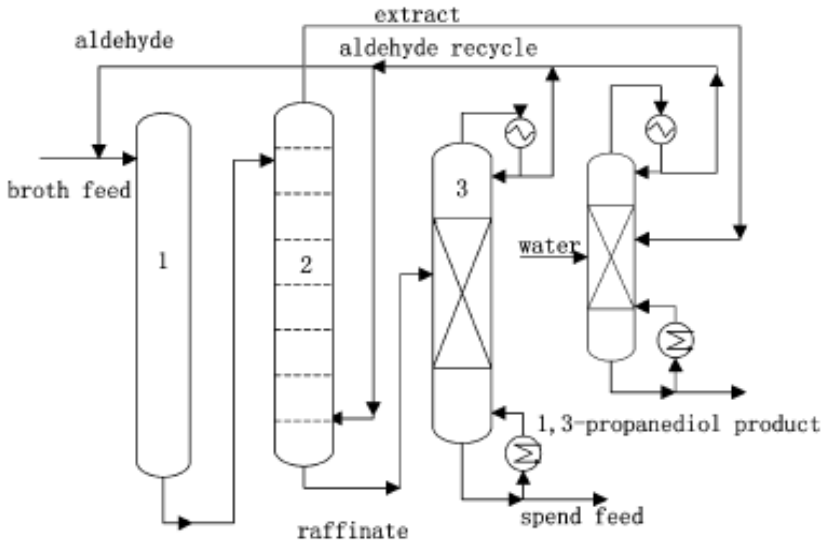


Figure 2.3 Schematic of diagram reactive extraction process:(1) reaction column; (2) reactive extraction column; (3) aldehyderecovery column; (4) acetal hydrolysis distillation column.

2.7 Catalysts for acetalization reaction

To convert 1,3-PDO to dioxane, a catalyst is needed to reduce the activation energy of the reaction. Catalyst used here can be either solid catalyst or liquid catalysts. The liquid catalyst may be: a) at least one organic acid, such as carboxylic acids, formic acid, acetic acid, propionic acid, butanoic acid, isobutanoic acid, pentanoic acid, caproic acid, caprylic acid, capric acid, benzoic acid and oxalic acid or b) at least one inorganic acid, such as the salts of hydroacids, hydrochloric acid, hydrobromic acid and hydrofluoric acid; salts of oxoacids, sulfuric acid, nitric acid, phosphoric acid, carbonic acid, boric acid, chloric acid, silicic acid, perchloric acid, chlorous acid, hypochlorous acid, chlorosulfuric acid, amidosulfuric acid, disulfuric acid and tripolyphosphoric acid; salts of thioacids, and thiosulfuric acid. Obviously, the catalyst may be of mixtures or combinations of any of these.

In practice, heterogeneous catalyst is more often used such as Dowex ion exchange resin, to avoid problem of removal acid from sample. Dowex ion exchange resins are based on crosslinked polystyrene. The required active groups can be introduced after polymerization, or substituted monomers can be used. The

crosslinking is achieved by adding 0.5-25% of divinyl benzene to styrene at the polymerization process. Non-crosslinked polymers are used only rarely because they are less stable. Crosslinking decreases ion exchange capacity of the resin and prolongs the time needed to accomplish the ion exchange processes. Particle size also influences the resin parameters; smaller particles have larger outer surface, but cause larger head loss in the column processes. Although Dowex ion exchange resin is a superior proton source but it is an expensive material.

Alternatively, the application of solid catalyst such as novel carbon based catalyst is an interesting. This type of catalyst has been applied for the acetalization of carbonyl compounds [GAO Shan., 2007] in which different kinds of diols and carbonyl compounds were subjected to acetalization reaction in the presence of novel carbon based catalyst (Figure 2.4 and Table 2.7-2.8). After the completion of the reaction, the catalyst could be reused expediently without further treatment except filtration and drying.

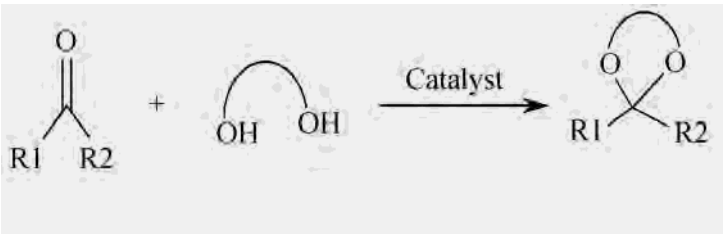


Figure 2.4 Acetalization of diols under heterogeneous condition.

Table 2.7 acetalization of carbonyl compounds with 1,2-ethanediol

Entry	Aldehydes or ketones	Conversion (%)	Selectivity (%)
1	cyclohexanone	99.6	100
2	cyclopentanone	99.4	100
3	butanone	94.1	99.1
4	propionaldehyde	98.9	99.6
5	*n*-butylaldehyde	98.1	98.9
6	*n*-valeraldehyde	97.2	98.5
7	*n*-hexylaldehyde	96.5	98.6
8	*n*-octylaldehyde	96.2	98.7
9	benzaldehyde	95.1	98.3

Table 2.8 acetalization of carbonyl compounds with 1,4-butanediol

Entry	Aldehydes or ketones	Conversion (%)	Selectivity (%)
1	cyclohexanone	97.9	97.8
2	cyclopentanone	97.1	97.6
3	butanone	92.3	95.6
4	propionaldehyde	97.5	96.3
5	*n*-butylaldehyde	95.3	96.2
6	*n*-valeraldehyde	94.8	95.9
7	*n*-hexylaldehyde	93.9	95.6
8	*n*-octylaldehyde	93.2	95.4
9	benzaldehyde	91.4	97.6

CHAPTER III
MATERIALS AND METHODS

3.1 Materials

1,3-propanediol (98% purity) was purchased from Acros Organic Co, Singapore. Glycerol (99% purity) was supplied from Ajax Finechem. Acetaldehyde (99% purity), ethyl benzene (99% purity) and Dowex 50-WX4-200 ion-exchange resins were obtained from Aldrich (Sigma-Aldrich, Singapore). Ambelite IR120 hydrogen form was purchased from Aldrich (Sigma-Aldrich, Singapore). Sulfuric acid and naphthalene were purchased from Fluka and Merck, Singapore. 2-methyl-1,2-dioxane (2MD) and sufonated carbon based catalyst were prepared following the procedures subsequently described.

3.2 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 so, 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 (0.53mm diameter, 0.88mm 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. [Hao, 2005]

3.3 Preparation of catalyst

Naphthalene (20 g) was heated in concentrated sulfuric acid (>96%, 200 mL) at 523 K under a flow of nitrogen, in a 4-neck round bottom flask as shown in Figure 3.1. It is noted that a 1000 ml flask containing about 300 g of activated carbon for was connected to the heated flask to adsorb acid vapor during the entire heating period. The round bottom flask and all the connections are made of PYREX® tubings were made of glass. After heating for 15 hours, the nitrogen inlet flow was closed and the excess sulfuric acid was removed from the dark brown tar. This was done by connecting the flask containing activated carbon to a vacuum pump, and the dark brown tar was heated at 523 K under vacuum for 8 hours. The resulted black solid was then ground to powder, and was washed repeatedly in boiling water until sulfate ions were no longer detected in the washing water.

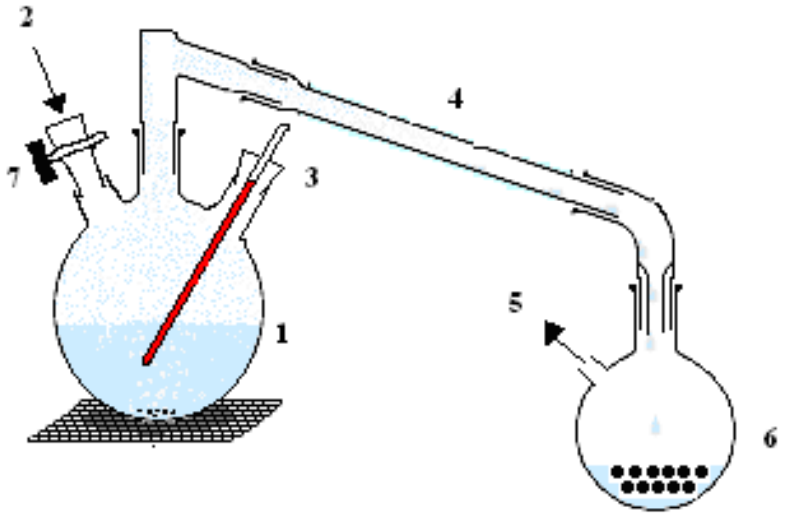


Figure.3.1 Apparatus setup for catalyst preparation instrument
(1 : round bottom 4-neck flask, 2 : nitrogen inlet, 3 : thermometer, 4 : connection tube, 5 : vacuum pump, 6 : flask contained the activated carbon)

3.4 Catalyst reactivity for acetalization of 1,3 PDO and acetaldehyde

A total 0.5 ml 1,3-PDO was added with of 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 sufonated 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 reason for preparing acetaldehyde first in an aqueous solution was to minimize the vaporization of low boiling acetaldehyde (b.p=20°C) and in this way, the reaction temperature was more easily controlled once the reaction started. To carry out the acetalization, the acetaldehyde solution was first brought to the set temperature of 35°C in a water bath shaker. Then 1,3-PDO was added and 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 experiment. For the evaluation of catalyst deactivation for possible recycling of the catalyst, acetalization was carried out 2 more times after the initial use. The reactivity as well as reusability of the synthesized carobon based catalyst was compared with those of commercial Dowex and Amberlite ion-exchange resin.

3.5 Reactive Extraction

To carry out the reactive extraction, a specified amount of catalyst (determined from 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 aqueous solution was added, and the reaction mixture was, and acetaldehyde were stirred vigorously (150 rpm) in a 125-mL shake flask. The reaction was catalyzed by novel carbon based catalyst, and the reaction was allowed to take placed for a specified reaction time (0-60 min) in a water bath at constant temperature. After the reaction, the catalyst was immediately separated from

the reaction product, which was then separated into 2 phases, the aqueous phase and extract (ethyl benzene) phase by a separation funnel. The samples were then kept in a refrigerator (4°C) until the analysis of 2-MD produced and the unreacted 1, 3 PDO. Here, the effect of reaction temperature and theh initial concentrations of 1,3-PDO solution in the range specified in Table 3.3 were examined. After the specified time of reactive extraction, sample solutions from both the organic and the aqueous phase were taken for GC analysis. From the analysais of aqueous phase, the quantitiy of unreacted 1,3-PDO remained was determined, while the quantity of 2-MD produced and its distribution would be obtained from the analysis of both phases.

Table 3.1 studied variation of thesis

Studied variation	
Reactive extraction temperature	15,20,25,25,30,35°C
Initial concentration of 1,3-PDO	20,40,60,80,100 g/l

3.6 Hydrolysis of 2-MD to obtain 1,3-PDO

The possibility of employing the novel carbon based catalyast for hydrolysis of 2-MD back to 1,3-PDO was determined. Here, equal molar quantities of 2-MD and water were placed in the distillation equipment in which the novel carbon based catalyst was added. The reaction was allowed to take place at 90 °C for 20 min, and the hydrolysis products were analyzed by a GC.

3.7 Catalyst characterization

The total surface area, pore volume and pore size of catalysts were determined using a Micromeritrics model ASAP 2020. The sample cell which contained 0.5 g of sample was placed into Micromeritrics model ASAP 2020. After degassing step, N_2 physisorption was carried out for measuring the surface area and pore volume of catalyst. The neutralization titration was applied in order to calculate the amount of the acidity. Here, mixture of iso-propyl-alcohol 12.5 ml and tolene 12.5 ml was

replaced in 100 ml flask then added 1 gram of novel carbon based catalysts and 0.5 ml of phenopthalene. This solution was titrated with 0.25 molar of KOH [ASTM D6751]. It is noted that 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). In detail, the catalyst was digested with 5 mL of HNO_3 (Suprapure, 65% v/v, Merck, Germany) and made up to 25 mL with ultrapure water at 18.2 mΩ, using Anton Paar Microwave Digester (Anton Paar, Austria) for testing. In addition, the sulfonic group on the catalyst was confirmed by the Nicolet NEXUS 670 FTIR using KBr Discs. The IR spectra of the catalyst showed the sulfonic absorbability at 3300 and 3500 cm^{-1} [Mo, 2008]. Lastly, the thermal behavior of catalyst was analyzed by thermogravimetric analyzer (PerkinElmer, Pyris 1 TGA, USA). The catalyst with the total weight of 10 mg was used, while the air flow at 10 ml/min was employed. The temperature was ramped from room temperature to 1000 C with the rate of 10 C/min.

3.8 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, 0.88μm 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. [Hao,2005].

CHAPTER IV
RESULTS AND DISCUSSION

The reactive extraction is the process in which reaction and extraction take place simultaneously. In consideration of reaction, the rate of reaction is the key concept. With this in mind, it follows that the type and quantity of catalyst would play important roles as these factors directly affect reactivity of the system of interest. Moreover, temperature of the reaction system and the initial concentration of the reactants are other significant factors to be considered in reactive extraction process as both can influence the reaction as well as the extraction kinetics of the system altogether. In this thesis, we evaluated the reactivity for acetalization of aqueous solution of 1,3-PDO and acetaldehyde to 2-MD, using the novel carbon based catalyst synthesized by incomplete carbonization of naphthalene in sulfuric acid. In this chapter, the results on the catalyst characterization, its reactivity and the reusability were reported and compared with those of commercial Dowex 50-WX4-200 and Ambelite IR120 hydrogen form ion exchange resins. In addition, the effects of temperature and initial concentration of 1,3-PDO on actual reactive extraction process and the possibility of employing the carbon based catalyst for hydrolysis of 2 MD back to 1,3 PDO were evaluated and reported.

4.1 Catalyst characterization

The physical properties of the novel carbon based catalyst are shown in Table 4.1. The BET measurement indicates that the catalyst shows 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) was found to be 1.46 mmol/g. The result agreed with the neutralization titration in which 1 g of catalyst was completely neutralized with 11 ml 0.25 mol/l of KOH solution. From this, the acidity of the catalyst was estimated to be approximately 161.14 mg (KOH)/g. These values,

although determined on different basis, showed rather high acidity of the synthesized carbon based catalyst.

Table 4.1 Physical properties of catalyst

Catalyst type	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Sulfur content (mmol/g)
Novel catalyst[1]	1.1	0.07	1.46*
Dowex [2]	200-300	1.2	4.6**
Amberite [2]	1000-1300	1.0-1.2	3.8**

1 this work

2 commercial catalysts (Sigma-Aldrich, Singapore)

* From elemental analysis

** From company data (Sigma-Aldrich, Singapore), reported as mEq/g

The sulfonic group on the catalyst was confirmed by the Nicolet NEXUS 670 FTIR. As shown in the IR spectra in Figure 4.1, showed strong absorption at 3300 - 3500 cm^{-1} which confirmed the existence of the sulfonic functional group of the catalyst [Mo, 2008].

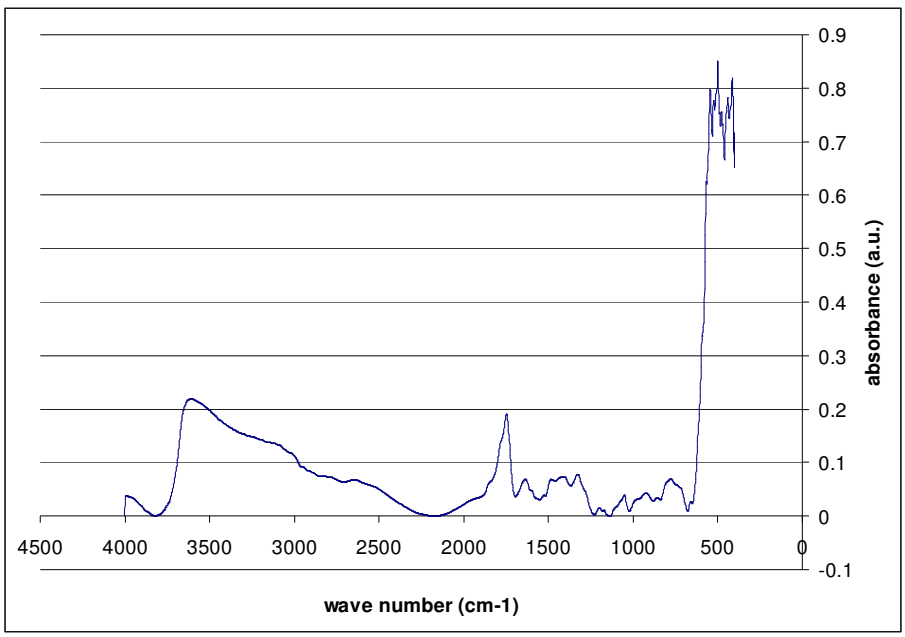


Figure 4.1 FTIR spectra of sulfonated carbon based catalyst.

The TGA analysis was performed to investigate the thermal behavior of catalyst. The result indicates that most of the catalyst start decompose at above 200°C and decompose with the rapid weight loss until 400°C. At the temperature higher than 700°C, no catalyst is left due to the thermal decomposition.

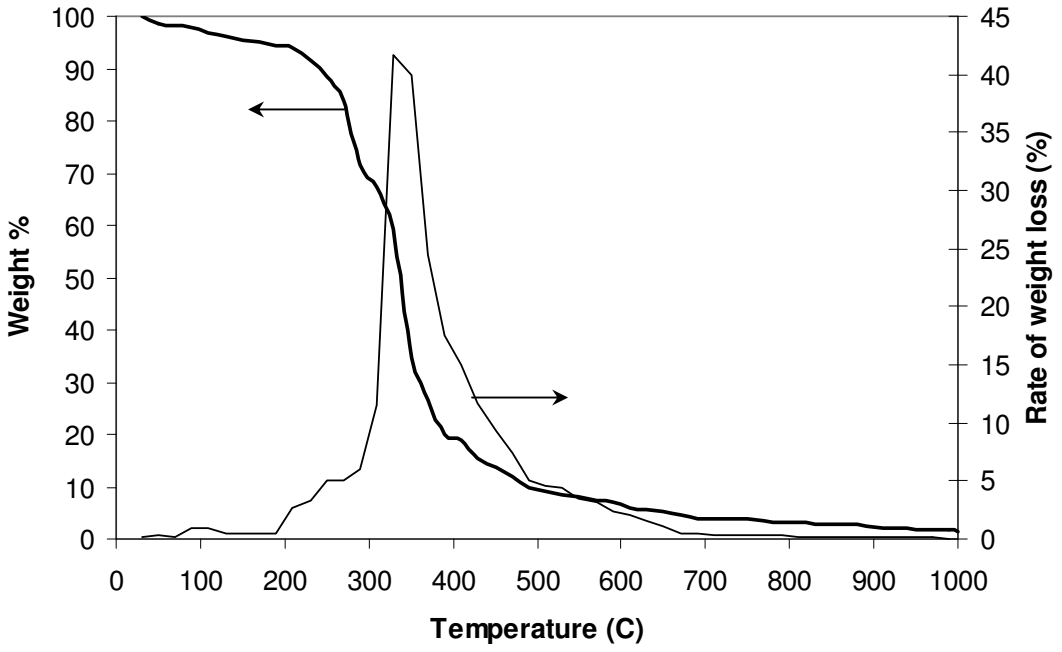


Figure 4.2 TGA analysis of sulfonated carbon based catalyst

4.2 Catalyst reactivity for acetalization of 1,3-PDO and acetaldehyde in aqueous solution

4.2.1 Preliminary results of catalyst reactivity

The feasibility of novel carbon based catalyst for acetalization of 1,3-PDO and acetaldehyde was tested. A total 0.5 ml 1,3-PDO was added with of 15.7 ml of acetaldehyde solution (containing 3.7 ml acetaldehyde and 12 ml of water) in a 125-mL shaken flask with a 0.35 g of sufonated carbon based catalysts. The reaction temperature was controlled at 35°C and the reaction time was 2 hours in the water bath shaker following the procedure described in Section 3.6. After the 2 hours of reaction, the solution was filtered to separate the solid catalyst, and the liquid phase was then analyzed with gas chromatography.

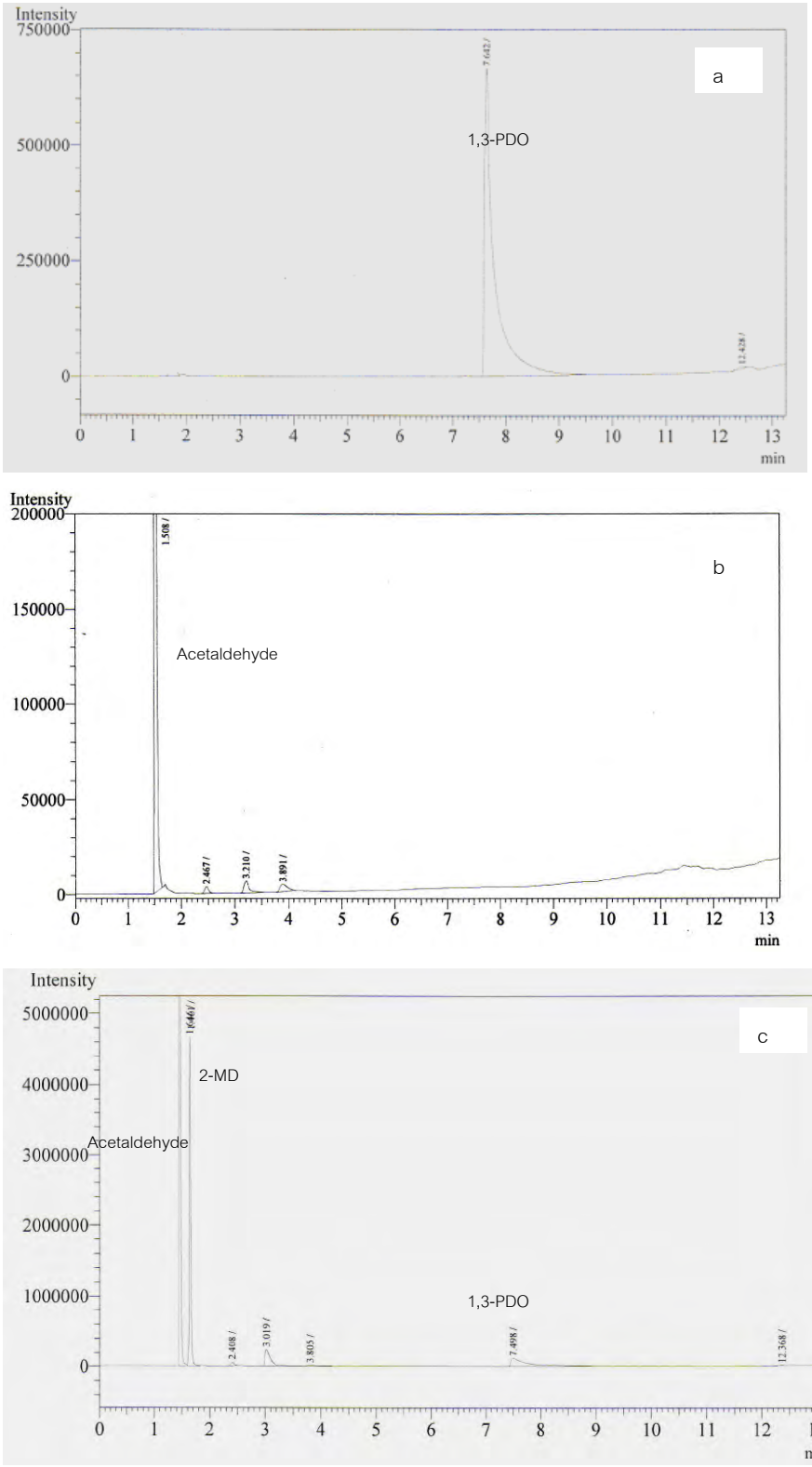


Figure.4.3 Chromatogram of reactants and product in aqueous solution

(a = 1,3-PDO, b = acetaldehyde, c = product)

The chromatograms of the reactants: 1,3-PDO and acetaldehyde in aqueous solution are shown in Figure 4.3a and 4.3b, which indicated that the retention times for 1,3-PDO and acetaldehyde were at about 7.5 minutes 1.4 minutes, respectively. The chromatogram of the product after the 2 hour of reaction shown Figure 4.3c indicated the presence of 2-MD (retention time = 1.6 minutes) as well as unreacted acetaldehyde, which was originally present in excess. It is seen from the same figure however that only a small amount the unreacted 1,3-PDO was found , indicating that the majority of 1,3-PDO was reacted with acetaldehyde to form 2-MD. Thus, it can be drawn from this preliminary result that the novel carbon based catalyst was effective catalyst for acetalization of 1,3-PDO and acetaldehyde in aqueous solution.

4.2.2 Determination of suitable catalyst to 1,3-PDO mass ratio for acetalization

This experiment was carried out to determine the suitable quantity of novel carbon based catalyst required for acetalization. Here the reaction was carried out at 35°C for 2 hours following the method described in section 3.6. The effect of catalysts to 1,3-PDO mass ratio in the range between 0.1 to 0.9 g/g on the conversion of 1,3-PDO was shown in Figure 4.4 From this result, the conversion increased to the maximum value of 92% as the catalysts mass ratio increased from 0.1 to 0.7 g/g. Higher amount of catalyst however caused no obvious change in the reaction conversion. All subsequent experiments were therefore carried out with 0.7 g catalysts mass per g of 1, 3-PDO.

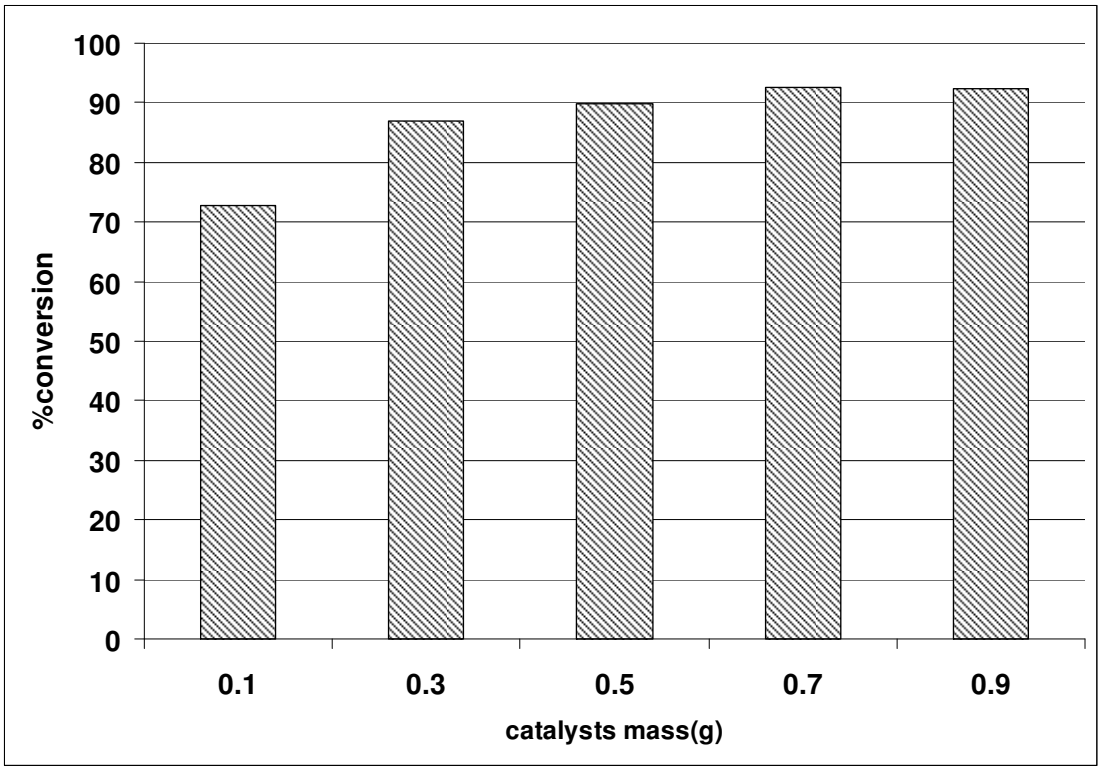


Figure.4.4 Effect of catalysts mass in the aqueous solution

4.2.3 Comparison of catalyst reactivity

The reactivity of novel carbon based catalyst was compared with those of commercial catalysts: Dowex 50-WX4-200and Ambelite IR120 hydrogen form. The reaction was carried out at 35°C for various times (60, 90 and 120 minutes), following the method described in section 3.6, using the different catalysts at the same 0.7 g catalyts/g1,3-PDO mass ratio. After the reaction, the resulted solution was analyzed by gas chromatography and the results are shown in Figure 4.5. From these results, Dowex 50-WX4-200and Ambelite IR120 hydrogen form were found to have higher reactivity compared with the novel carbon based catalysts. Specifically, the reactions in the commercial catalysts took only about 60 minutes (or less) while that in the carbon based catalyst took about120 minutes to achieve comparable converstion of about 90%. The lower reactivity could be due to lower acidity and porosity, and thus surface area of the novel carbon based catalyst compared with the polymeric ion

exchange resin. (Table 4.1) However, the low cost of carbon based catalyst makes it attractive and the development of catalysts with enhanced reactivity is underway.

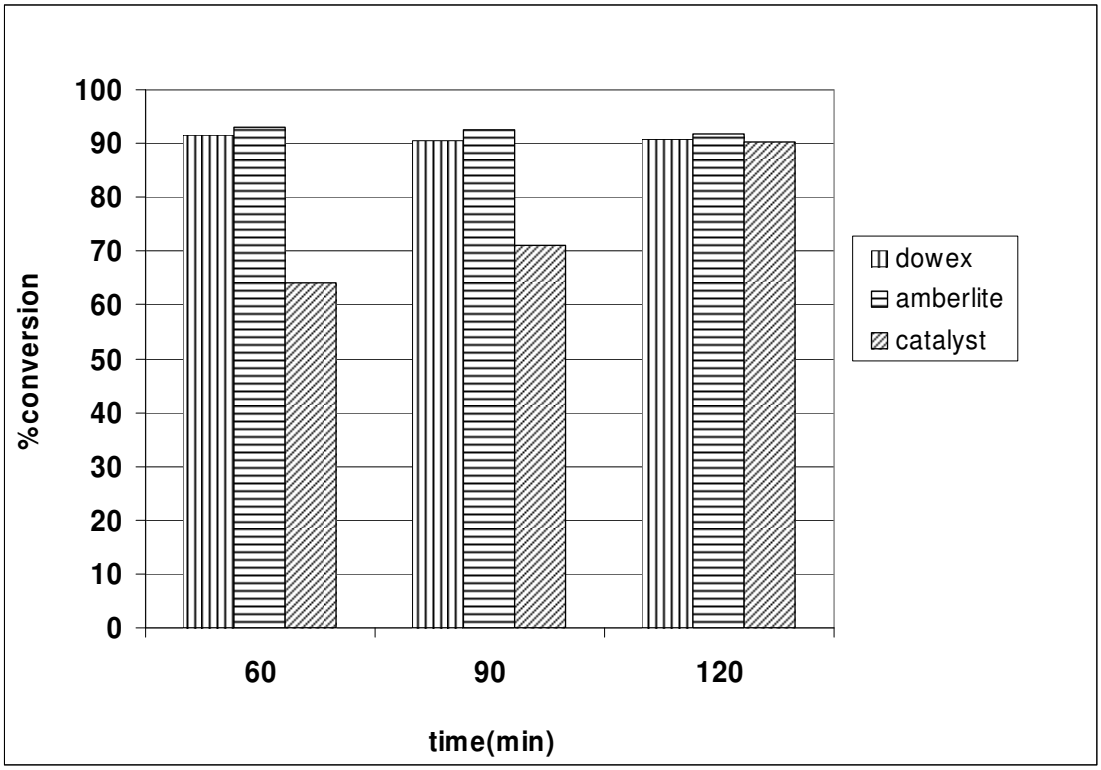


Figure.4.5 Compare catalysts with the commercials catalysts

4.3 Reactive extraction of 2-MD

In the separation of 1,3-PDO from aqueous solution by reactive extraction, both acetalization reaction and extraction of its reaction product, 2-MD, were carried out simultaneously. In this section, the results of some process conditions such as temperature and initial concentration of 1,3-PDO on the reactive extraction behavior were reported.

4.3.1 Preliminary results of reactive extraction

As a preliminary experiment, the possibility of separation of 1, 3 PDO from aqueous solution by reactive extraction in presence of novel carbon based catalyst was investigated. In this set of experiment, ethyl-benzene was used and an extractant for 2-MD that was produced from the acetalization of 1,3-PDO and acetaldehyde. Since ethyl-benzene is not soluble in aqueous solution, it could be separated from aqueous solution after reactive extraction using a separation funnel. The ethyl-benzene phase was analyzed for the quantity of 2-MD, while the aqueous phase was analyzed for the quantity of 2-MD and unreacted 1,3-PDO by gas chromatography.

The chromatograms of the resulted aqueous phase and extract phase are shown in Figure 4.6a and 4.6b, respectively. The small amount of 1,3-PDO in aqueous phase indicated 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 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).

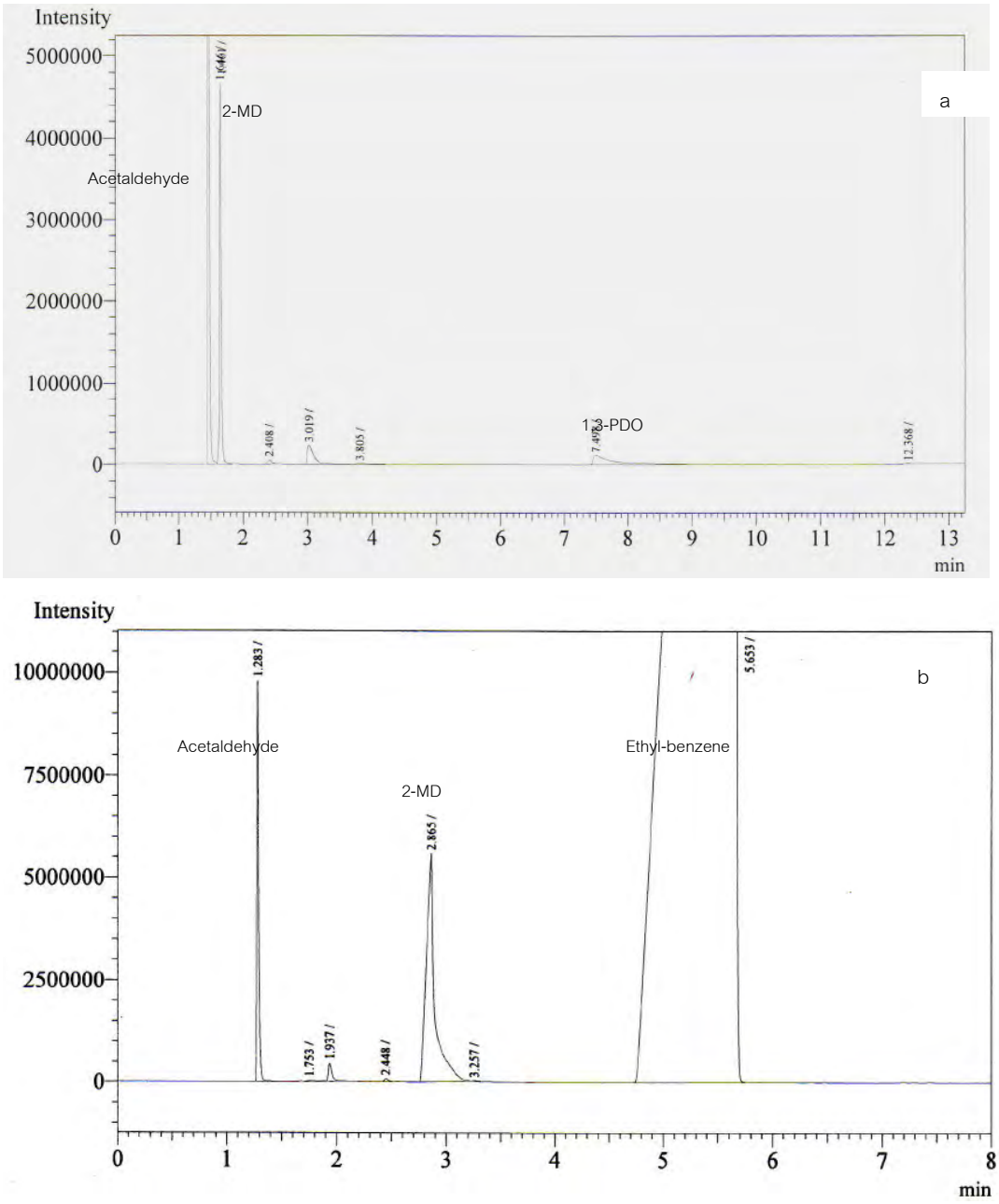


Figure.4.6 Chromatogram of sample in both phases

(a = aqueous phase, b = solvent phase)

4.3.2 Effect of temperature

To determine the effect of temperature, the reactive extraction was carried out in a 125-mL shake flask containing 0.5 ml 1,3-PDO and the equal volumes (15.7 mL) of ethyl-benzene as a solvent and acetaldehyde aqueous solution (3.7 ml of acetaldehyde in 12 ml of water), in the presence of the carbon based catalyst (0.7 g/g catalyst to 1,3-PDO mass ratio) for a 0-60 min. The range of reaction temperature between 15° C and 35 °C was studied. The profiles of 2 MD in the aqueous and extract phases, and of 1, 3 PDO in the aqueous phase for these reactions are shown in Figure 4.10a-4.10e.

From these figures, 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 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 became lower. The initial rates of reaction determined from the slope of 1,3-PDO in the first 5 min for the reactive extraction at various temperatures (15-35°C) and the corresponding reaction conversions (after 60 min), are summarized in Table 4.2. These results, which are in agreements with the collision theory, revealed that the rate of reaction increased with increasing temperature. That is, when two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place. Increasing the reaction temperature increased the energy levels of the molecules involved in the reaction, thus resulting higher reaction rate.

Apart from the result on reaction rate, the consideration of the concentration profiles of the 1,3-PDO in the aqueous phase and of 2-MD in the two phases would suggest relative importance of the rate of reaction and that of mass transfer in the system. At lower temperatures (15 and 20°C, Figure 4.10a and 4.10b), the concentration of 2-MD in the extract phase increased slowly due to the corresponding slow rate of reaction. At these temperatures, the concentration of 2-MD in the extract phase was always lower that in the aqueous phase. At higher temperatures (25, 30, 35

°C) on the other hand, the 2-MD concentration in the aqueous phase was higher than the extract phase initially, but its concentration in the aqueous phase decreased while continuing to be extracted into the extract phase. This indicated that at high temperatures, the initial rate of reaction was higher than the rate of mass transfer into the extract phase. As the reactive extraction proceeded, the rate of reaction became slower as a result of lower reactant concentrations, while the rate of mass transfer increased as a result of lower viscosity of the reaction mixture which was richer in less viscous 2-MD product. In such case, the mass transfer exceeded the reaction rate, resulting in the cross-over of the concentration profiles of 2-MD in the two phases. This cross-over was not observed at lower temperatures, which suggested that at these temperatures, the reaction rate and the mass transfer rate between the two phases were relatively close to each other.

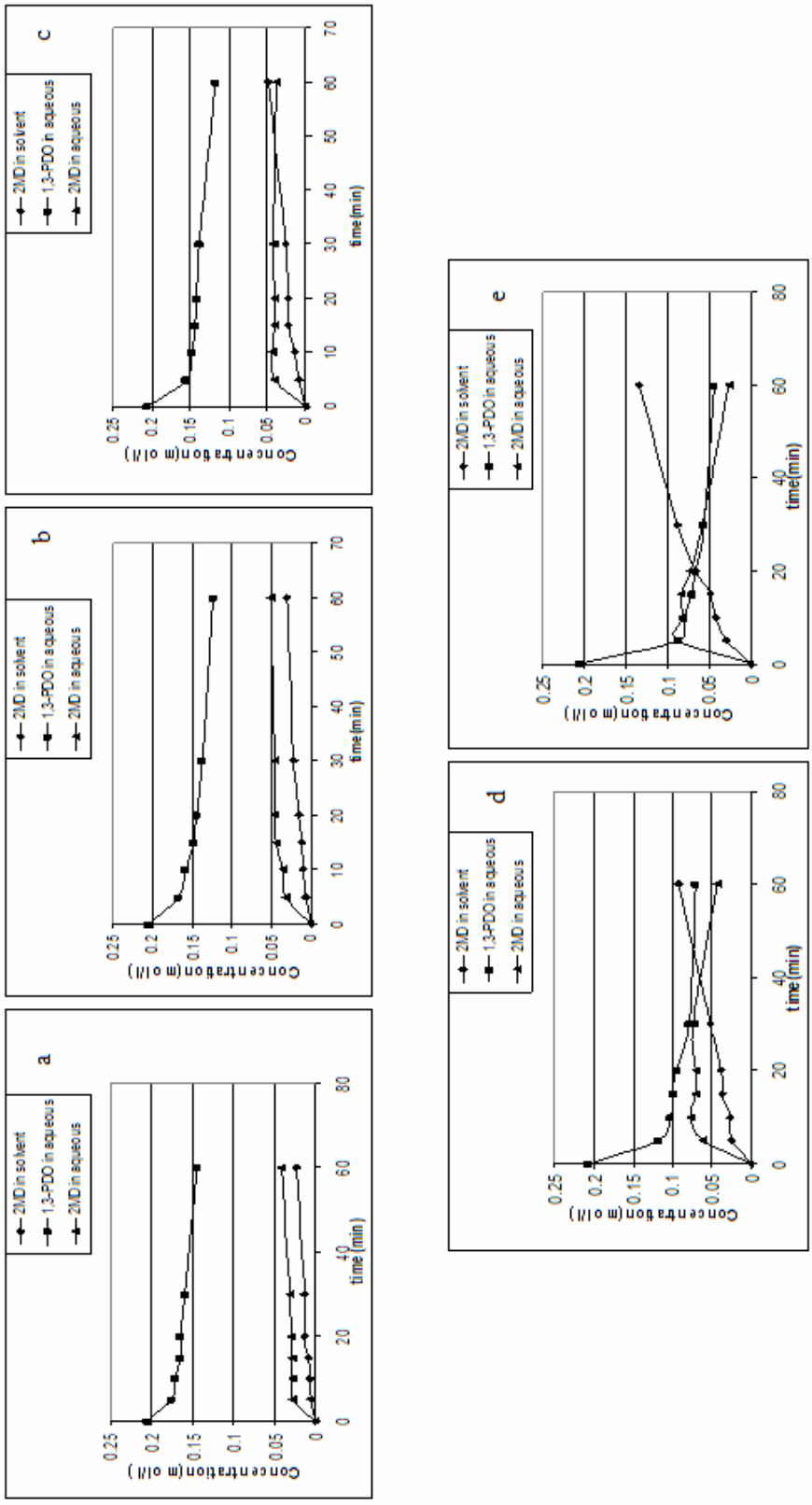


Figure.4.7 Effect of temperature on reactive extraction at initial concentration 40 g/L (a = 15°C, b = 20°C, c = 25°C, d = 30°C, e = 35°C)

Table 4.2 %conversion of 1,3-PDO with varied reactive extraction temperature

Reactive Extraction temperature (°C)	Initial rate (mol/L/min)	%conversion at 60 min.
15	0.0062	30.02 %
20	0.0077	39.57 %
25	0.0099	42.90 %
30	0.0178	65.75 %
35	0.0239	78.92 %

4.3.3 Effect of initial concentration of 1,3-PDO

Also based on the collision theory, increasing the concentration of the reactants will increase the frequency of collisions between the two reactants. Thus, it would generally be expected that the increase in initial concentration of reactant increases the reaction rate. Here, the effect of initial concentration of 1,3-PDO solution was determined on reactive extraction carried out at 35°C. The concentration range studied was between 20 – 100 g/L of 1,3-PDO solution. Specifically, the reaction was carried out in 125 ml flask, which contained 0.35 g of novel carbon based catalyst, 0.25, 0.5, 0.75, 1.0, 1.25 g of 1,3-PDO, 3.7 ml of acetaldehyde dilute in 12 ml of water and 15.7 ml of ethyl-benzene.

Since in all cases here, the reactive extraction was carried out at 35°C, the concentration profiles of the 1,3-PDO and 2-MD follow relatively the same behaviors as those in Figure 4.10a-4.10e. The initial rates of the reaction and the reaction conversion after 60 min of reactive extraction obtained with different initial 1,3-PDO concentrations are summarized in Table 4.3. It should be noted that the initial reaction rate was found to increase as the initial 1,3-PDO concentration increased according to the collision theory. However, the overall reaction conversion after 60 min decreased as the initial concentration of 1,3-PDO increased. These results indicated that the overall conversion was controlled by the mixing rate, which in turns influenced by the viscosity of the reaction mixture, particularly at high 1,3-PDO concentration.

It is noted that, for the reactive extraction with the initial 1,3-PDO concentration of 40 g/L (the typical concentration of the fermentation broth), the reaction conversion was found to be 78.92 %. This was higher than the conversion that would be achieved by acetalization in the aqueous solution alone (65%). The 20% increased in the conversion observed here confirmed the advantage of having extraction performed simultaneously with the reaction in order to shift the reaction equilibrium forward.

It should be noted that conversion as well as the recovery of the 2-MD into the extract phase could be further improved, given that the reactive extraction would be for longer time period, or that the mass transfer rate (both in terms of mixing rate of the reactants and the partitioning of the 2-MD reaction product into the extract pahse), would be improved. Nevertheless, the results here suggested the high potential of employing the novel carbon based catalyst of reactive extraction to separate 1,3-PDO from the aqueous solution. In addition, the improvement the performance of this system could also be achieved by enhancing the catalysts properties such as acidity, surface area and pore volume, by optimizing the preparative conditions of the carbon based catalyst. This study is currently underway.

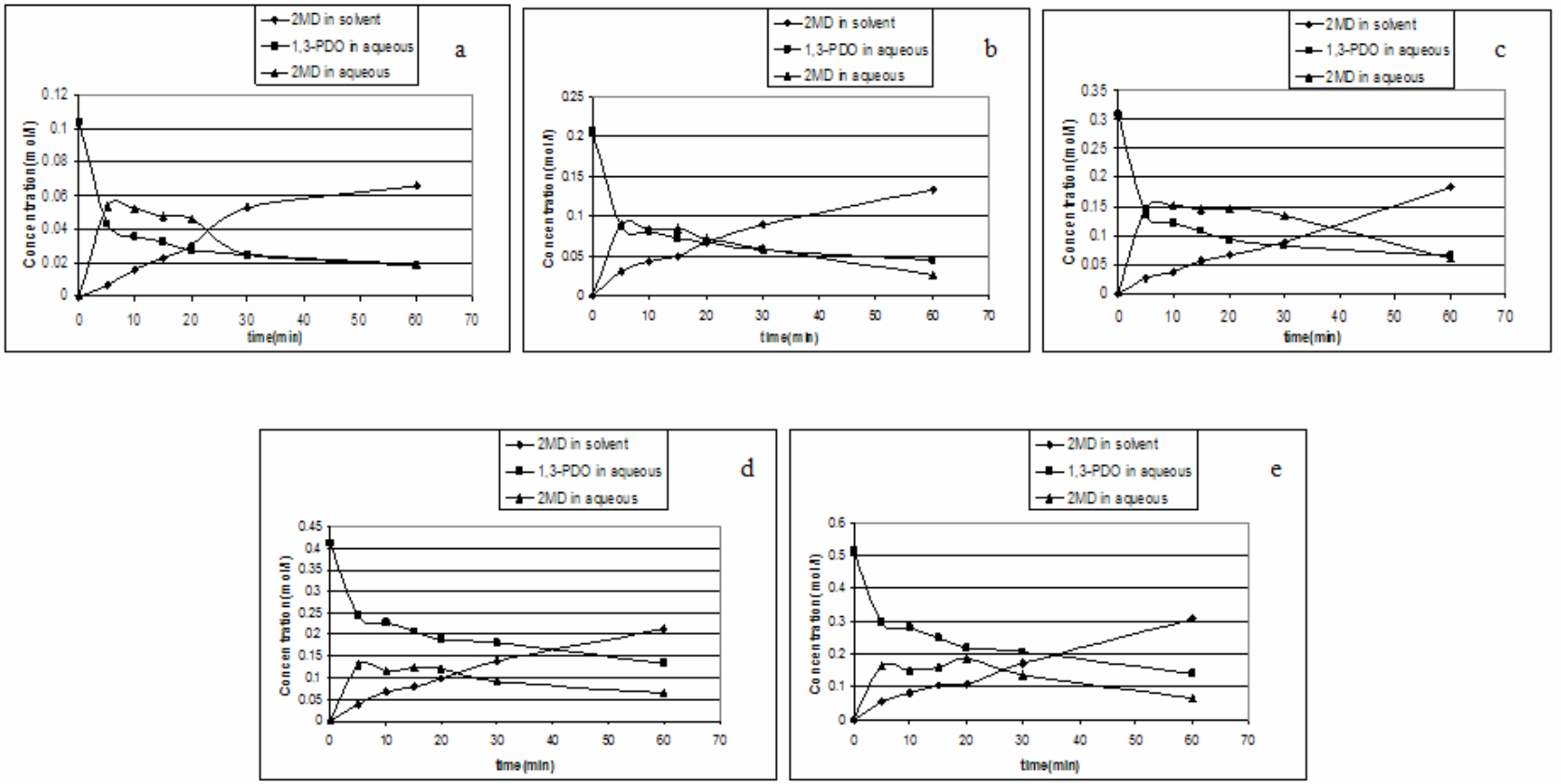


Figure.4.8 Effect of initial 1,3-PDO concentration on reactive extraction at 35°C (a = 20g/L, b = 40 g/L, c = 60 g/L, d = 80 g/L, e = 100 g/L)

Table 4.3 %conversion of 1,3-PDO with varied 1,3-PDO initial concentration

Initial concentration of 1,3-PDO (g/L)	Initial rate (mol/L/min)	%conversion at 60 min
20	0.0119	82.33 %
40	**0.0239**	**78.92 %**
60	0.0338	78.17 %
80	0.0348	72.65 %
100	0.0436	67.61 %

4.4 Evaluation of catalyst deactivation

In this set of experiment, multiple acetalization of 1,3 PDO solution and acetaldehyde was carried out according to the procedure described in Section 3.6 to evaluate the catalyst deactivation. Each time, the reaction took place at 35°C for 2 hours. The results on the percent conversions resulted from these multiple reactions are shown in Figure 4.9 for the novel carbon based catalyst, compared with those obtained with commercial Dowex 50-WX4-200 and Ambelite IR120 hydrogen form solid ion exchange resins. From the experiment data, novel carbon based catalysts deactivated more easily than the commercial catalysts. The %conversion of 2-MD with novel carbon based catalysts decreased from 90% to 63% in the third time of use, while that with the commercial catalysts (both Dowex 50-WX4-200 and Ambelite IR120 hydrogen form) decreased from 92% to approximately 87%.

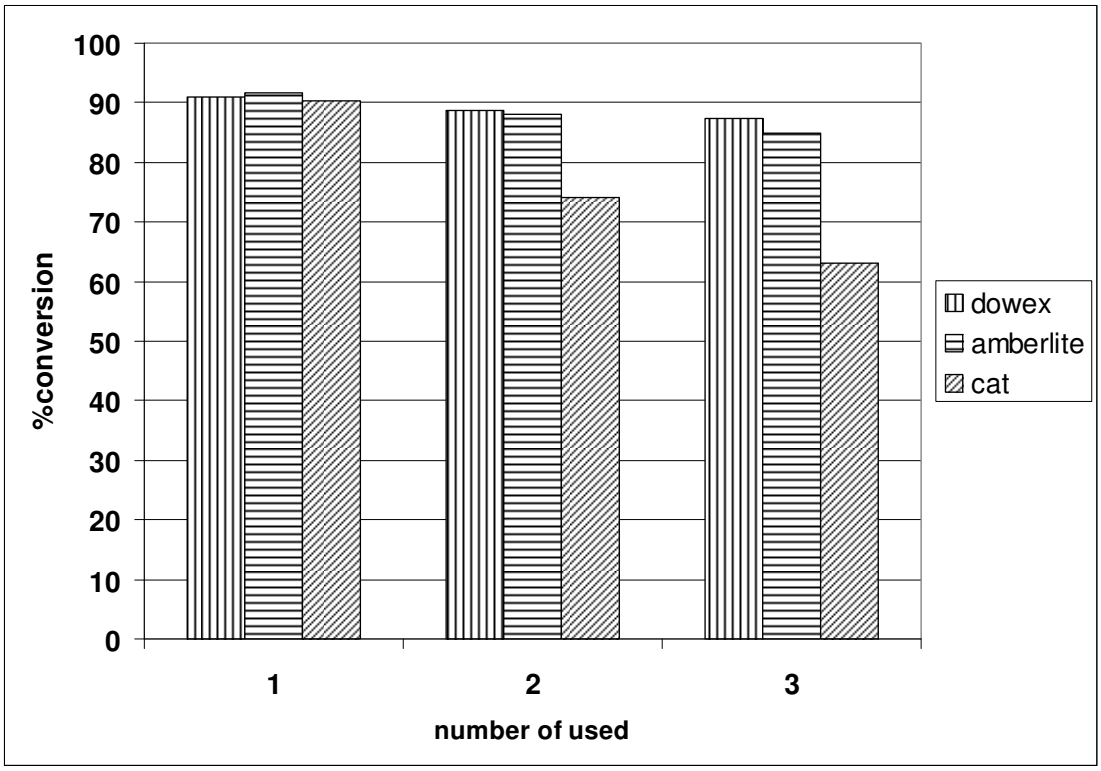


Figure.4.9 Conversions of multiple reactions for various solid catalysts

4.5 Hydrolysis reaction

For the investigation of the feasibility of 2-MD hydrolysis to 1,3-PDO employing the novel carbon based catalyst, equal molar quantities of 2-MD and water were reacted in a volumetric flask connected to distillation column with added novel carbon based catalyst. Specifically, 3 g of 2-MD was reacted with 0.53 g of water in the presence of 0.1 g of novel carbon based catalyst. The reaction was allowed to take place at 90 °C for 20 min. After hydrolysis reaction, the resulted 1,3-PDO was diluted with water and filtrated to separate the catalysts, and the solution was analyzed for the amount of 1,3-PDO produced.

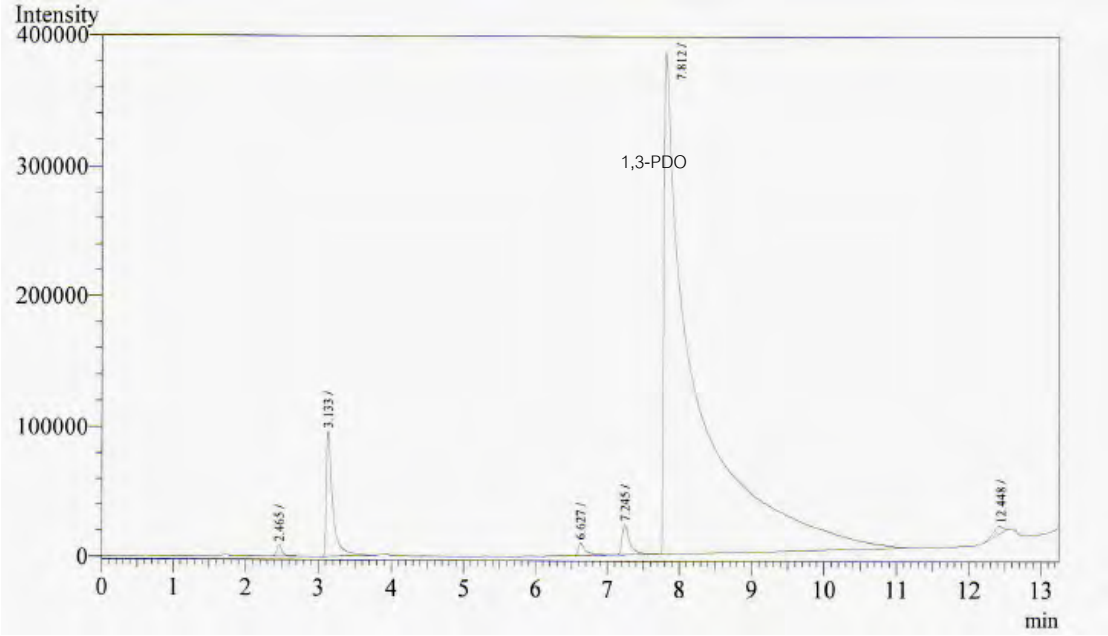


Figure 4.10 Chromatogram of 1,3-PDO after hydrolysis reaction.

From the chromatogram of the hydrolysis reaction product shown in Figure 4.10, 2-MD could not be detected. This result as well as the large 1,3-PDO peak in the chromatogram indicated that the conversion of the reaction was quite high. The purity of the 1,3-PDO product was also determined form the percentage of peak area to be around 92-93%. However, only approximately 73.82% recovery was achieved when attempting to recover 1, 3-PDO. The highly viscous product makes it difficult to remove it from the reaction vessel and to separate it from the solid catalyst. Nevertheless, in view of the fact that no 2-MD peak was present after the reaction, it is expected that the actual % conversion of 1,3-PDO by hydrolysis in the carbon based catalyst was indeed no less than 99%. This result supports the potential application of the novel low cost carbon based catalyst to entire separation process of 1,3-PDO by reactive extraction.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

In this thesis, the application of a novel carbon based solid catalyst was investigated on reactive extraction for the recovery of 1,3-PDO from a dilute aqueous solution. Acetaldehyde was used as a reactant and ethyl-benzene as a solvent. First acetalization of 1,3-PDO and acetaldehyde (without solvent extraction) was carried out to determine the suitable amount of catalysts for the reaction was . This 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%. Commercial catalysts: Dowex 50-WX4-200 and Ambelite IR120 (hydrogen form), required shorter reaction time, thus have higher reactivity compared with the novel carbon based catalysts. However, the low cost of carbon based catalyst makes it attractive and the development of catalysts with enhanced reactivity is underway.

Reactive extraction was then carried out at 35°C for up to 60 min with 1, 3-PDO solution of 40 g/L of initial concentration, a typical concentration of 1, 3-PDO derived from the fermentation process. The conversion was found to be 78.92% after 60 min of the reactive extraction. Compared with the conversion of acetalization alone at the same reaction condition, the conversion of acetalization was approximately 65%. A 20% increase in the conversion was due to the shifting of the reaction equilibrium in the forward direction as the 2-MD was partitioned into the extract phase.

The use of novel carbon based catalysts for multiple reactions indicated that the catalyst deactivated more easily than the commercial catalysts (Dowex 50-WX4-200 and Ambelite IR120 (hydrogen form)). The % conversion of 2-MD with novel carbon based catalysts decreased from 90% to 63% in the third time of use, while that with both commercial catalysts decreased from 92% to approximately 87%.

In addition, the feasibility of applying the carbon based catalyst for 2-MD hydrolysis to recover 1,3-PDO was investigated. The purity of the resulted 1,3-PDO was found to be around 92-93% and as high as 99% conversion was expected to be

achieved. This result supports the potential application of the novel low cost carbon based catalyst to the entire separation process of 1,3-PDO by reactive extraction.

Recommendations

From the experimental results on reactive extraction, it was found that the reactive extraction was limited by reaction kinetics at lower time but it was limited by mass transfer at the later time. This therefore suggested two possibilities for the improvement of the performance of the system. Firstly, the reactivity of the carbon based catalysts could be enhanced through optimizing the preparation conditions, to provide better properties such as the porosity, surface area, and acidity. Secondly, the process could be improving providing better mixing, i.e., increasing the rotational speed, or through the better design of the reactive extractor. Once the optimal system was found, it is advisable to determine the reaction kinetics for further system design and scale-up.

REFERENCES

A. Reimann, H. Biebl, W. D. Deckwer. Production of 1,3-propanediol by Clostridium butyricum in continuous culture with cell recycling. Appl Microbiol Biotechnol 49 (1998): 359-363.

A. Reimann, S. Abbad-Andaloussi, H. Biebl and H. Petitdemange 1,3-Propanediol formation with product-tolerant mutants of *Clostridium butyricum* DSM 5431 in continuous culture: productivity, carbon and electron flow. Journal of Applied Microbiology 84 (1998): 1125-1130.

Ames TT. Process for the isolation of 1,3-propanediol from fermentation broth. US Patent 6.361.983 B1 (2002).

Boonsongsawat T. Separation of 1,3-propanediol from model mixture and fermentation broth by solvent extraction. Master of Engineering Program in Chemical Engineering Department of Chemical Engineering Faculty of Engineering Chulalongkorn University, 2007.

Fabien Barborato, El Hassan H., Theirry C., Andre B. 1,3-propanediol production by fermentation: An interesting way to valorize glycerin from the ester and ethanol industries. Industrial Crops and Products 7 (1998): 281-289.

GAO Shan. High efficient acetalization of carbonyl compounds with diols catalyzed by novel carbon-based solid strong acid catalyst. Chinese Science Bulletin. 52 (2007): 2892-2895.

Hilaly AD, Thomas PB. Method of recovering 1,3-propanediol from fermentation broth. US Patent 6.479.716 (2002).

Jian Hao, Hongjuan Liu, and Dehua Liu. Novel Route of Reactive Extraction To Recover 1,3-Propanediol from a Dilute Aqueous Solution. Ind. Eng. Chem. Res. 44 (2005) **:** 4380-4385.

Luerruk W. Adsorption of 1,3-propanediol from synthetic mixture using polymeric resin as adsorbents. Master of Engineering Program in Chemical Engineering Department of Chemical Engineering Faculty of Engineering Chulalongkorn University, 2008.

Malinowski J. Evaluation of liquid extraction potentials for downstream separation of 1,3-propanediol. Biotechnology Techniques 13 (1999): 127-130.

Malinowski J. Reactive extraction for downstream separation of 1,3-propanediol. Biotechnol. Prog. (2000).

Mi-Hae Cho, Sun Im Joen, Sang-Hyun Pyo, Sungyong Mun, Jin-Hyun Kim. A novel separation and purification process for 1,3-propanediol. Process Biochem 41 (2006): 739-744.

Roturier JM, Fouache C, Berghmans E. Process for the purification of 1,3-propanediol from a fermentation medium. US Patent 6.428.992 B1 (2002).

Shiguang Li, Vu A. Tuan, John L. Falconer, Richard D. Noble. Separation of 1,3-propanediol from glycerol and glucose using a ZSM-5 zeolite membrane. Microporous and Mesoporous Materials. 53 (2002) :59–70.

Shiguang Li, Vu A. Tuan, John L. Falconer, Richard D. Noble. X-type zeolite membranes: preparation, characterization, and pervaporation performance. J. Membr. Sci. 191 (2001): 53-59

Takagaki A. Esterification of higher fatty acids by a novel strong solid acid. Catalysis Today. 116 (2006) :157–161

Xunhua Mo. A Novel Sulfonated Carbon Composite Solid Acid Catalyst for Biodiesel Synthesis. Catal Lett. (2008) 123:1–6.

Zeng AP, Biebl H. Bulk chemicals from biotechnology: the case of 1,3-propanediol production and the new trends. Adv Biochem Eng. 74 (2002): 239-5

APPENDICES

APPENDIX A

EXPERIMENTAL DATA FOR ANALYSIS

A-1 Standard calibration curve of 2-MD in aqueous solution from Gas chromatography analysis

Table A-1 Standard calibration curve data of 2-MD in aqueous solution from Gas chromatography analysis

2-MD peak area	2-MD concentration (ppm)
0	0
530035	2500
1045711	5000
2256835	10000
4520051	20000
8300782	40000

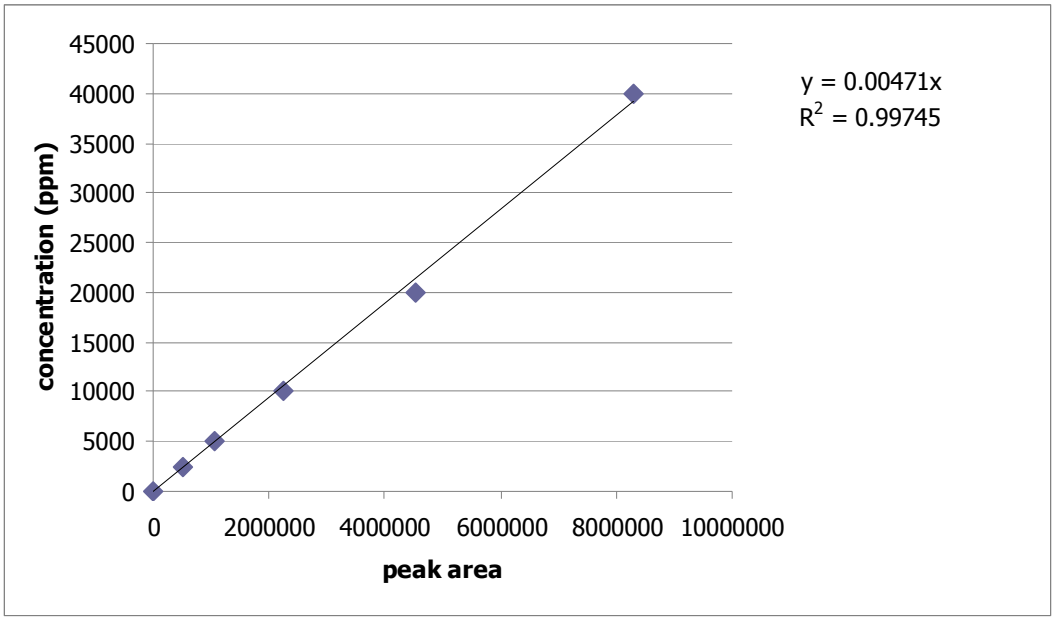


Figure A-1.1 Standard calibration curve data of 2-MD in aqueous solution from Gas chromatography analysis

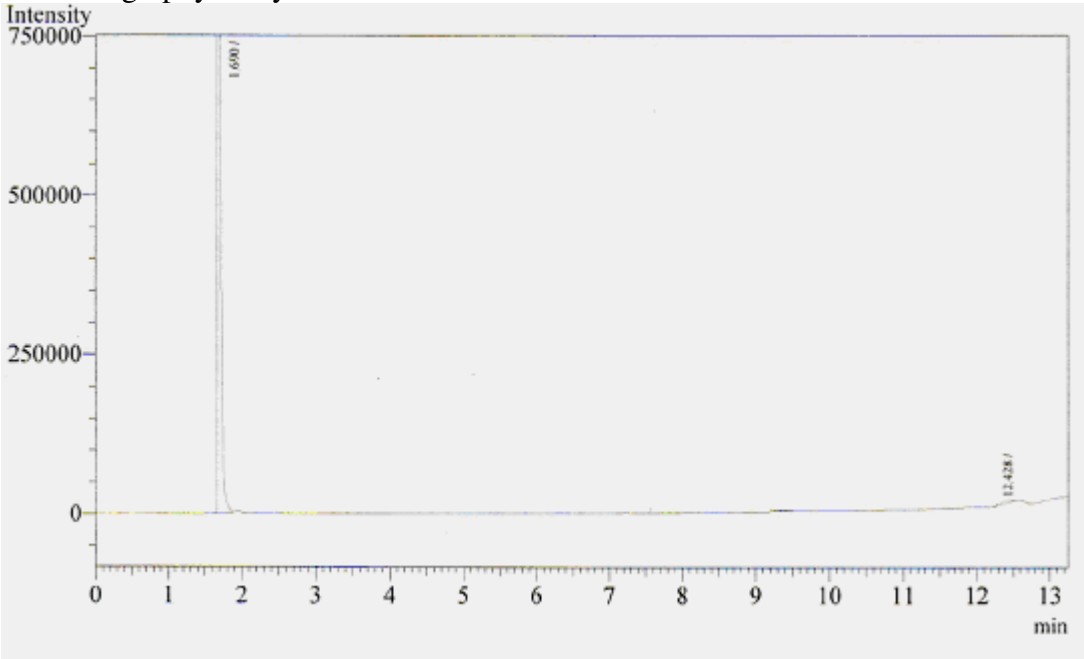


Figure A-1.2 Gas chromatography chromatogram of 2-MD standard in aqueous solution

A-2 Standard calibration curve of 1,3-PDO in aqueous solution from Gas chromatography analysis

Table A-2 Standard calibration curve data of 1,3-PDO in aqueous solution from Gas chromatography analysis

1,3-PDO peak area	1,3-PDO concentration (ppm)
0	0
254775	2500
835217	5000
1735629	10000
3691104	20000
8681455	40000

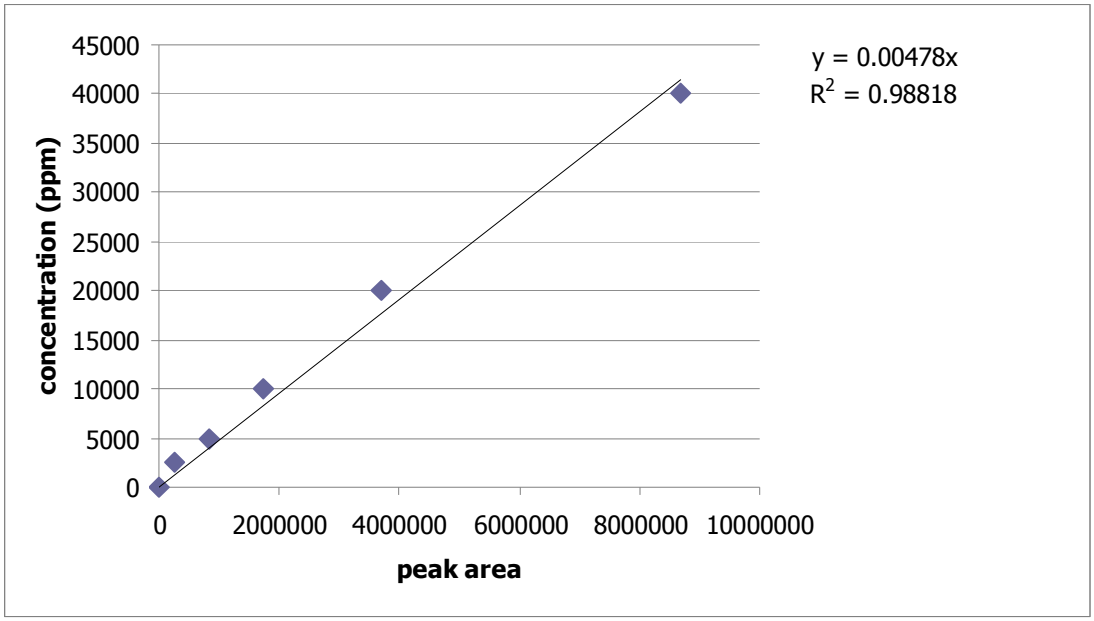


Figure A-2.1 Standard calibration curve data of 1,3-PDO in aqueous solution from Gas chromatography analysis

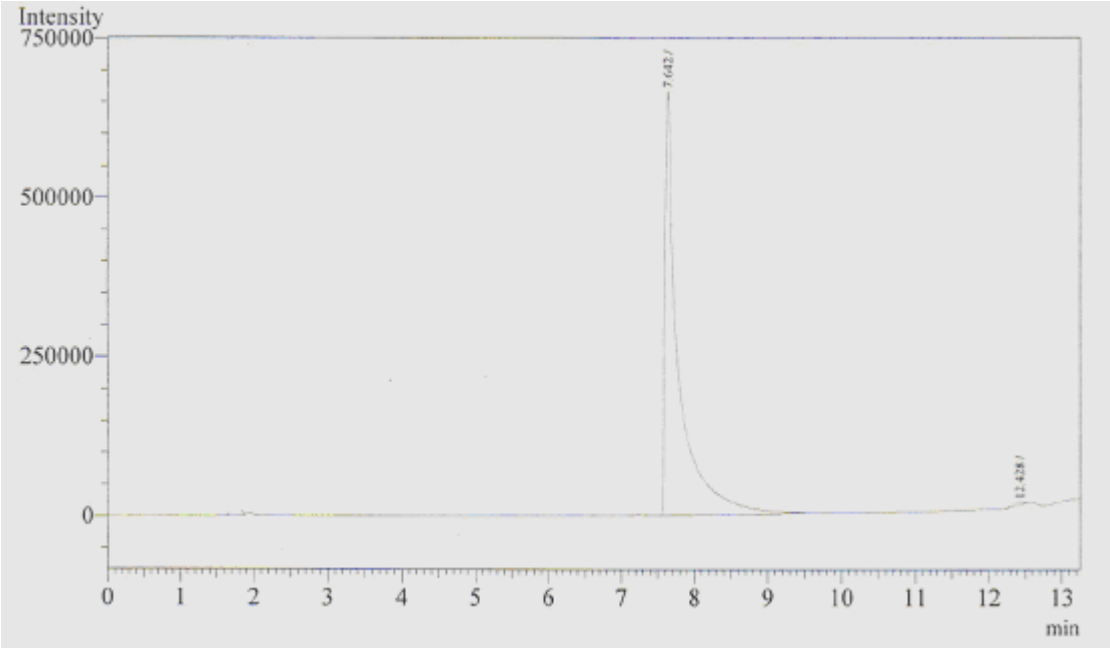


Figure A-2.2 Gas chromatography chromatogram of 1,3-PDO standard in aqueous solution

A-3 Standard calibration curve of 2-MD in ethyl-benzene from Gas chromatography analysis

Table A-3 Standard calibration curve data of 2-MD in ethyl-benzene from Gas chromatography analysis

2-MD peak area	2-MD concentration (ppm)
0	0
520572	2205
1619722	5379
4825476	13120
12016675	32000
30862318	80000

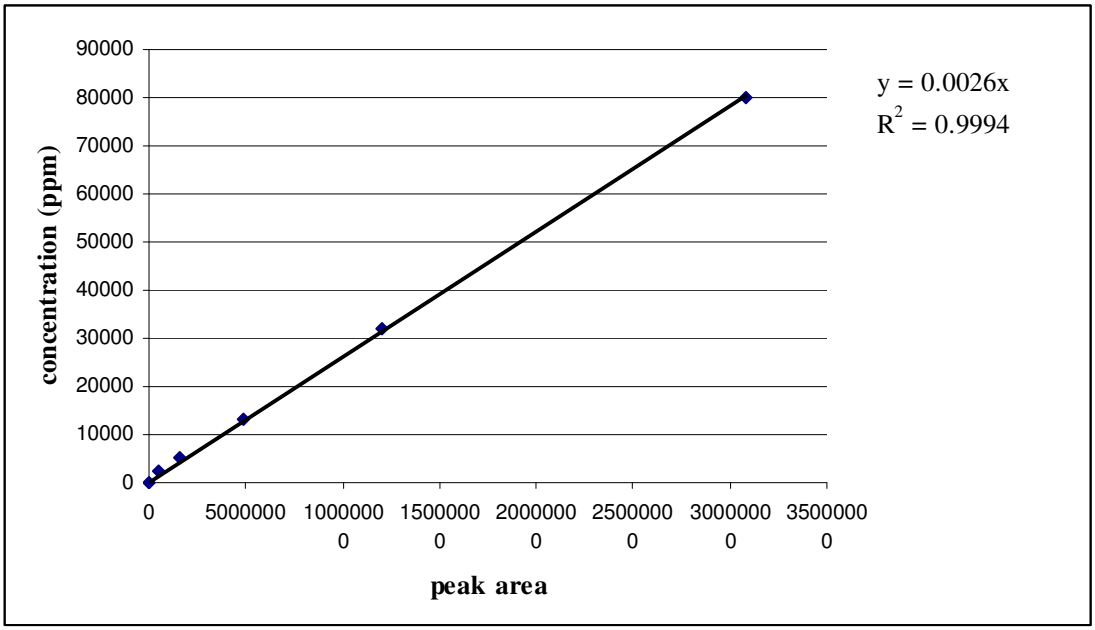


Figure A-3.1 Standard calibration curve data of 2-MD in ethyl-benzene from Gas chromatography analysis

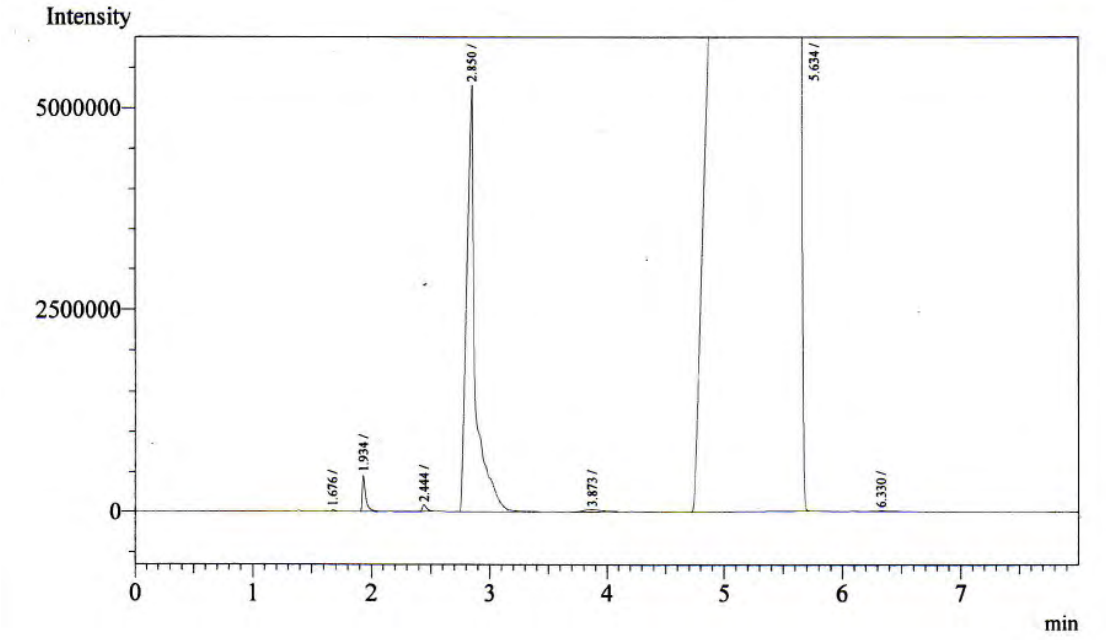


Figure A-3.2 Gas chromatography chromatogram of 2-MD standard ethyl-benzene

APPENDIX B

EXPERIMENTAL DATA

B-1 Calculation of %conversion and concentration of 1,3-PDO and 2-MD

$$\%\text{conversion of 1,3-PDO} = \frac{\text{initial 1,3-PDO mass} - \text{last 1,3-PDO mass}}{\text{initial 1,3-PDO mass}} * 100$$

$$\text{Concentration of 1,3-PDO or 2-MD} = \frac{\text{gram of 1,3-PDO or 2-MD}}{\text{M.W} \times \text{Volume}}$$

B-2 Experimental data of Catalyst reactivity for acetalization of 1,3-PDO and acetaldehyde in aqueous solution

Table B-1 Determination of suitable catalyst to 1,3-PDO mass ratio for acetalization

catalyst mass (g)	1,3-PDO (g)	%conversion
0.1	0.27300	72.70
0.3	0.13027	86.97
0.5	0.10140	89.86
0.7	0.07326	92.67
0.9	0.07587	92.41

Table B-2 Comparison of catalyst reactivity

time (min)	dowex		amberlite		novel carbon based	
	1,3-PDO (g)	%conversion	1,3-PDO (g)	%conversion	1,3-PDO (g)	%conversion
60	0.0421	91.57	0.0346	93.08	0.1790	64.21
90	0.0469	90.61	0.0379	92.43	0.1444	71.11
120	0.0456	90.88	0.0413	91.74	0.0489	90.23

Table B-3 Evaluation of catalyst deactivation

time used	dowex		amberlite		novel carbon based	
	1,3-PDO (g)	%conversion	1,3-PDO (g)	%conversion	1,3-PDO (g)	%conversion
1	0.0456	90.88	0.0413	91.74	0.0456	90.23
2	0.0559	88.82	0.0592	88.17	0.1290	74.19
3	0.0635	87.30	0.0753	84.93	0.1846	63.08

Table B-4 1,3-PDO and 2-MD in aqueous phase on effect of temperature

Temperature (°C)	time (min)	1,3-PDO (g)	1,3-PDO concentration (mol/l)	2-MD (g)	2-MD concentration (mol/l)
15					
	0	0.500	0.206	0.000	0.000
	5	0.425	0.175	0.088	0.027
	10	0.416	0.172	0.091	0.028
	15	0.400	0.165	0.093	0.029
	20	0.399	0.164	0.099	0.030
	30	0.388	0.160	0.101	0.031
	60	0.350	0.144	0.134	0.041
20					
	0	0.500	0.206	0.000	0.000
	5	0.406	0.168	0.106	0.033
	10	0.385	0.159	0.116	0.036
	15	0.359	0.148	0.141	0.043
	20	0.350	0.144	0.149	0.046
	30	0.335	0.138	0.149	0.046
	60	0.302	0.125	0.163	0.050
25					
	0	0.500	0.206	0.000	0.000
	5	0.379	0.156	0.129	0.040
	10	0.361	0.149	0.141	0.043
	15	0.347	0.143	0.133	0.041
	20	0.345	0.142	0.133	0.041
	30	0.335	0.138	0.134	0.041
	60	0.285	0.118	0.123	0.038
30					
	0	0.500	0.206	0.000	0.000
	5	0.284	0.117	0.204	0.063
	10	0.247	0.102	0.253	0.078
	15	0.241	0.099	0.231	0.071
	20	0.234	0.096	0.227	0.070
	30	0.193	0.079	0.243	0.075
	60	0.171	0.071	0.143	0.044
35					
	0	0.500	0.206	0.000	0.000
	5	0.210	0.087	0.288	0.089
	10	0.195	0.081	0.267	0.082
	15	0.174	0.072	0.274	0.084
	20	0.163	0.067	0.235	0.072
	30	0.139	0.058	0.193	0.059
	60	0.109	0.045	0.085	0.026

Table B-5 1,3-PDO and 2-MD in ethyl-benzene phase on effect of temperature

Temperature (°C)	time (min)	2-MD (g)	2-MD concentration (mol/l)
15			
	0	0.000	0.000
	5	0.018	0.006
	10	0.021	0.006
	15	0.029	0.009
	20	0.042	0.013
	30	0.045	0.014
	60	0.076	0.024
20			
	0	0.000	0.000
	5	0.022	0.007
	10	0.036	0.011
	15	0.041	0.012
	20	0.049	0.015
	30	0.070	0.022
	60	0.100	0.031
25			
	0	0.000	0.000
	5	0.031	0.010
	10	0.044	0.013
	15	0.072	0.022
	20	0.074	0.023
	30	0.084	0.026
	60	0.162	0.050
30			
	0	0.000	0.000
	5	0.084	0.026
	10	0.087	0.027
	15	0.118	0.036
	20	0.128	0.039
	30	0.168	0.051
	60	0.298	0.092
35			
	0	0.000	0.000
	5	0.100	0.031
	10	0.140	0.043
	15	0.161	0.049
	20	0.215	0.066
	30	0.288	0.089
	60	0.437	0.134

Table B-6 1,3-PDO and 2-MD in aqueous phase on effect of initial 1,3-PDO concentration

Initial 1,3-PDO concentration (g/L)	time (min)	1,3-PDO (g)	1,3-PDO concentration (mol/l)	2-MD (g)	2-MD concentration (mol/l)
20					
	0	0.250	0.103	0.000	0.000
	5	0.105	0.043	0.174	0.054
	10	0.085	0.035	0.170	0.052
	15	0.078	0.032	0.156	0.048
	20	0.065	0.027	0.149	0.046
	30	0.060	0.025	0.082	0.025
	60	0.044	0.018	0.062	0.019
40					
	0	0.500	0.206	0.000	0.000
	5	0.210	0.087	0.288	0.089
	10	0.195	0.081	0.267	0.082
	15	0.174	0.072	0.274	0.084
	20	0.163	0.067	0.235	0.072
	30	0.139	0.058	0.193	0.059
	60	0.109	0.045	0.085	0.026
60					
	0	0.750	0.309	0.000	0.000
	5	0.328	0.135	0.477	0.147
	10	0.293	0.121	0.490	0.151
	15	0.260	0.107	0.474	0.146
	20	0.226	0.093	0.481	0.148
	30	0.200	0.082	0.438	0.135
	60	0.158	0.065	0.196	0.060
80					
	0	1.000	0.412	0.000	0.000
	5	0.591	0.244	0.421	0.129
	10	0.554	0.229	0.371	0.114
	15	0.504	0.208	0.404	0.124
	20	0.460	0.190	0.398	0.122
	30	0.440	0.182	0.298	0.092
	60	0.324	0.134	0.212	0.065
100					
	0	1.250	0.516	0.000	0.000
	5	0.721	0.297	0.534	0.164
	10	0.676	0.279	0.498	0.153
	15	0.604	0.249	0.516	0.159
	20	0.525	0.216	0.613	0.188
	30	0.502	0.207	0.441	0.135
	60	0.342	0.141	0.216	0.066

Table B-7 1,3-PDO and 2-MD in ethyl-benzene phase on effect of initial 1,3-PDO concentration

Initial 1,3-PDO concentration (g/L)	time (min)	2-MD (g)	2-MD concentration (mol/l)
20			
	0	0.000	0.000
	5	0.021	0.007
	10	0.051	0.016
	15	0.075	0.023
	20	0.099	0.031
	30	0.172	0.053
	60	0.214	0.066
40			
	0	0.000	0.000
	5	0.100	0.031
	10	0.140	0.043
	15	0.161	0.049
	20	0.215	0.066
	30	0.288	0.089
	60	0.437	0.134
60			
	0	0.000	0.000
	5	0.083	0.026
	10	0.118	0.036
	15	0.180	0.055
	20	0.221	0.068
	30	0.291	0.090
	60	0.597	0.184
80			
	0	0.000	0.000
	5	0.129	0.040
	10	0.222	0.068
	15	0.262	0.081
	20	0.320	0.098
	30	0.454	0.139
	60	0.695	0.213
100			
	0	0.000	0.000
	5	0.174	0.054
	10	0.272	0.084
	15	0.344	0.106
	20	0.349	0.107
	30	0.561	0.172
	60	0.996	0.306

APPENDIX C

The 18th Thailand Chemical Engineering and Applied Chemistry Conference

(TICHE 18 th)

20-21 October 2008, The Jomtain palmbeach Hotel, Pattaya, Thailand

Separation of 1,3-propanediol from model mixture and fermentation broth by solvent extraction

Boonnoun P[1]., Boonsongsawat T[1]., Muangnapoh C[1]., Prasitchoke P[2]., Tantayakom V[2].,and Shotipruk A[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 1 Road,Tambon Map Ta Phut,Amphoe Mueang Rayong,Rayong 21150,Thailand

The 18h Thailand Chemical Engineering and Applied Chemistry Conference October 20-21,2008,Pattaya Thailand

Separation of 1,3-propanediol from model mixture and fermentation broth by solvent extraction

*Boonnoun P[1]., Boonsongsawat T[1]., Muangnapoh C[1]., Prasitchoke P[2]., Tantayakom V[2]., and Shotipruk A[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 1 Road,Tambon Map Ta Phut,Amphoe Mueang Rayong,Rayong 21150,Thailand

Abstract

For the recovery of 1,3-propanediol from aqueous solution by solvent extraction, a suitable solvent was selected and the experimental equilibrium data on 1,3-propanediol-water-solvent mixture was investigated. The theoretical solvent screening using Hansen model was first applied to select the possible solvents for extracting 1,3-propanediol from aqueous solution. Then the experiments were conducted to evaluate the selected solvents based on the distribution coefficients and mutual solubilities of the solvents. The experimental data were then compared with the calculated data obtained using unifac equation. The results revealed that ethyl acetate was a suitable solvent and the distribution coefficient of 1,3-propanediol was 0.22 at temperature of 303.15 K. In this study, the tie line data were also correlated using the methods of Othmer-Tobias and Hand and their correlation coefficient (R^2) were 0.94 and 0.99, respectively. Furthermore, the effects of temperature (303.15 to 323.15 K) and glycerol addition in feed aqueous stream (4, 8, 12 g/L) were studied. In presence of glycerol in the feed mixture, the distribution coefficient of 1,3-propanediol increased .

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

1. Introduction

For decade, 1,3-Propanediol (PDO) is one of the major monomer components for the production of high performance polyester such as polytrimethylene terephthalate (PTT). The PTT produced from 1,3-propanediol has excellent physical properties and is suitable for fiber and textile applications. In addition, PTT can be produced in an environmentally friendly way and at a price very competitive to that of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). Nowadays, 1,3-propanediol (PDO) can be produced either by a chemical method or a biotechnological method.This study focused on separation and concentration of 1,3-PDO produced by the biological process. Separation and purification of 1,3-PDO from fermentation broth is not straightforward because 1,3-PDO has low volatility and high hydrophilic characteristics in dilute aqueous solutions. Ames (2002) disclosed a process for separation and purification of 1,3-propanediol by evaporation and distillation but the necessity for a large amount of heat energy made this process unprofitable. Compared with distillation, solvent extraction requires lower energy consumption. Malinowski (1999) reported the theoretical evaluation of the downstream separation of 1,3-propanediol from dilute aqueous solutions by liquid-liquid extraction with aliphatic aldehydes and alcohols. However, the distribution of 1,3-PDO into aldehydes and alcohols appeared not to be sufficient to make simple extraction efficient. Alternatively, Malinowski (2000) developed the 1,3-propanediol purification process based on the reactive extraction, using aldehydes as a reactant to first convert 1,3-PDO to alkyl 1,3-dioxane, which was then extracted with organic solvent such as toluene, o-xylene, and ethylbenzene. Yan et al. (2005) proposed a similar but improved reactive extraction process using aldehydes as both the reactant and the extraction solvent. Although high extraction yield was resulted, the 1,3-dioxane product needs to be converted back to 1,3-PDO by hydrolysis, which is operated at high temperature. Furthermore, the separation of 1,3-propanediol from the mixture of 1,3-propaneidol and aldehyde is then required. Such procedures were too complicated to achieve a satisfactory yield. Alternatively, Shiguang Li et al. (2001) applied pervaporation using a ZSM-5 zeolite membrane for the separation of 1,3-propanediol from glycerol and glucose in aqueous solution, however this method has some drawbacks such as low flux and low selectivity. Roturier et al. (2002) and Hilaly et al. (2002) used the chromatographic column packed with cation exchange resin for the recovery of 1,3-propanediol. This method consumed less energy and satisfied the environmental protection standards, however, it was difficult to obtain 1,3-propanediol with high purity and the process required the dewatering step. Corbin et al. (2003) suggested the separation of 1,3-propanediol, glycerol, and a mixture of 1,3-propanediol and glycerol from a biological mixture using a molecular sieve. They discovered that using any of molecular sieves and ethanol in an elution step achieves the yield greater than 90%. However, the mixture must still be purified further using conventional separation methods such as distillation. In this work, we proposed to concentrate 1,3-PDO from the fermentation broth using solvent extraction. First, the theoretical solvent screening using Hansen model was applied to select the possible solvents for extracting 1,3-propanediol from aqueous solution. Then the experiments were conducted to determine the distribution coefficients and mutual solubilities of selected solvent system. The

experimental data were then compared with the calculated data obtained using unifac equation.

2. Materials and Methods

2.1 Chemicals

The feed material in this study was a mixture of 1,3-propanediol and glycerol in aqueous solution. 1,3-propanediol (98% purity) was purchased from Acros Organic Co. Glycerol (99.5% purity) was supplied from Ajax Finechem. Ethyl acetate analytical grade was obtained from Fisher Scientific, UK.

2.2 Solvent selection

To assist the solvent selection, the Hansen solubility parameters are usually considered, in which the parameters are plotted on a normal three-dimensional graph. For simplicity, the graphical representation can be reduced to a two-dimensional plot of the polar parameter, δp, versus the hydrogen bonding parameter, δh. This is generally an acceptable practice because the dispersive component parameter, δd of many common solvents are quite similar. In this experiment, Hansen model was employed by plotting the polar parameter, δp, against the hydrogen bonding parameter, δh, of a number of possible solvents and the components in the feed mixture including of 1,3-propanediol, glycerol, and water.

2.3 Experimental measurements of equilibrium data

Determinations of binodal curve data were made at isothermal condition in a 100 mL equilibrium cell equipped with a magnetic stirrer. The cell was filled with homogeneous water-1,3-propanediol mixtures. Then the solvent was added into the cell until the end point was reached, as indicated by the onset of permanent turbidity (Ozmen et al., 2004). The tie lines data were obtained using the equilibrium cell into which 20 mL of an organic solvent and 20 mL of an aqueous mixture containing 1,3-propanediol are introduced. In this experiments, the mixture were prepared in five different concentrations of 1,3-propanediol. The temperature was controlled by refrigerated bath. The content of the two phases was stirred at 150 rpm until the system reached equilibrium (see section 2.4 for the determination of appropriate mixing time). The mixture was then centrifuged for 30 min at 30 °C and 500 rpm to obtain complete phase separation. The organic phase and the aqueous phase were separated and the volumes were measured. To separate remaining solvent, the aqueous phase was evaporated by a vacuum rotary evaporator at 35 °C for 10 min, and the solvent free aqueous phase was then analyzed with an HPLC analytic column. This procedure allows for the determination of partition coefficients of 1,3-propanediol between various organic phase and aqueous phase, thus the selection of the most suitable extraction solvent.

2.3.1 Mixing time for 1,3-propanediol extraction

To determine the time of agitation for extraction, the change in 1,3-propanediol and glycerol concentration in the organic and aqueous phases was determined at different stirring times (20, 40, 60 min). 20 mL ethyl acetate and 20 mL of an aqueous 1,3-propanediol and glycerol solution were introduced in the cell in which the concentration of 1,3-propanediol and glycerol in the initial aqueous solution were 60 g/L and 10 g/L, respectively. The mixture was then stirred at 150 rpm for a specified period of stirring time, after which the mixture was centrifuged to achieve complete

phase separation. The aqueous phase was separated from the mixture, and the remaining solvent mixture was analyzed by HPLC.

2.3.2 Temperature effect on extraction of 1,3-propanediol

Extraction of 1,3-propanediol with selected solvent was investigated at three different temperatures: 30, 40, 50 °C. At each temperature, the equilibrium data were taken using the same procedure described earlier, in which 20 mL of solvent and 20 mL of 1,3-propanediol aqueous solution were introduced into the equilibrium cell. The mixture was then stirred at 150 rpm, after which the concentration of 1,3-propanediol in the aqueous phase was analyzed. For each temperature, the experiments were carried at five different concentrations of 1,3-propanediol aqueous mixtures.

2.3.3 Effect of presence of glycerol in feed mixture

To determine the effect of the presence of glycerol in the feed, the experiment was conducted by adding an amount of glycerol into initial mixture at three different glycerol mass fractions. The mixture was then extracted with solvent at 303.15 K. The different feed mixtures in this experiment had the mass ratios of 60 g 1,3-propanediol to 12 g glycerol, 60 g 1,3-propanediol to 8 g glycerol, and 60 g 1,3-propanediol to 4 g glycerol, respectively in 1 L solution, and were extracted with solvent at the volume ratio of 20 mL feed to 20 mL solvent at 303.15 K, with the stirring speed of 150 rpm for 40 min.

2.4 Analysis

2.4.1 Chemical analysis

An HPLC (Lichrocart-C18) system was used to measure the concentration of 1,3-propanediol and glycerol in the aqueous (raffinate) phase. Lichrocart-C18 column (250 mm x 4 mm I.D.) was used as an HPLC analytic column and the mobile phase was 5%MeOH. The flow rate of mobile phase was maintained at 0.5 ml/min and an injection volume of 20 µL was used. The column effluent was monitored with RI detector. Each analysis was carried out using isocratic mode at room temperature.

2.4.2 Data analysis

Using the described analytical methods, the mass fraction of solute was determined in the aqueous phase. The mass balance was calculated in the mass fraction of solute in the solvent phase. The distribution ratio of a solute i, $K_{D,i}$, was calculated based on its definition as the ratio of the determined solute mass fraction in the organic phase, $w_{i,org}$, and that in the aqueous phase, $w_{i,aq}$, at equilibrium:

$$K_{D,i} = \frac{w_{i,org}}{w_{i,aq}}$$

The distribution ratio represents the capacity of a solvent system in the extraction of 1,3-propanediol and was used for evaluation of the experimental results.

The number of theoretical stages, NTS, for extraction of 1,3-propanediol from aqueous solutions was calculated for ethyl acetate, the most suitable solvent. Using a graphical method

3. Results and Discussion

3.1 Solvent selection for 1,3-propanediol extraction

Ethyl acetate, proposed by Cho et al. (2006) was used for extraction of 1,3-propanediol from mixture and was claimed to be good for glycerol and glucose separation. A group of possible solvents whose points are located close to ethyl acetate such as butanol, pentanol, cyclohexanol, butyraldehyde, and ethyl acetate itself. These point lie close to 1,3-propanediol but they are far from glycerol and water.

In general solvent selection, the solvent must preferably be chemically stable, of low toxicity, non-corrosive, inexpensive, available in large quantities, and easily recoverable from the extract. pentanol and cyclohexanol are difficult to recover from the extract phase because of their high boiling point. Furthermore, butyraldehyde has low flash point and highly flammable solvent are not appropriate solvents. Of the selected solvents, ethyl acetate and 1-butanol might be most suitable for 1,3-propanediol extraction from dilute aqueous phase due to low boiling point.

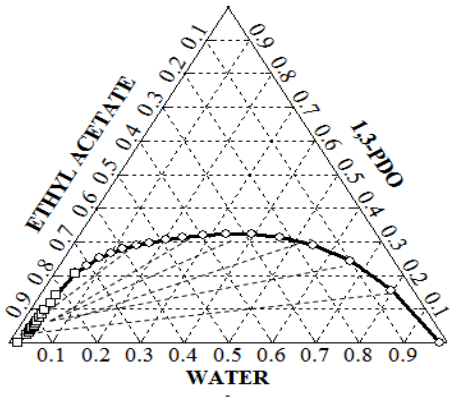


Figure 1 Predicted ternary diagram for the 1,3-propanediol-water-ethyl acetate using the Unifac model at 303.15 K

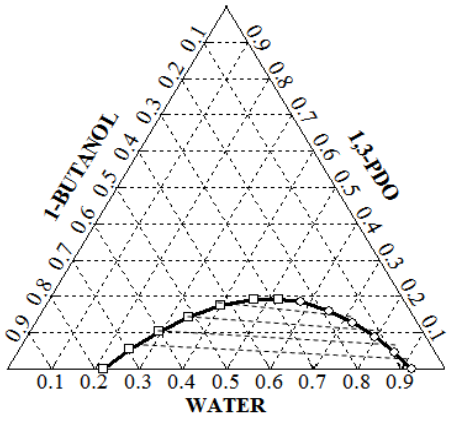


Figure 2 Predicted ternary diagram for the 1,3-propanediol-water-1-Butanol using the Unifac model at 303.15 K

Figure 1 shows that the binodal curve of 1,3-propanediol-water-ethyl acetate system has a large two-phase area, with a minimum mutual solubility but the distribution of 1,3-propanediol is in favor of aqueous phase. On the other hand, the mutual solubility of 1,3-propanediol-water-1-butanol system as shown in Figure 2 was higher due to the smaller two-phase area than one. Although the distribution of 1,3-propanediol is in favor of the butanol phase, the high mutual solubility of 1-butanol in 1,3-propanediol makes it unsuitable for extraction of 1,3-propanediol from aqueous solution. Ethyl acetate however, is more suitable for extracting 1,3-propaendiol due to lower mutual solubility and was therefore evaluated for the further experimental investigation for the separation of 1,3-propanediol from the fermentation mixture.

3.2 Preliminary equilibrium measurements

The liquid-liquid equilibrium phase composition data was measured for the system of water+1,3-propanediol+ethyl acetate at 303.15 K to investigate the equilibrium distribution and mutual solvent solubility. Initially, the time of agitation required to reach equilibrium was determined by measuring the change in 1,3-propanediol and glycerol concentration for different stirring times (20, 40, 60 min). The mass fraction of 1,3-propanediol and glycerol in the aqueous phase at different stirring times are shown in Figure 3.

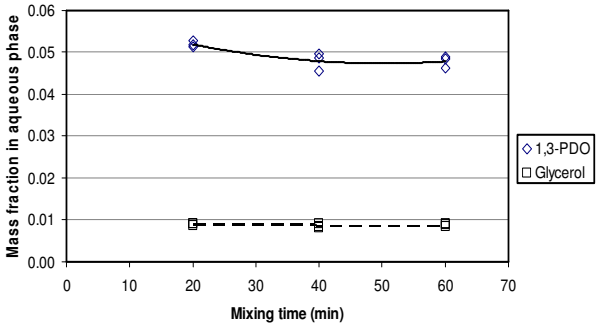


Figure 3 Mass fraction of 1,3-propanediol and glycerol in raffinate phase versus stirring time.

Figure 3 shows that mass fraction of 1,3-propanediol in raffinate phase tends to decrease slightly when the time of agitation increased and reached a constant value after 40 min, while the mass fraction of glycerol in the raffinate phase achieves to equilibrium at 20 min. From these results, we concluded that 40 min of mixing time would experimentally be sufficient to approach the equilibrium state. Thus the experimental liquid-liquid equilibrium data would be taken after 40 min of extraction time, provided the same degree of mixing degree was applied.

3.3 Effect of temperature for 1,3-propanediol extraction

To study the distribution of 1,3-Propanediol as function of temperature, the extraction temperature was varied at 303.15 K, 313.15 K, and 323.15 K. The experimental distribution coefficients are summarized in Table 1.

Table 1 Experimental partition coefficients at 303.15 K, 313.15 K, and 323.15 K..

Temperature (K)	$K_{1,3\text{-PDO}}$	NTS (99%)
303.15	0.220	5.1
313.15	0.192	5.9
323.15	0.185	6.2

When the temperature increases, the partition coefficients of 1,3-propanediol decreases only slightly. With these results, the calculated number of theoretical stages required to achieve 99% extraction showed almost no difference. From this result, the extraction temperature at 303.15 K is the most suitable for extraction of 1,3-propanediol from aqueous solution.

3.4 Influence of residual glycerol from fermentation

Table 2 The calculated distribution ratio of 1,3-propanediol and glycerol from extraction at 303.15 K

Glycerol in feed Mass ratio (1,3-PDO:Glycerol)	$K_{1,3\text{-PDO}}$	NTS (99%)	K_{gly}	Selectivity
60:0 g/L	0.220	5.1	-	-
60:4 g/L	0.229	4.9	0.08	2.9
60:8 g/L	0.251	4.5	0.20	1.3
60:12 g/L	0.277	4.1	0.20	1.4

As seen in Table 13, the distribution ratio of 1,3-propanediol was slightly increased at low concentration of glycerol and was increased to 0.28 at high concentration of glycerol. Furthermore, the distribution ratio of glycerol at high glycerol concentration was higher than the distribution ratio of glycerol at low concentration due to the increased amounts of glycerol in water. From these, the selectivity was determined and was found to decrease with increasing glycerol concentration. Based on these results, the number of theoretical stages, NTS, to achieve 99% extraction was not found to be significantly different while the selectivity was decreased considerably. It was therefore recommended that glycerol concentration in the aqueous phase should be kept at minimum.

4. Conclusions

1. From theoretical screening methods, ethyl acetate would be suitable for recovery of 1,3-propanediol from aqueous solution.
2. In this study, ethyl acetate was used in extraction of 1,3-propanediol and the distribution

ratio of 1,3-propanediol at 303.15 K was found to be 0.22.

3. The experimental distribution ratio of 1,3-propanediol were only slightly decreased when the extraction temperature, and the number of stages required for extracting 99% of 1,3-propanediol calculated from such data were not significantly different.

4. The addition of glycerol in feed aqueous stream effects did not increase the distribution ratio of 1,3-propanediol significantly, however the selectivity decreased when the concentration of glycerol increased.

5. References

[1] A. Reimann, H. Biebl, W. D. Deckwer. Production of 1,3-propanediol by Clostridium butyricum in continuous culture with cell recycling. Appl Microbiol Biotechnol 49 (1998): 359-363.

(n-hexane, cyclohexane, cyclohexanol and cyclohexyl acetate) ternaries at 298.15 K. Brazilian journal of chemical engineering 21 (2004): 647-657.

[3] F.S. Mohammad Doulabi, M. Mohsen-Nia, H. Modarres. Measurements and modeling of quanternary (liquid+liquid) equilibria for mixtures of (methanol or ethanol+water+toluene+n-dodecane). J. Chem. Thermodynamics 38 (2006): 405-412.

[9] Fabien Barborato, El Hassan H., Theirry C., Andre B. 1,3-propanediol production by fermentation: An interesting way to valorize glycerin from the ester and ethanol industries. Industrial Crops and Products 7 (1998): 281-289.

[10] Fredenslund, Aa., R.L. Jones and J.M. Prausnitz, Group-Contribution Estimation of

[2] A. Reimann, S. Abbad-Andaloussi, H. Biebl and H. Petitdemange 1,3-Propanediol formation with product-tolerant mutants of *Clostridium butyricum* DSM 5431 in continuous culture: productivity, carbon and electron flow. Journal of Applied Microbiology 84 (1998): 1125-1130.

[4] Ames TT. Process for the isolation of 1,3-propanediol from fermentation broth. US Patent 6.361.983 B1 (2002).

[5] Avraham M. Baniel, Robert P. Jansen, Asher Vitner, Anthony Baiada. Process for producing 1,3-propanediol. US Patent 7.056.439 B2 (2006).

[6] Barton, Allan F.M. Handbook of Solubility Parameters, CSC Press, (1983): 153-157

[7] Corbin DR, Norton T. Process to separate 1,3-propanediol or glycerol, or a mixture thereof from a biological mixture. US Patent 6.603.048 (2003).

[8] D. Ozman, U. Dramur, B. Tatli. Liquid-liquid equilibria of propionic acid-water-solvent Activity Coefficients in Nonideal Liquid Mixtures, AIChe J. 21 (1975): 1086-1099.

[11] G. S. Laddha, T. E. Degaleesan. Transport phenomena in liquid extraction. McGraw-Hill Book Company. New York, (1978): 26-28.

[12] Hilaly AD, Thomas PB. Method of recovering 1,3-propanediol from fermentation broth. US Patent 6.479.716 (2002).

[13] John Burke. Solubility Parameter: Theory and Application. AIC Book and Paper Group Annual 3 (1984): 13-58.

[14] Malinowski J. Evaluation of liquid extraction potentials for downstream separation of 1,3-propanediol. Biotechnology Techniques 13 (1999): 127-130.

[15] Malinowski J. Reactive extraction for downstream separation of 1,3-propanediol. Biotechnol. Prog. (2000).

[16] Maria Gonzalez-Pajuelo, I. Meynial-Salles, F. Mendes, J. Carlo Andrade, I. Vasconcelos, P. Soucaille Metabolic of *Clostridium acetobutylicum* for the industrial production of 1,3-propanediol from glycerol. Metabolic Eng. 7 (2005): 329-336.

[17] Mi-Hae Cho, Sun Im Joen, Sang-Hyun Pyo, Sungyong Mun, Jin-Hyun Kim. A novel separation and purification process for 1,3-propanediol. Process Biochem 41 (2006): 739-744.

[18] Roturier JM, Fouache C, Berghmans E. Process for the purification of 1,3-propanediol from a fermentation medium. US Patent 6.428.992 B1 (2002).

[19] S. Papanikolaou, P. Ruiz-Sanchez, B. Pariset, F. Blanchard, M. Fick High production of 1,3-propanediol from industial glycerol by a newly isolated *Clostridium butyricum* strain. Journal of Biotechnology 77 (2000): 191-208.

[20] S. Saint-Amans, P. Perlot, G. Goma and P. Soucaille High production of 1,3-propanediol by *Clostridium butyricum* VPI 3266 in a simply controlled fed-batch system. Biotechnol. Lett 16 (1994): 831-836.

[21] Seader J. D., Ernest J. Henley, Separation Process Principles, John wiley & Sons, Inc. New York (1998): 163-198

[22] Shiguang Li, Vu A. Tuan, John L. Falconer, Richard D. Noble. Separation of 1,3-propanediol from glycerol and glucose using a ZSM-5 zeolite membrane. J. Membr. Sci. 191 (2001): 53-59

[23] Yan G,Yu T, Xiao-lin W, Li-xin Y, De-hua Liu. The possibility of the desalination of actual 1,3-propanediol fermentation broth by electrodialysis. Desalination 161 (2004): 169-178.

[24] Zeng AP, Biebl H. Bulk chemicals from biotechnology: the case of 1,3-propanediol production and the new trends. Adv Biochem Eng. 74 (2002): 239-5

Journal of Sustainable Energy & Environment

The joint Graduate School of Energy and Enviironment (JGSEE)
King Mongkut's University of Technology Thonuri (KMUTT)
126 Prachauthit Road, Bangmod, Tungkru, Bangkok 10140 Thailand
Tel: 66 2470 8309-10 ext. 4120
Fax: 66 2872 6736
E-mail : ajee@jgsee.kmutt.ac.th

Asst. Prof. Artiwan Shotipruk
Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University,
Patumwan, Phayathai Road, Bangkok 10330, Thailand

28 April 2009

Dear Asst. Prof. Artiwan Shotipruk,

Reactive extraction of 1,3-propanediol from model mixture of fermentation broth using novel carbon based catalyst
By
Boonnoun P., Muangnapoh C., Prasitchoke P., Tantayakom V., and Shotipruk A.

From your submission of the above paper for publication in Journal of Sustainable Energy & Environment (JSEE), we are very pleased to inform you that your paper has been accepted for publication in Journal of Sustainable Energy & Environment (2009) Volume 1, Issues 1.

Enclosed, please find the "master proof" of your paper for your final correction before publication. Please send your approval and copyright transfer to us before 4 May 2009.

Thank you very much for your cooperation.

Yours sincerely,

Surapong C.

(Prof. Dr. Surapong Chairattanon)
Editor-in-Chief

Reactive extraction of 1,3-propanediol from model mixture of fermentation broth using novel carbon based catalyst

*Boonnoun P[1]., Muangnapoh C[1]., Prasitchoke P[2]., Tantayakom V[2].,and Shotipruk A[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 1 Road, Tambon Map Ta Phut, Amphoe Mueang Rayong, Rayong 21150,Thailand

Abstract

This study deals with the development of 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 $m^2 g^{-1}$ and 0.07 $cm^3 g^{-1}$, 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 aqueous solution indicated its applicability for such reaction, and the optimal quantity of the catalyst required for this reaction was 0.7 g/ g 1,3-PDO, giving the conversion of approximately 92% after 2 h of reaction at 35°C. In addition to acetalization reaction, 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 derived from the fermentation process, the conversion was found to be 78.92% after 60 min for 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

Biodiesel is among the most promising alternatives for renewable energy that has recently gained much interest because it is a green energy and its properties are closed to those of petroleum diesel. Biodiesel is typically produced by transesterification of plant oils or animal fats, whose process 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 cosmetic industry or as animal feeds, 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 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 biological process of glycerol conversion to 1,3-PDO using various types of microorganism such as *Klebsiella pneumoniae, Citobacter frundii, Enterobacter agglomerans,*and *Clostridium butyricum.* Among these microorganisms, *Clostridium butyricum* leads to the highest yield of 1,3-PDO.

Beside 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 a 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 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 shorter operating time and smaller amount of reactant and extractant, which could also be recovered and reused. Malinowski et al. (2000) used UNIFAC program to select an appropriate solvent for extraction of dioxane. Three solvents that have 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 researcher later investigated the effect of two types of ion exchange catalysts for reactive extraction of 1,3-propanediol: Dowex and Amberlite ion exchange resins (Malinowski et al. 2002). Dowex ion exchange resin was found to be 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) proposed a reactive extraction process with use of the 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 researches on reactive extraction, either a homogeneous liquid acid or ion exchange acid resin was used as catalyst. Homogeneous acid catalysts are corrosive and cannot be reused. Furthermore, its use, particularly in aqueous system such as this, leads to large amount of waste water. This problem can be solved with use of solid acid catalysts, and those currently used are such as Dowex and Amberite ion exchange polymeric resions. 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 the low cost, simple preparation, high acid density and stability. The dense acidity endues its 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 of the simple sugars, Gao et al (2007) 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 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 organic phase, these results suggested potential application of such catalysts for the reactive extraction of 1,3 PDO from the aqueous solution, in which 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. Materials and Methods

2.1 Chemicals

1,3-propanediol (98% purity) was purchased from 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 sufonated carbon based catalyst were prepared following the procedures subsequently described.

2.2 Preparation of 2-mthyl-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 so, 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 (0.53mm diameter, 0.88mm 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. [Hao, 2005]

2.3 Preparation of catalyst

Naphthalene (20 g) was heated in concentrated sulfuric acid (>96%, 200 mL) at 523 K under a flow of N2. 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.[Shan et al.,2007]

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

A total 0.5 ml 1,3-PDO was added with of 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 sufonated 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 experiment.

2.5 Reactive extrtaction

To carry out the reactive extraction, a specified amount of catalyst (determined from 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 aqueous solution was added, and the reaction mixture was, and acetaldehyde were stirred vigorously (150 rpm) in a 125-mL shake flask. The reaction was catalyzed by novel carbon based catalyst, and the reaction was allowed to take placed 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 Micromeritrics model ASAP 2020. The sample cell which contained 0.5 g of sample was placed into Micromeritrics model ASAP 2020. After degassing step, N_2 physisorption was carried out for measuring 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, 0.88μm 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. [Hao,2005].

3. Results and Discussion

3.1 Catalyst characterize

The physical properties of the novel carbon based catalyst are shown in Table 3.1. The BET measurement indicates that the catalyst shows 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) was found to be 1.46 mmol/g.

Table 3.1 Physical properties of 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 acetalization of acetaldehyde and 1,3-PDO

The chromatograms of the reactants: 1,3-PDO and acetaldehyde in aqueous solution are shown in Figure 3.1a and 3.1b, which indicated that the retention times for 1,3-PDO and acetaldehyde were at about 7.5 minutes 1.4 minutes, respectively. The chromatogram of the product after the 2 hour of reaction shown Figure 3.1c indicated the presence of 2-MD (retention time = 1.6 minutes) as well as unreacted acetaldehyde, which was originally present in excess. It is seen from the same figure however that only a small amount the unreacted 1,3-PDO was found , indicating that the majority of 1,3-PDO was reacted with acetaldehyde to form 2-MD. Thus, it can be drawn from this preliminary result that the novel carbon based catalyst was effective catalyst for acetalization of 1,3-PDO and acetaldehyde in 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%.

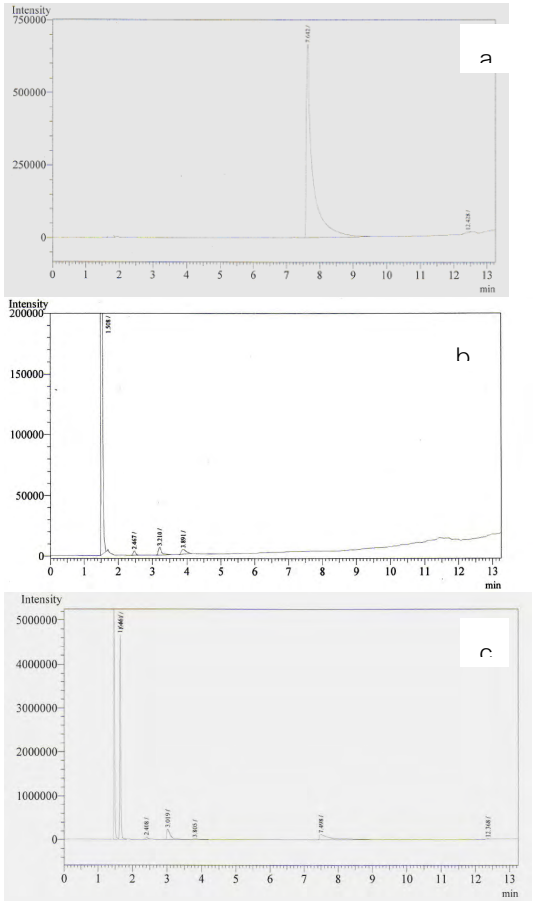


Figure.3.1 Chromatogram of reactants and product in aqueous solution (a = 1,3-PDO, b = acetaldehyde, c = product)

3.3 Reactive extraction

The chromatograms of the resulted aqueous phase and extract phase are shown in Figure 3.2a and 3.2b, respectively. The small amount of 1,3-PDO in aqueous phase indicated 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

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).

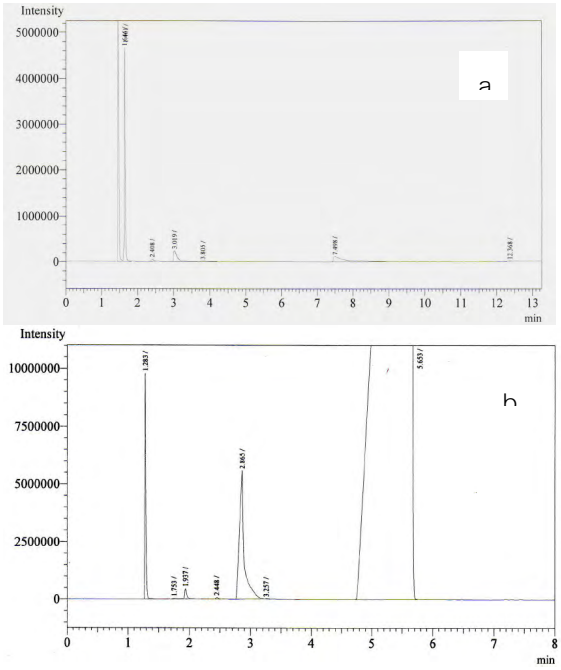


Figure.3.2 Chromatogram of sample in both phases

(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 3.3. 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 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 became lower. The reaction conversion calucaluted from the rate of 1,3-PDO decreased was found to be 79% after 60 min. However, as seen from the contuningly decresing 1,3-PDO concentration, it conversion would be expected that higher conversion could be achieved providing that longer reactive extraction time is allowed.

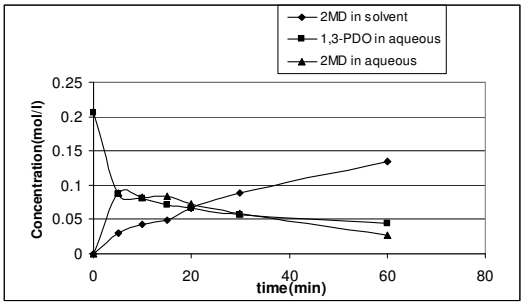


Figure 3.3 reactive extraction at 35°C

4. Conclusions

A small amount the unreacted 1,3-PDO was found , indicating that the majority of 1,3-PDO was reacted with acetaldehyde to form 2-MD. Thus, it can be drawn from this preliminary result that the novel carbon based catalyst was effective catalyst for acetalization of 1,3-PDO and acetaldehyde in 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%.

5. References

[1] Ames TT. Process for the isolation of 1,3-propanediol from fermentation broth. US Patent 6.361.983 B1, 2002.

[2] Gao Shan. High efficient acetalization of carbonyl compounds with diols catalyzed by novel carbon-based solid
strong acid catalyst, 21, 2007, 2892-2895

[3] Malinowski J. Evaluation of liquid extraction potentials for downstream separation of 1,3-propanediol. Biotechnology Techniques. 13, 1999, 127-130.

[4] Malinowski J. Reactive extraction for downstream separation of 1,3-propanediol. Biotechnol. Prog, 2000.

[5] Fang YJ, Study on Reactive Extraction Kinetics of
1,3-Propanediol in Dilute Aqueous Solutions. Separation Science and Technology. 41, 2006, 329–340.

[6] Li S., Vu A. Tuan, John L. Falconer, Richard D. Noble. Separation of 1,3-propanediol from glycerol and glucose using a ZSM-5 zeolite membrane. J. Membr. Sci. 191, 2001, 53-59.

[7] Hilaly AD, Thomas PB. Method of recovering 1,3-propanediol from fermentation broth. US Patent 6.479.716, 2002.

[8] Corbin DR, Norton T. Process to separate 1,3-propanediol or glycerol, or a mixture thereof from a biological mixture. US Patent 6.603.048, 2003.

[9] Ozman D., Dramur D., Tatli B. Liquid-liquid equilibria of propionic acid-water-solvent (n-hexane, cyclohexane, cyclohexanol and cyclohexyl acetate) ternaries at 298.15 K. Brazilian journal of chemical engineering. 21, 2004, 647-657.

VITA

Panatpong Boonaul was born on October 5th, 1984, in Pitsanulok, Thailand. He earned a Bachelor of Engineering Degree from the Department of Chemical Engineering, Thammasat University., Thailand, in 2006. He then subsequently fulfilled the requirements for a Master of Engineering Degree at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Thailand, in 2008