การเตรียมพอลิออลเอสเทอร์โดยใช้ตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดกรด

นายปิยะวัฒน์ แปงพั๊วะ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2554

PREPARATION OF POLYOL ESTERS USING ACIDIC HETEROGENEOUS CATALYSTS

Mr. Piyawat Paengphua

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2011

Thesis Title	PREPARATION OF POLYOL ESTERS USING ACIDIC HETEROGENEOUS CATALYSTS
By	Mr. Piyawat Paengphua
Field of Study	Chemistry
Thesis Advisor	Duangamol Tungasmita, Ph.D.

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

……………………………………..Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr. rer. nat.)

THESIS COMMITTEE

……………………………………………..Chairman
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

……………………………………………..Thesis Advisor
(Duangamol Tungasmita, Ph.D.)

……………………………………………..Examiner
(Assistant Professor Preecha Phuwapraisirisan, Ph.D.)

……………………………………………..External Examiner
(Suchada Butnark, Ph.D.)

ปิยะวัฒน์ แปงพั๊วะ : การเตรียมพอลิออลเอสเทอร์โดยใช้ตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดกรด (PREPARATION OF POLYOL ESTERS USING ACIDIC HETEROGENEOUS CATALYSTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร. ดวงกมล ตุงคะสมิต, 119 หน้า

ได้สังเคราะห์ตัวเร่งปฏิกิริยาเอสบีเอ-15 ที่มีหมู่โพรพิลซัลโฟนิก ด้วยวิธีทางความร้อนและการเติมหมู่ความเป็นกรดภายหลัง จากนั้นตรวจสอบลักษณะเฉพาะของวัสดุที่สังเคราะห์ได้ด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ เทคนิคการดูดซับไนโตรเจน และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ทำการเปรียบเทียบประสิทธิภาพของตัวเร่งปฏิกิริยาที่สังเคราะห์กับตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดอื่นๆ ที่ภาวะเดียวกันกับปฏิกิริยาเอสเทอริฟิเคชันของนีโอเพนทิลไกลคอลกับกรดออกทาโนอิกต้นแบบที่ถูกเร่งปฏิกิริยาด้วยแอมเบอลิสต์-15 พบว่า เอสบีเอ-15 ที่มีหมู่โพรพิลซัลโฟนิกเป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสูงสุดซึ่งสามารถให้ประสิทธิภาพเทียบเท่ากับแอมเบอลิสต์-15 โดยใช้เวลาเพียงสองชั่วโมง ภาวะที่เหมาะสมในการเตรียมสารหล่อลื่นคือ ปริมาณตัวเร่งปฏิกิริยา 3% โดยน้ำหนักสารตั้งต้น ที่อุณหภูมิ 80 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง ด้วยอัตราเร็วในการกวน 200 รอบต่อนาที การใช้อัตราส่วยโดยโมลระหว่างของกรดออกทาโนอิกต่อนีโอเพนทิลไกลคอลเท่ากับ 2 สารละลายหลังปฏิกิริยาให้ผลได้ของเอสเทอร์รวมที่ 74.0% และมีความจำเพาะต่อไดเอสเทอร์ 73.3% การเพิ่มอัตราส่วนโดยโมลของ2-เอทิลเฮกซานอลต่อกรดออกทาโนอิกต่อนีโอเพนทิลไกลคอลเท่ากับ 4 ช่วยเพิ่มความเลือกจำเพาะต่อไดเอสเทอร์สูงสุดถึง 89.1 และผลได้ของเอสเทอร์รวมเท่ากับ 78.1% นอกจากนี้ขนาดของกรดคาร์บอกซิลิกมีผลต่อผลได้เอสเทอร์และความเลือกจำเพาะอย่างมีนัยสำคัญ ทั้งนี้เนื่องจากความต้องการพลังงานในการทำปฏิกิริยาไม่เท่ากัน เอสบีเอ-15 ที่มีหมู่โพรพิลซัลโฟนิกถูกนำมาใช้สองครั้งเพื่อทดสอบการนำกลับมาใช้ใหม่ชี้ให้เห็นว่าเป็นตัวเร่งปฏิกิริยาที่ถูกล้างด้วยเฮกเซนสามารถนำกลับมาใช้ใหม่ได้แต่ให้ผลได้ลดลงในขณะที่ไม่มีผลต่อความเลือกจำเพาะอย่างมีนัยสำคัญ ทั้งนี้การเพิ่มความเป็นกรดให้แก่วัสดุจะทำให้ผลได้มีค่าสูงขึ้น

ภาควิชา.........เคมี.........   ลายมือชื่อนิสิต..
สาขาวิชา.........เคมี.........   ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก............................
ปีการศึกษา.......2554.........

5272429023: MAJOR CHEMISTRY

KEYWORDS: SBA-15 / SBA-15-PrSO_3H / NEOPENTYL GLYCOL / NPG / OCTANOIC ACID / ESTERIFICATION / LUBRICANTING OIL

PIYAWAT PAENGPHUA: PREPARATION OF POLYOL ESTERS USING ACIDIC HETEROGENEOUS CATALYSTS. THESIS ADVISOR: DUANGAMOL TUNGASMITA, Ph.D., 119 pp.

The sulfonic functionalized SBA-15, SBA-15-PrSO_3H, was prepared by hydrothermal method and post-grafting synthesis. The synthesized materials were characterized by X-ray powder diffraction, nitrogen sorption analysis and scanning electron microscopy. The synthesized catalyst was studied its performance comparing to several heterogeneous catalysts in the esterification of neopentyl glycol and octanoic acid which was firstly optimized the suitable condition using Amberlyst-15 as a catalyst. The synthesized material performed the best efficient catalyst which could reduce reaction time from 4 to 2 hours. Thus, the optimal condition performed at 80 ^{o}C for 2 hours with stirring speed 200 rpm using 3 wt. % of SBA-15-PrSO_3H based on total reaction weight in stainless steel batch reactor which gave high total ester yield as 74.1% and 76.9% of NPG dioctanoate ester selectivity in order to using the octanoic acid to neopentyl glycol mole ratio as 2. Moreover, the reaction mixtures exhibited highest NPG dioctanoate ester selectivity as 89.1% with 78.1% of total ester yield in case the octanoic acid to neopentyl glycol mole ratio increased to 4. Additionally, the esterification with difference molecular size of monocarboxylic acid and alcohol type significantly affected to the total ester yield and diester selectivity due to the difference requirement of energy. For reusability test, the SBA-15-PrSO_3H was used two times to examine its reusability. It was indicated that the hexane washed catalyst obtained the best performance in reusability experiment. Moreover, the catalyst regeneration could improve its reactivity.

Department:.........Chemistry.........
Field of Study:.......Chemistry.........
Academic Year: ....2011.............

Student's Signature: ....
Advisor's Signature: ....

ACKNOWLEDGEMENTS

The accomplishment of this thesis can be attributed to the extensive support and assistance from Dr. Duangamol Tungasmita, my thesis advisor. I would like to sincere gratitude to her for valuable advice and guidance in this research as well as extraordinary experiences throughout the work.

I would like to deeply thank Assistant Professor Warinthorn Chavasiri, Ph.D., Assistant Professor Preecha Phuwapraisirisan, Ph.D., and Suchada Butnark, Ph.D., the external examiner from PTT Research and Technology Institute for all of their kindness and useful advice in the research.

I would like to appreciatively thank PTT Research and Technology Institute and Center for Petroleum, Petrochemicals, and Advanced Materials for partial lab expense supporting. Moreover, I would like to thank Department of Chemistry, Faculty of Science, Chulalongkorn University for supporting a teacher assistant fund and the valuable knowledge and experience. Furthermore, I would like to thank the Science Achievement Scholarship of Thailand “Human Resource Development in Science project” grant for financial support. In addition, Thailand Japan Technology Transfer Project a loan supported by Japan Banks for International Cooperation (TJTTP-JBIC) for instrument support.

Many thanks go in particular to the members of Materials Chemistry and Catalysis Research Unit for their help and encouragement throughout the course of my research and study. Finally, I greatly thank to my family and all of my friends for their help and encouragement during my graduate study.

CONTENTS

CHAPTER **Page**

LIST OF TABLES

Table **Page**

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

Å	Angstrom
a.u.	Arbitrary unit
BET	Brunauer-Emmett-Teller
BJH	Barret, Joyner, and Halenda
^{o}C	Degree Celsius
CMC	critical micelle concentration
CSPTMS	2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane
GC	Gas chromatography
g	Gram (s)
hr	Hour (s)
MPTMS	(3-mercaptopropyl)trimethoxysilane
MS	Mass spectroscopy
μm	Micrometer (s)
ml	Milliliter (s)
min	Minute (s)
M	Molarity
nm	Nanometer (s)
%	Percentage
SEM	Scanning electron microscopy
TEOS	Tetraethyl orthosilicate
TOF	Turnover frequency
TON	Turnover number
XRD	X-ray diffraction

CHAPTER I

INTRODUCTION

1.1 Statement of problems

As a few decades, an environmental issue is established as the world's major problem which has to be concerned, whereas a rapid development of technology causes requiring extreme conditions to applying in many modern engines. Thus, to accomplish this problem, using environmental friendly chemicals is a challenging in a modern engine.

Polyolesters, the esterified polyhydric alcohol with carboxylic acid, serve as an important role in lubricant application. Since it provides many excellent properties such as high viscosity index, high flash point, low volatility and low pour point which can be applied to many applications by modified with respect to viscosity grade, temperature characteristic and pressure stability of the applications. Besides the mentioned excellent properties, these esters also obtain other marvelous properties especially their high thermal stability due to absence of ß-hydrogen on their molecules. Moreover, the esters are not outstanding only on their properties, but they also enhance the biodegradability which would promote more environmental cleanness.

Despite numerous advantages of polyolesters, these esters synthesis come up with many troubles especially the reaction catalysis which typically use acid homogenous catalysts such as sulfuric acid and *p*-toluene sulfonic acid. Although it accelerate high activity, but using these catalyst type is often concerned to be proposed for an industrial usage due to uneconomic problems such as corrosive equipment and separating problem. Nowadays, heterogeneous catalyst becomes a powerful material which many industries pay attention to using in their plant because it has many advantages. For example, it contained high reaction accelerating behavior which is probably similar to the homogeneous catalyst. Furthermore, heterogeneous catalyst might give a vast profit to the factory because of non-destructive instrument and its facile separation between catalyst and reaction medium. The facile separation not only advantage to the factory, it is also friendly to environment which is an essential topic for dealing with industry.

1.2 Literature reviews

1.2.1 Synthesis of polyolesters

1.2.1.1 Esterification

In 1997, Suwanwuttiwat [1] investigated esterification between poly hydric alcohols such as neopentyl glycol (NPG), trimethylol propane (TMP) and pentaerythritol (PE) and monobasic acids with amount of carbon atom as 7-8 in straight and branch structure such as n-heptanoic acid, n-octanoic acid and 2-ethyl-hexanol. All experiments were carried out at 130^{o}C for 3 hours in the presence of toluene. In addition, the reactions were optimized by varying amount of concentrated sulfuric acid at 0.5-1.0 % by weight of total reaction. The optimum condition was obtained at 0.5 % of catalyst amount which gave over all yields higher than 89 %. The resulted products were also characterized in physical and chemical properties which concluded that trimethylol propane ester performed good properties for used as refrigeration oil.

After that, in 1999 Panchoowong [2] studied synthesis of lubricating diester via esterfication of fatty acid such as lauric acid, myristic acid and stearic acid with dihydric alcohol (diols) such as 1,2-ethanediol and 1,2-propanediol by using concentrated sulfuric acid as catalyst. The result exhibited that the most synthetic reactions promoted waxes products except the esterified lauric acid with 1,2-propanediol product. In addition, the obtained laurate ester products were determined in physical and chemical properties which showed high flash point and excellent thermal stability and oxidative stability.

In 2008, The Chevron U.S.A. inc. [3,4], had owned patents involving polyol ester, including diester and triester synthesis, from olefin and various types of fatty acid. For diester synthesis, the method had begun with epoxidizing step of olefin by using peroxide species such as hydrogen peroxide, peroxyacetic acid and potassium permanganate to convert double bonds to epoxide ring. Secondly, the rings were opened by hydrolysis using acid or base catalyst which gave mainly diol products. Next, the obtained diols were esterified by coupling with fatty acid via esterification reaction. The reactions were catalyzed by acid homogeneous catalysts such as sulfuric acid, sulfonic acid and hydrochloric acid. On the other hand, the patent proposed triester by firstly reacted unsaturated fatty acid with alcohol to form ester species. Then, the unsaturated esters were epoxidized with the same method as diester to give epoxidester. After epoxidation, the epoxide rings were hydrolyzed to form dihydroxyesters which could be esterified in next step to obtain trimester as the final product. According to all mentioned reactions, they caused environmental problems together with uneconomical by working up processes.

Moreover, in 2008, Vahteristo [5] investigated the estimation of kinetic parameters in esterfication of NPG and propionic acid. The experiment utilized the Markov chain Monte Carlo (MCMC) method to analyze the reliability of the parameters estimation. The reactions were performed in glass batch reactor and used Dowex 50 WX 2 resin as catalyst to study the esterification of NPG with propionic acid and disproportionation of neopentyl glycol monoester. The catalyst was fixed at 0.29 wt% of total substrate, whereas temperature and time were varied at 100 - 150^{o}C and 0-27.5 hours, respectively. The results in esterification reaction exhibited that the experiment, performed at 135^{o}C for 1.5 hours, promoted highest diester selectivity and total ester yield as 22.6 % and 75.3 %, respectively. In another section, the result showed that higher temperature accelerated the disproportionation reaction.

1.2.1.2 Transesterification

Polyolesters are not only synthesized via esterification but they can be also synthesized by transesterification. In 2003, Yunus [6] studied trimethylol propane ester synthesis via transesterification. The substrates, palm kernel oil methyl ester and trimethylol propane were performed to transesterified using sodium methoxide as catalyst at 150 – 180^{o}C. In addition, the studies were also investigated vacuum pressure parameters which affect on the reactions. The results concluded that both temperature and vacuum pressure had effect on the reaction rate and reversibility. So, the optimum condition was carried out at 150^{o}C with reduced pressure at least 20 mbar which obtained high conversion of palm kernel oil trimester as 98%.

1.2.2 Catalysts in esterification

Since polyolesters can be synthesized via esterification, there are many researches had focused on the performance of catalyst in this kind of reaction. These reactions are probably facile reactions if they were catalyzed by acidic catalysts. Homogenous acidic catalyst such as sulfuric acid, *p*-toluene sulfonic acid, nitric acid, phosphorous oxide and stannous octanoate, serve as firstly used catalyst but it caused a number of trouble especially in difficulty separation. So, heterogeneous catalyst has gained more attention to apply in various kinds of reactions due to their numerous advantages such as easy separation and fewer side reactions. The heterogeneous catalysts consist of many types, for example, microporous material, mesoporous metarial, ion-exchange resin, clay and heteropolyacid supported silica.

There are various types of heterogeneous microporous catalyst such as ZSM-5 and β-zeolite which was investigated in this kind of reaction. In 2010, Viswanadham [7] studied effect of nanosized ZSM-5 on cyclohexanol esterification with acetic acid and compared with commercial ZSM-5 and β-zeolite. The reactions were performed at 100^{o}C and varied time 0.5 – 10 hours. The experimental results appeared that nanosized ZSM-5 could convert amount of substrates at 69 % which was higher than commercial ZSM-5. However, this reaction ranked β-zeolite as the best catalyst which gave high substrate conversion as 73 %.

Besides microporous catalyst, the mesoporous silica, such as MCM-41, was also gained attention to study in thisthe reaction. For example, in 2007, Pandurangan [8] studied the catalytic activity of Al-MCM-41 on gas phase esterification of butyric acid and pentanol. The calalysts were synthesized by varied amount of Aluminium in the MCM-41 structure in term of silica to alumina ration as 25, 50, 75 and 100. The obtained catalysts were tested their activity in the reaction and compared with commercial ZSM-5 and β-zeolite. As a result, the optimum condition which hit highest conversion at 96 % was using catalyst with silica to alumina ratio at 100 and reaction temperature at 250^{o}C.

In addition, the ion-exchange resin was obtained as a low cost catalyst which was also employed in esterification and numerous reactions. In 2007, Ali et al.

[9] stimulated the kinetic of propionic acid esterification with propanol by comparison three types of resin catalysts, Dowex 50Wx8-400, Amberlite IR-120 and Amberlyst-15. The reactions were studied in various parameters, for instance, temperature, catalyst loading and acid to alcohol molar ratio as 130–160^{o}C, 10-60 g dry catalyst/L and 0.25-4, respectively. The experiment used various model to estimate the activation energy such as the pseudo-homogeneous (P-H) model, the Eley–Rideal (E–R) model, the Langmuir–Hinshelwood (L–H) model, the modified Eley–Rideal (M-E–R) model and the modified Langmuir–Hinshelwood (M-L–H) model. The result showed that the activation energy from M-E-R model estimation, which suitable for estimating in esterification, is 67.3 kJ/mol. The optimal condition performed at 160^{o}C, 60 g of dry Dowex 50Wx8-400 catalyst with acid to alcohol molar ratio as 4.

In another type of heterogeneous catalyst was heteropoly acid which was mostly supported on various materials, for example, amorphous silica or clay. In 2010, Bhorodwaj et al. [10] investigated heteropoly acid (dodecatungstophosphoric) supported montmorillonite activity on esterification between acetic acid and sec-butanol. The studies varied modification of acid amount on supporter as 5 – 30 %. Then, the modified catalysts were test in esterification with varied time 15 minute to 4 hours to optimize the reaction. The experiment exhibited the optimal condition which gave the highest conversion at 80 %, employed at 98^{o}C by using least time at 15 min under this condition.

1.3 Objective

To investigate the optimum conditions and heterogeneous catalyst for esterification of polyols and monocarboxylic acid.

1.4 Scopes of work

1. Investigate the optimum condition of esterification between neopentylglycol (NPG) and octanoic acid which were depended on effect of reaction time, reaction temperature, catalyst to total substrates weight ratio, stirring speed and molar ratio of substrates by using Amberlyst-15 as catalyst.

2. Study on catalytic activity of various catalysts.
3. Synthesize the chosen catalyst which gave the highest activity.
4. Characterize the prepared catalyst.
5. Adjust the optimum condition which was catalyzed by synthesized catalyst from the previous optimal condition.
6. Focus on the optimum condition for esterification of lauric acid and neopentyl glycol by using Amberlyst-15 and prepared catalyst.
7. Test the synthesized catalyst activity on esterification of octanoic acid with trimethylol propane (TMP).
8. Study on reusability and activity of reused and regenerated catalysts.

CHAPTER II

THEORY

2.1 Lubricating oil [11, 12]

There are two essential sources from which the base lubricant fluids are obtained. There are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties suitable for lubricant purposes.

A lubricant is used to reduce the coefficient of friction between the rubbing surfaces in machinery, thereby reducing energy losses. The lubricant also prevents direct contact of the rubbing surface since under proper condition of lubrication a film of the lubricant is maintained between these surfaces. This prevents failure due to seizure and also reduces wear. The friction heat generated by the rubbing surfaces is removed by the lubricant acting as a coolant or heat transfer medium. In internal combustion engines the lubricant also seals the piston and cylinder wall at the compression rings do that the high pressure gases in the combustion chamber will not leak past the rings and cause power losses. Briefly, the lubricant reduces energy losses from friction, reduces wear, serves as a coolant and may also seal. Most lubricating oils are derived from petroleum; however, some synthetic lubricants are also important in use.

Essential properties of the lubricating oil are viscosity, viscosity temperature relation, viscosity-pressure relation, and oiliness. The changes in these properties are minimized when the oil dose not undergo chemical change during use. Therefore, characteristics such as the following are important: stability toward oxidation and other chemical change, resistance to decomposition when exposed to elevated temperatures, and ability to resist emulsification. For various applications special properties are important such as detergency for severe operating conditions in internal combustion engines or extreme pressure load-carrying properties for hypoid gear lubrication.

2.1.1. The Basic Function of Lubricant [12, 13]

2.1.1.1 The reduction of friction Friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of lubricating oil is its viscosity. It forms lubricating films under both thick and thin films conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils to reduce the rate of oil consumption. It go determines that machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equipment, satisfactory results are obtained only with the use of an oil of proper viscosity under the operated condition.

The basic concept of viscosity is shown in Figure 2.1 where a plate is being drawn at uniform speed over a film of oil. The oil adheres to both the moving surface and the stationary surface. Contacting oil with the moving surface travel at the same velocity (U) as that on surface, while oil at contact with the stationary surface is at zero velocity.

In between, the oil film may be visualized as made up of many longer, each being drawn by the layer above it is friction of velocity “U” that is proportional to its distance above the stationary plate (Figure 2.1 : lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the results of viscosity, the force is proportional to viscosity.

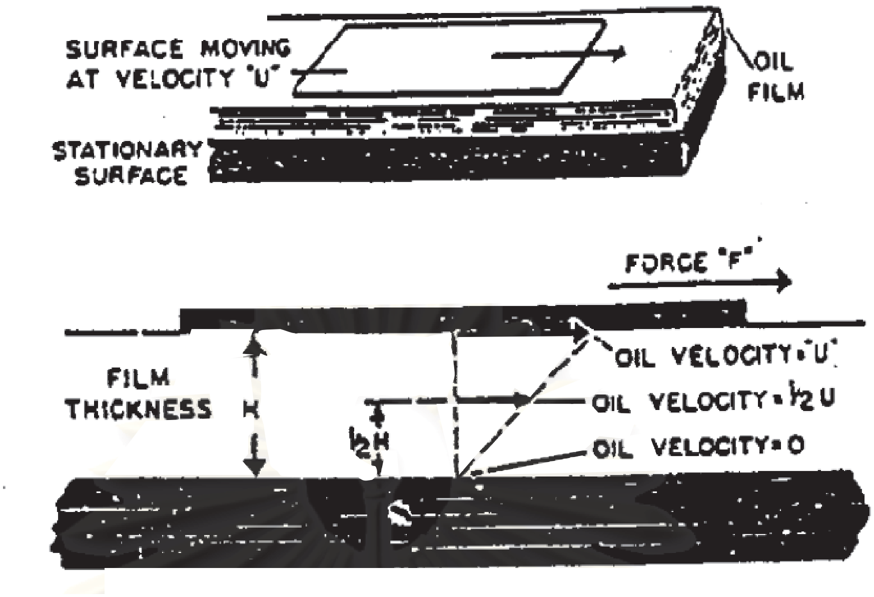


Figure 2.1 Concept of dynamic viscosity [13]

2.1.1.2 Heat removal Another important function of a lubricant is to act as coolant, removing heat generation either by friction or other sources such as via combustion process or transfer by contacting with substances at higher temperatures. In performing this function, it is important that the lubricant remain in a relatively unchanged condition. Change in thermal and oxidation stability which affect its ability to reach the areas involved will materially decreases its efficiency in this respect.

2.1.1.3 Containment of contaminants The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic combustion products, particulate matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

2.1.2 Lubricating oil classification [14]

Lubricating oils are classified into three categories as following:

- Animal fat / vegetable oils
- Mineral oils
- Synthetic lubricants

2.1.2.1 Animal fat/vegetable oil

The animal fat and/or vegetable oils are not utilized for industrial bearing applications, due to acid formation after a short period of use. The acid is detrimental to the bearing surface performance. The natural fat and oils are generally reserved for cooking purposes.

2.1.2.2 Mineral oils

The majority of lubricating oil using these days is derived from refined crude petroleum. The refining method is either by the solvent refining process or by the hydrotreating process. Both processes consist of a number of stages designed to remove undesired components, such as aromatic hydrocarbons, acid components, organic sulfur compounds and wax. They were improved desirable properties, including viscosity index, pour point and stability. After refining, the oils are finished with base stock oil to which additives are blended to enhance the lubricating performance. For example, molybdenum dialkylphosphorodithioates are added into the mineral oil to reduce oxidation property and foaming formation.

2.1.2.3 Synthetic lubricants

Synthetic lubricants are man-made chemicals designed to work under conditions where normal petroleum base oils would find limitations. They possess well-defined functional groups to serve specific applications. They are usually more consistent and uniform in structure than petroleum base stocks. For some types, the use of synthetic lubes has the following features.

- ***Advantages***
  - No waxes are present at very low temperatures.
  - Petroleum-based oils have a temperature application limit of approximately 320 °C, whereas synthetic lubes can also be used at much higher temperatures.

- At higher temperatures, sludging and acid buildup are less apparent due to their improved oxidation stability.
- Synthetics have a more stable viscosity index (VI) and can be relied upon to be a more stable lubricant over different temperature value.

- ***Disadvantages***
  - Synthetics are much more expensive to purchase. Prices range from five times to mineral base lubricant cost.
  - Many synthetics are not compatible with certain sealing materials and may require replacement of seal, hoses, and paint.

Table 2.1 Physical properties comparisons of important lubricants [14]

Property	Mineral Oil	Polyalphaolefin	Diester	Polyol ester
Viscosity characteristics (temperature)	Moderate	Good	Excellence	Excellence
V.I.	Moderate	Very good	Good	Very good
Low temperature pour point	Good	Very good	Very good	Good
Oxidation stability	Moderate	Very good	Good	Very good
Volatility	Moderate	Good	Very good	Very good
Lubricating properties	Good	Good	Very good	Very good
Mineral oil compatibility	-	Excellence	Good	Poor
Cost	Low	Medium	Medium	Medium

The primary performance advantage of synthetic lubricants is the extended service life capability and handling a wider range of application temperatures. Their outstanding flow characteristics at low temperature and their stability at high temperatures mark the preferred use of these lubricants. Figure 2.2 compares the operating temperature limits of mineral oil and synthetic lubricants.

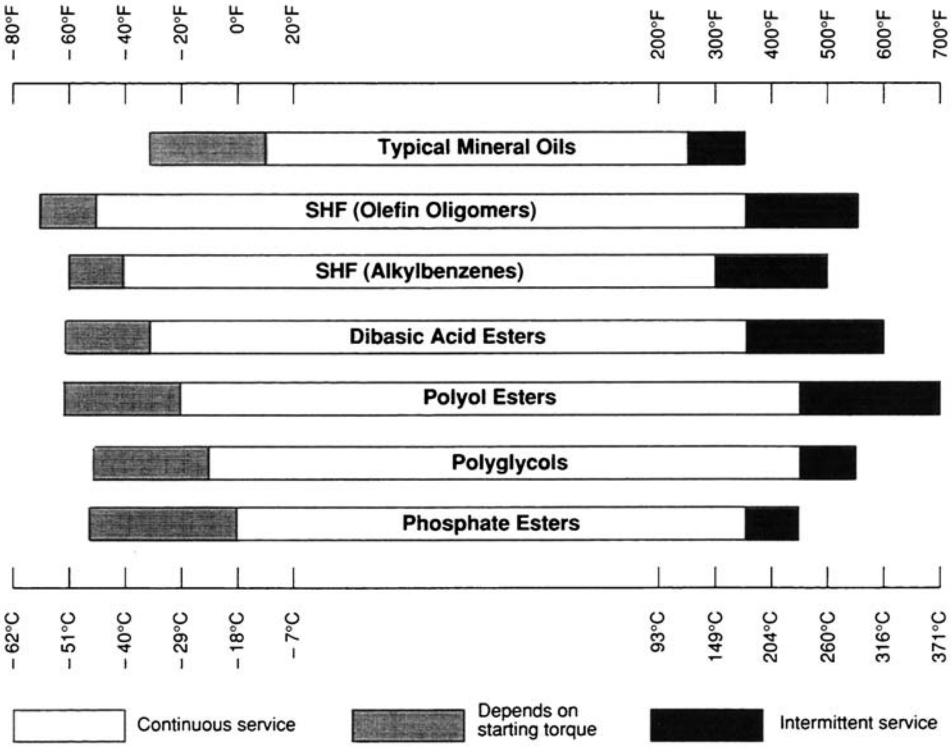


Figure 2.2 Comparative temperature limits of mineral oil and synthetic lubricants. [15]

2.2 Synthetic ester lubricants [15]

Considerable attention has been focused on synthetic lubricants since the introduction into the retail market of synthetic-based or synthesized automotive engine oils. The use of synthetic-based lubricants in aviation and industrial applications extends back over many years. Past interests in synthetic lubricants were due to their ability to resist burning to a greater degree than mineral oils and to provide equipment protection advantages under extremes of operating conditions. These conditions included very low or very high temperatures. More recent interest still entails taking advantage of these performance capabilities, but researchers also want to see how synthetic lubricants may be able to minimize direct or indirect effect on the environment.

Organic esters have been an important class of synthesized base fluids longer than any of the other materials now in use. Their use dates back to World War II, when German chemists used them in mineral oil blends to improve low temperature properties and to supplement scarce supplies of mineral oils. They were first used as aircraft jet engine lubricants in the 1950s and are now used as the base fluid for essentially all aircraft jet engine lubricants. They are also used as the base fluid in many wide temperature range aircraft greases.

Organic esters are oxygen-containing compounds that result from the reaction of an alcohol with an organic acid. The two commonly use classes of organic esters are dibasic acid esters and polyol esters.

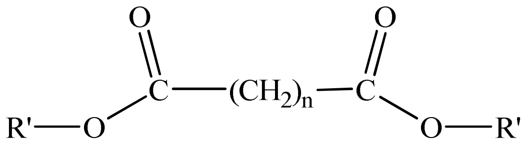
2.2.1 Classification of organic ester [15]

2.2.1.1 Dibasic acid ester

The various diesters differ in their acid and alcohol components. For all diesters, the acid and alcohol are reacted either thermally or in the presence of a catalyst in an esterification reactor. After the ester has been formed, the water by-product is distilled off and unreacted dibasic acid is neutralized and removed by filtration. The base stock is then suitable for final product blending. As shown in Figure 5.6, the backbone of the structure is formed by the acid, with the alcohol radicals joined to its ends.

Dibasic acid esters exhibit good metal-wetting ability, high film strength, high oxidation and thermal stability, and good shear stability. Diesters will dissolve system deposits and keep metal surfaces clean. This property could be a disadvantage in dirty systems. The hydrolytic stability and antirust properties of diesters are fair. In changing over to diesters from another family of products, care should be taken to assure a thorough cleaning and flushing of the system prior to their installation. Also the compatibility with elastomers and paints used in the system should be reviewed. Diesters are compatible with mineral oils.

Dibasic acid esters have been used as the base fluid for older type I jet engine oils. Generally the use of these oils has been restricted mainly to older military jet engines, and some very limited use in jet engines for industrial service. Diesters are used as the base oils, or components of the base oil, for automotive engine oils and air compressor lubricants. They are also used as the base fluid in some aircraft greases. These products were developed originally for use as jet engine oils, but now have been replaced, to a large extent, by polyol esters.



n = 4 – 10, R' = C7-C10 linear or branched alkyl groups

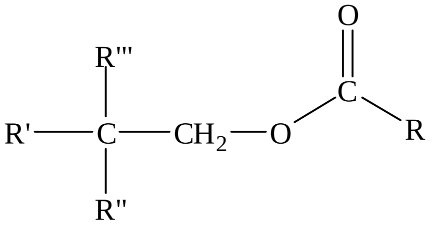
Figure 2.3 Chemical structure of dibasic acid ester.

2.2.1.2 Polyol Esters

Polyol esters are made by reacting a polyhydric alcohol with a monobasic acid to give the desired ester. In contrast to diesters, as shown in Figure 2.4, in the polyol esters, the polyol forms the backbone of the structure with the acid radical attached to it. As with diesters, the physical properties of polyol esters can be varied by using different polyps or acids. Trimethylol propane and pentaerithritol are two of the polyols that are commonly used. Usually, the acids are obtained from animal or vegetable oils.

Polyol esters have better high temperature stability than diesters. Their low temperature properties and hydrolytic stability are about the same, but their VIs may be lower. Their volatility is equal or lower. The polyol esters also may have more effect on paints and cause more swelling of elastomers.

The primary use of polyol diesters is in type II jet engine oils. They also are used in air compressor oils and as components in some synthesized hydrocarbon blends. More recently, polyol esters have become widely used as refrigeration lubricants, to take advantage of their miscibility with hydrofluorocarbon (HFC) refrigerants. Polyol esters are also the lubricant of choice in refrigeration systems where nonchlorine HFC refrigerants such as R134a are used. They are also used in environmentally sensitive products such as hydraulic fluids and other lubricants for which biodegradable structures are required.



PE; pentaerythritol; R' = R'' =R''' = CH_2OCOR

TMP; Trimethyol propane;

R' = R''' = CH_2OCOR, R'' = Ethyl

NPG; Neopentyl glycol;

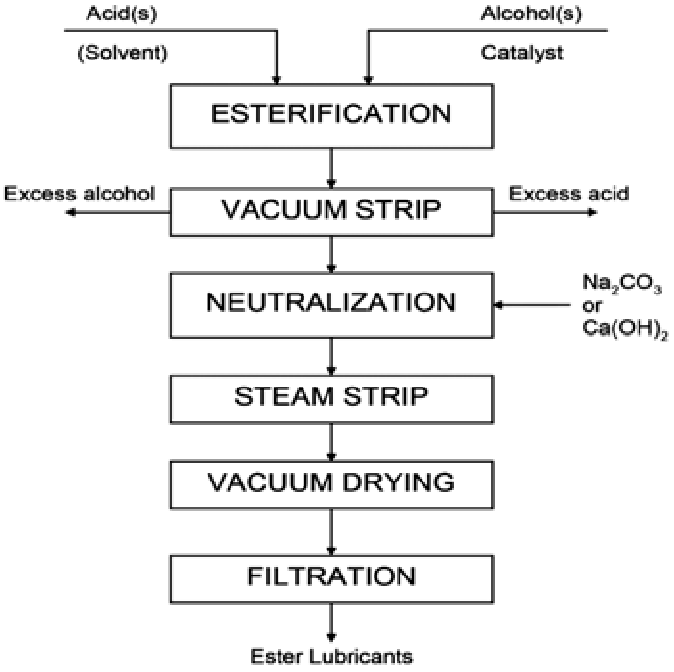
R' = CH_2OCOR, R'' = R''' = Methyl

R = C4-C17 linear or branched alkyl groups

Figure 2.4 Chemical structure of polyol ester.

Typical polyol esters: acid radicals R typically used contain 6–10 carbons, with those containing an odd number of carbon atoms being generally favored.

2.2.2 Manufacture of ester lubricants [16]



The manufacturing process of esters consists of three distinct stages; esterification, neutralization and filtration

Figure 2.5 Synthesis of ester lubricants.

A schematic manufacturing process is given in Figure 2.5. The production of ester is based on the following reaction: acid + alcohol → ester + water.

For diesters, the reaction can be driven to a high level of completion by using excess alcohol to remove the water of reaction. This usually takes several hours, during which the reaction is monitored by taking samples periodically for acid number determination. The use of an azeotroping agent such as xylene or toluene (to aid water removal) is optional. The acid and alcohol can be reacted directly or in the presence of a catalyst. Possible catalysts include: sulfuric acid, paratoluenesulfonic acid, tetraalkyl titanate, anhydrous sodium sulfate, phosphorous oxides and stannous octanoate.

After the ester has been formed, unreacted acid is neutralized by means of sodium carbonate or calcium hydroxide and removed by filtration. Typical reaction conditions for titanium catalysts are 230ºC in vacuum; acid catalysts require milder conditions, since side reactions (e.g., color formation) become prominent at higher temperatures. A significant amount of alcohol vaporizes along with the water and must be recovered. This is accomplished by condensing the reactor vapors and decanting the resulting two-phase liquid mixture. The alcohol is then refluxed and return to the reactor.

Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NPG), trimethylol propane (TMP), pentaerythritol (PE), or dipentaerythritol (diPE) with a monobasic acid to give a desired ester.

Polyol esters can also be made via a transesterification (alcoholysis) route. Here, monoesters (usually methyl) are transesterified with a neopentyl alcohol in the presence of a catalyst. Catalysts specifically designed to help the transesterification process are now available.

Variations in raw materials dominate a major influence on the final physical properties of the ester. For example, the monofunctional alcohols used to make monoesters, diesters, phthalates, trimellitates and pyromellitates are often mixtures of varying chain lengths, degrees of branching of isomers for example:

Isotridecanol, which is a mixture of branched carbon chain lengths C_{11} to C_{14}, rich in C_{13} alkyl caains.

Isodecanol, which is a mixture of branched carbon chain lengths C_9 to C_{11}, rich in C_{10} alkyl caains.

The degree of branching, the chain length, and the ratio of isomers are highly dependent on the feedstock and catalyst used to make the alcohol. Batches of the same alcohol purchased from different companies or from different plants of same company can vary significantly. Therefore, the typical properties of a given ester may differ from supplier to supplier. Even if exactly the same raw materials are used, the processing specification is a major impact on the physical properties and the performance of ester. The following properties of the ester should be tightly controlled: residual unreacted acid, hydroxyl number (degree of esterification), residual unreacted alcohol, cross-contamination of other esters made on plant, residual catalyst and residual neutralizing agents

Guidelines for the recommended levels of these ester properties are listed in Table 2.2. These are only guidelines and may need to be adjusted depending on the application of use.

Table 2.2 The effect of specification on the performance of an ester lubricant.

Property	Effects	Typical value
Total acid number	Hydrolytic stability Thermal stability Wear	< 0.1 mg KOH/g
Hydroxyl number	Hydrolytic stability Deposit formation Foaming Volatility Flash point	< 4 mg KOH/g
Iodine number	Thermal stability Color stability Deposit formation Low temperature flow	As low as possible
Water content	Hydrolytic stability	< 0.1 % w/w
Process residuals (e.g. catalyst, neutralizing agents, azeotrope, etc.)	Thermal stability Deposit formation Hydrolytic stability Foaming	< 5 ppm metals
Purity	All of the above	

2.2.3 Principal properties of ester lubricants [17]

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of long-chain hydrocarbons. Synthetic ester lubricants, on the other hand, are prepared from raw materials having uniform molecular structures. This uniformity yields well-defined properties that can be tailored for specific applications.

Many lubricant requirements are translated into specific properties of an oil measurable by conventional laboratory tests, e.g. viscosity, evaporation, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricant and many of these can be measured satisfactorily only by elaborate and expensive apparatus specially developed to simulate performance. A wide variety of raw materials can be used for the preparation of ester-type base fluids and this affects a number of lubricant properties including: viscosity, flow properties, lubricity, thermal stability, hydrolytic stability, solvency, and biodegradability.

Viscosity*, *ASTM D445 [18]

Viscosity is one of the most important for characterization of lubricants and their flow and transport properties. The viscosity of a fluid is a measurement of its internal resistance to flow of cohesion between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extent of the viscosity change depends on the crude source of the oil and molecular weight of the constituent components. The instrument used to determine the viscosity of oil is called the viscometer. Kinematic viscosity is the more common and measured by timing the flow of a fixed amount of oil through a capillary tube under gravitational force at a standard temperature. Test temperatures are usually at 40 and 100^{o}C for centistokes units

The viscosity of an ester lubricant can be altered by:

- increasing the molecular weight of the molecule by:
  – increasing the carbon chain length of the acid
  – increasing the carbon chain length of the alcohol
  – increasing the number of ester groups
- increasing the size or degree of branching
- including cyclic groups in the molecular backbone

- maximising dipolar interactions

One disadvantage of very long-chain molecules is their tendency to shear into smaller fragments under stress.

Viscosity index (VI), ASTM D2270 [19]

The relationship of viscosity to temperature of fluid, high viscosity index fluids tends to display less change in viscosity with temperature than low viscosity index fluids. The viscosity index of lubricant is calculated from viscosities determined at low temperatures at 40^{o}C and 100^{o}C

The viscosity index (VI) of an ester lubricant can be increased by:

- increasing the acid chain length
- increasing the alcohol chain length
- increasing the linearity of the molecule
- not using cyclic groups in the backbone, which lowers the VI even more than aliphatic branches
- by molecular configuration-viscosity indices of polyol esters tend to be lower than their diester analogues, from more compact configurations of the polyol molecules

The pour point, ASTM D97 [20]

The pour point is the lowest temperature expressed as a multiple of 3^{o}C at which the test fluid is observed to flow when it is cooled and examined under defined conditions.

The pour point of an ester lubricant can be decreased by:

- increasing branching
- positioning of the branch-branching in the centre of the molecule gives better pour points than branches near to the chain ends
- decreasing the acid chain length
- decreasing the internal symmetry of the molecule

From the above lists, there is a natural trade-off between viscosity index and pour point, e.g. by increasing the linearity of the ester, the viscosity index improves but the pour point increases. Esters made from mixtures of normal and branched acids with the same carbon number have viscosity indices between those of the normal and branched acid esters. But their pour points are lower than those esters formed separately from either branched or normal acids.

Lubricity; ester groups are polar and therefore affect the efficiency of anti-wear additives. When a base fluid is used which is too polar, the anti-wear additives will be adsorbed onto, and cover, the metal surfaces, giving higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives. Esters are classified in terms of polarity or non-polarity by the Van der Waal formula, Equation (2.1):

$$\text{Non-polarity index} = \frac{[\text{Total number of C atoms} \times \text{Molecular weight}]}{[\text{Number of carboxylic group} \times 100]} \qquad (2.1)$$

Generally, the higher the non-polarity index, the lower the affinity for the metal surface. Using the above formula it can be seen that as a general rule, increasing molecular weight improves overall lubricity. Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids/alcohols have lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/alcohols.

Thermal stability; the ester linkage is exceptionally stable; bond energy determinations predict that it is more thermally stable than the C−C bond. The thermal stability advantages of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. The absence of hydrogen atoms on the β-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of the β-hydrogen atom enables a low-energy decomposition mechanism to operate via a six-membered cyclic intermediate producing acids and 1-alkenes, Figure 2.6 (a). When β-hydrogen atoms are replaced by alkyl groups, this mechanism cannot operate and decomposition occurs by a free radical mechanism. This type of decomposition requires more energy and can occur only at higher temperatures, as in Figure 2.6 (b).

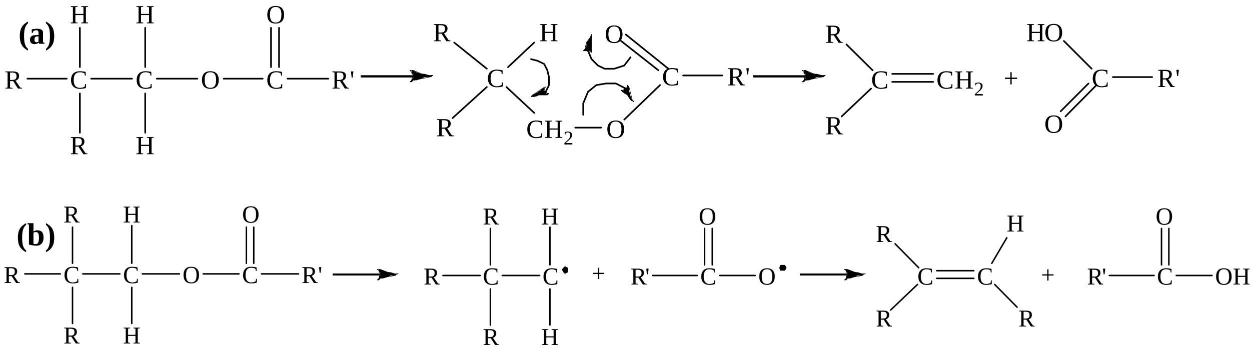


Figure 2.6 Thermal decomposition of (a) esters with β-hydrogens (e.g. dibasic acid esters) and (b) esters without β-hydrogens (e.g. polyol esters).

Primarily, the oxidative and thermal stabilities of polyol esters are dependent on:

- the absence of hydrogens on β-carbons, as stated above
- the number and type of hydrogens present in decreasing order of stability,

$$-CH_2- > -CH- > -\overset{|}{\underset{|}{C}}-$$

Thus, in general, linear acid esters are more stable than branched, and short-chain acids are more stable than long-chain acids,

- The stability of the alcohol used, which decreased in the following order of stability, PE > diPE > TMP > NPG.

One exception to the rule that branched acid esters give poorer stability than linear acids is the branched C9 acid 3,5,5-trimethylhexanoic acid. The weak tertiary hydrogen is sterically hindered and is more stable than would normally be expected. The structure has fewer secondary hydrogens than the linear form and is hence more stable. Esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight increases flash points.

Hydrolytic stability; the hydrolytic stability of esters depends on two main features:

- processing parameters
- molecular geometry

If the final processing parameters of esters are not tightly controlled, they dominate a major effect on the hydrolytic stability of the esters, such as the following:

- their acid value – which must be <0.05 mg KOH/g
- the degree of esterification, >98%
- the catalyst used during esterification and the level remaining in the ester after processing, as a low ash level

molecular geometry effects will assert themselves. Molecular geometry affects hydrolytic stability in several ways. By sterically hindering the acid portion of the molecule, because hindrance on the alcohol portion has relatively little effect, hydrolysis can be slowed down. For this purpose, geminal di- branched acids such as neoheptanoic acids have been used. However, with these feedstocks there are penalties, namely very long reaction times to achieve complete esterification and also poor pour points. The length of the acid chain is also very important, for acids shorter than pentanoic tend not to be used owing to their corrosion. The hydrolytic stability of neopolyol esters can generally be regarded as superior to that of dibasic esters.

Solvency; this can be divided into compatibility with additives and other lubricants, and also elastomer compatibility.

- *Compatibility with additives and other lubricants:* esters are generally fully compatible with mineral oils, which gives them three major advantages. First, there are no contamination problems and therefore esters can be used in machinery that previously used mineral oil. In addition, they can be blended with mineral oil (semi-synthetics) to boost their performance. Second, most additive technology is based on mineral oil experience and this technology is usually directly applicable to esters. Third, esters can be blended with other synthetics such as polyalphaolefins, PAOs, giving them great flexibility, whilst blending with other oils gives unrivalled opportunities to balance the cost of a lubricant blend against its performance.
- *Elastomer compatibility:* elastomers contacting liquid lubricants undergo an interaction with liquid diffusing through the polymer network. There are

two possible kinds of interaction, chemical (rare) and physical. During physical interactions two different, and opposing, processes occur:

1) extraction of soluble components out of the elastomer, causing shrinkage
2) adsorption of the lubricant by the elastomer, causing swelling. The degree of swelling of elastomeric materials depends on:
    - the size of the lubricant-the larger the lubricant, the smaller the degree of swelling
    - the molecular dynamics of the lubricant-linear lubricants diffuse into elastomers quicker than branched or cyclic lubricants
    - the closeness of the solubility parameters of the lubricant and the elastomer the ‘like-dissolves-like’ rule is followed
    - the polarity of the lubricant – it is known that some elastomers are sensitive to polar ester lubricants. The non-polarity index can be used to model elastomeric seal swelling trends for specific ester types.

Several polar esters are well-known industrial plasticisers. Non-polar base stocks, such as PAOs, have a tendency to shrink and harden elastomers. By carefully balancing these compounds with esters, lubricants with neutral physical behaviour towards elastomeric materials can be formulated. Table 2.3 shows the compatibility of elastomers and plastics with ester lubricants.

Table 2.3 Guidelines on the compatibility of elastomers and plastics with esters.

Compatible	Not compatible
Viton	PVC
Teflon	Polystyrene and styrene (ABS)
Nylon	SBR Rubber
High nitrile (>33%)	Low nitrile (<33%)
Fluorosilicone	Neoprene
Polysulfide	Ethylene propylene copolymers, natural rubber, BUNA-s

Environmental aspects; increasing environmental awareness has raised water pollution to a major issue. The environment can become polluted in many ways, for example, oils and oil-containing effluents in water can have devastating consequences on fish stocks and other water fauna.

Ecotoxicity; Germany classifies materials according to their potential to pollute water, or 'Wassergefährdungsklasse' (WGK) with substances given a ranking of between 0 and 3, where:

WGK 0 Not water endangering
WGK 1 Slightly water endangering
WGK 2 Water endangering
WGK 3 Highly water endangering

The esters generally having the ranking given below showing that esters have a low environmental impact.

Polyols, polyoleates, C36 dimer esters, diesters	WGK 0
Phthalates and trimellitates	WGK 0–2

Biodegradability; the general biochemistry of microbial attack on esters is well known and has been thoroughly reviewed. The main steps of ester hydrolysis, β-oxidation of long-chain hydrocarbons and oxygenase attack on aromatic nuclei have been extensively investigated. The main structural features which slow or reduce microbial breakdown are the following:

- the position and degree of branching, which reduces β-oxidation
- the degree to which ester hydrolysis is inhibited
- the degree of saturation in the molecule
- increasing of the ester molecular weight.

Table 2.4 Overview of physicochemical properties of ester lubricants.

	Diesters	Phthalates	Trimellitates	Polyols	Polyoleates
Viscosity at 40°C	6-46	29-84	47-366	14-35	8-95
Viscosity at 100°C	2-8	4-9	7-22	3-6	10-15
Viscosity index	90-170	40-90	60-120	120-130	130-180
Pour point (°C)	-70 to -40	-50 to -30	-55 to -25	-60 to -9	-40 to -5
Flash points	200/260	200/270	270/300	250/310	220/380
Thermal stability	Good	Very good	Very good	Excellent	Fair
Percentage biodegradable	75-100	46-88	0-69	90-100	80-100
Costs (PAO =1)	0.9-2.5	0.5-1.0	1.5-2.0	2.0-2.5	0.6-1.5

2.3 Catalysis

Catalysis is a way of accelerating the rate of a chemical reaction by means of contacting the reactants with a substance called a catalyst, which itself is not consumed by the overall reaction. More generally, one may at times call anything that accelerates a process, "catalyst". A catalyst provides an alternative route to products, the catalytic route being subject to lower activation energy (E_a) than in the non-catalyzed reaction. A lowered activation energy increases the reaction rate. Catalysts generally change in the course of a reaction but are regenerated. The energy profile with and without catalyst were shown in Figure 2.7.

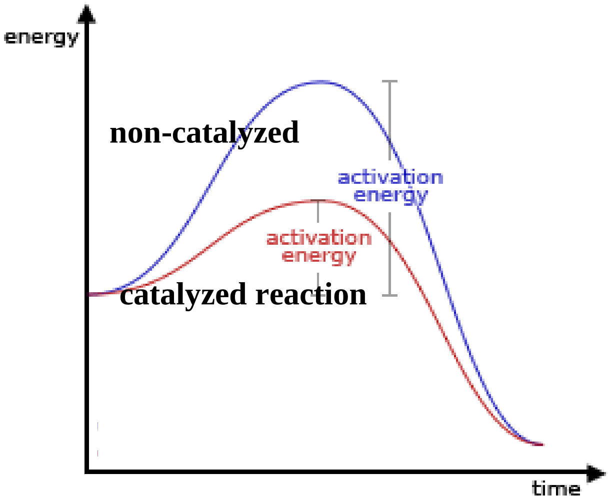


Figure 2.7 The potential energy profile of the reaction with and without catalyst

Catalysts generally react with one or more reactants to form an intermediate that subsequently give the final reaction product, in the process regenerating the catalyst. The following is a typical reaction scheme 2.1, where C represents the catalyst, A and B are reactants, and D is the product of the reaction of A and B:

$$A + C \rightarrow AC \qquad (1)$$

$$B + AC \rightarrow ABC \qquad (2)$$

$$ABC \rightarrow CD \qquad (3)$$

$$CD \rightarrow C + D \qquad (4)$$

Scheme 2.1 Typical reaction

Although the catalyst (C) is consumed by reaction (1), it is subsequently produced by reaction 4, so for the overall reaction:

$$A + B \rightarrow D$$

Industrial catalysts comprise wide variety of materials that was manufactured by a variety of methods. Many catalysts or porous structure were studied. The commercially useful catalyst particle size is determined by the process in which to be used, fixed beds and fluidized beds. In fluidized beds reactors, usually present in the catalyst powder supplied. The particles present generally range from about 20-300 μm in diameter. For fixed beds particles generally range from about 0.0625-0.5 inches in diameter. In general, 60% of commercially produced chemical products involve catalyst at some stage in the process of their manufacture [21].

2.4 Types of catalysts

Catalysts can be divided into two main types, heterogeneous and homogeneous catalysts. Biocatalyst is often seen as a separate group. In nature enzymes are catalyst in metabolic pathway whereas in biocatalysts enzymes are used as catalyst in organic chemistry. Heterogeneous catalyst is present in different phases from the reactants whereas homogeneous catalyst is in the same phase.

2.4.1 Homogeneous catalysts

Homogeneous catalysts are in the same phase as the reactants. The catalyst is a molecule which facilitates the reaction. The catalyst initiates reaction with one or more reactants to form intermediate and in some cases one or more products. Subsequent steps lead to the formation of remaining products and to the regeneration of the catalyst. Typically, everything will be presence as gas or contained in a single liquid phase. In addition, the catalysis of organic reactions by metal complexes in solution has grown rapidly in both scientific and industrial importance.

2.4.2 Heterogeneous catalysts

Heterogeneous catalyst is presented in different phases from the reactants e.g. a solid catalyst in a liquid reaction mixture. A simple model heterogeneous catalysis involves the catalyst providing a surface on which the reactants temporarily become adsorbed. Bonds in the reactants become weakened sufficiently for new bonds to be created. The bonds between the products and the catalyst are weaker, so the products are released. The mechanism of heterogeneous catalysis comprises five steps between compounds adsorbed on the surface of solid catalyst [22].

(1) Diffusion of the reacting substances over the catalyst particle.
(2) Adsorption of the reacting substances on the catalyst.
(3) Interaction of the reacting substances on the surface of catalyst.
(4) Desorption of the reaction products from the catalyst particle.
(5) Diffusion of the reaction products into the surrounding medium.

Furthermore, catalyst particles have internal pores that are accessible to the reactant molecules, so that diffusion proceeds in two steps, external and internal surface.

2.5 Properties of industrial catalysts

In general, the suitable catalysts for industrial processes are considered mainly on the three properties [23]:

a) Activity is a measure of how fast one or more reactions proceed which can be defined in terms of kinetics. A high activity catalyst will be given high productivity when the less amount of the catalyst is utilized or the reaction is performed in mild operating condition, particularly temperature, which enhances selectivity and stability if the thermodynamic is more favorable. It is appropriate to measure reaction rates in the temperature that will be occurred in the reactor.

b) Selectivity of a reaction is the fraction of the starting material that is converted to the expected product. High selectivity catalyst produces high yield of a desired product, whereas undesirable competitive and consecutive reactions are suppressed. This means that the texture of the catalyst (in particular pore size and pore volume) should be improved toward reducing limitation by internal diffusion, which in case of consecutive reactions rapidly reduces selectivity.

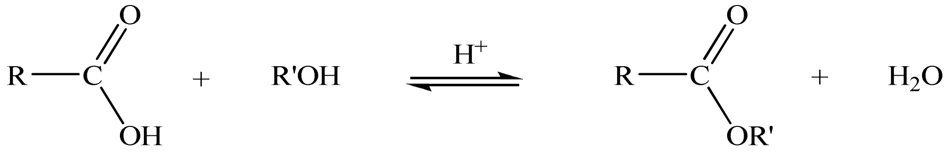
c) Stability of a catalyst determines its lifetime in industrial processes. Catalyst stability is influenced by various factors such as decomposition, coking and poisoning. Catalyst deactivation can be followed by measuring activity or selectivity as a function of time. Deactivated catalysts can often be regenerated before they ultimately have to be replaced. The catalyst lifetime is a crucial importance for the economics of process.

Nowadays, the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones. For various reasons, the target quantities should be given the following order of priority:

Selectivity > Stability > Activity

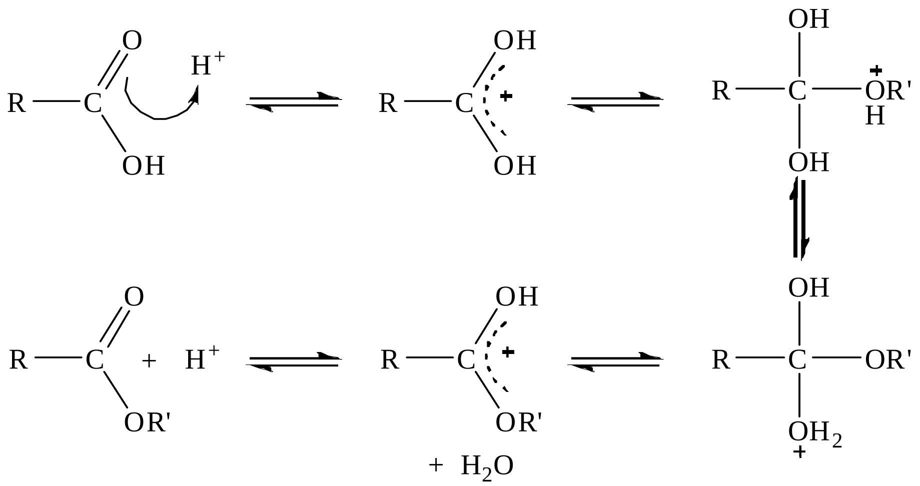
2.6 Acid catalyst in esterification [24]

The most usual method for the preparation of esters is the reaction of carboxylic acid and alcohol with elimination of water. Esterification is a reversible reaction, but is driven to completion by using of excess alcohol and removal of water as it forms by azeotroping agent, e.g. toluene.



The uncatalysed reaction is usually too slow to be useful. The acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reactor. Possible catalysts include sulfuric, *p*-toluene sulfonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulfate, phosphorous oxides and stannous octanoate.

- Mechanism for reaction for acid catalyzed esterification [25]



Step 1: An acid/base reaction, protonation of the carbonyl makes it more electrophilic

Step 2: The alcohol O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3: An acid/base reaction. Deprotonate the alcoholic oxygen.

Step 4: An acid/base reaction. Need to make an OH leave, it doesn’t matter which one, so convert it into a good leaving group by protonation.

Step 5: Use the electrons of an adjacent oxygen to help “push out” the leaving group, a neutral water molecule.

Step 6: An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the ester product.

2.6.1 Brønsted acids

Since acid catalysis is one of the most popular methods for esterification, numerous papers are available. When the substances are acid-resistant, the reaction is usually carried out in the presence of a Brønsted acid such as HCl, HBr, H_2SO_4, $NaHSO_4$, $ClSO_3H$, H_3PO_4, etc.

In case in which the acidity is not high enough to trigger the desired reaction, the acid is combined with an activator. Other ways to activate the acid catalysts are provided by the use of ultrasound and microwave. H_2SO_4-catalyzed esterification, which usually requires a long reaction time under refluxing conditions, is complete at room temperature in several hours on exposure to ultrasonic waves. Microwave irradiation accelerates the *p*-toluenesulfonic acid-catalyzed esterification, the reaction finishing within 10 min. Aqueous HCl is not employable for water-sensitive compounds. In such cases, dry HCl gas must be used, but generation of this is not operationally simple. Alternatively, generation of HCl under anhydrous conditions is conveniently feasible by addition of acetyl chloride to methanol or ethanol. Treatment of alcohol and carboxylic acid in the HCl solution obtained provides the desired ester. By this method, the concentration of HCl can be readily adjusted by changing the amount of acetyl chloride.

In situ generation of catalytic HCl is accessible photolytically. Photoirradiation of carboxylic acids in methanol containing CBr_4 furnishes the corresponding methyl esters. Interestingly, sp^3 carbon-tethered carboxylic acids undergo esterification smoothly under these conditions, while sp^2 or sp carbon-tethered carboxylic acids are not esterified. Similar photolytic esterification occurs in CCl_4 or $BrCCl_3$ in place of CBr_4. It has been proposed that HCl generated by abstraction of an α-hydrogen of alcohol by Cl radical is the real catalytic species in this reaction.

Hydrophobic polystyrene-supported sulfonic acids catalyze reaction between carboxylic acid and alcohol in water. The catalysts are recovered and reused for further reactions. The acidity of strong acids is moderated by forming the corresponding ammonium salts. Diphenylammonium triflate is an efficient catalyst for mediation of condensation between alcohol and carboxylic acid in a 1:1 ratio [26]. The reaction usually affords greater than 90 % yields of esters simply on treatment of the reactants with 1 mol% of the catalyst in refluxing toluene. After the reaction is complete, the solvent is evaporated and column chromatography of the residue furnishes the esters. Pentafluorophenylammonium triflate is also a good esterification catalyst. The pentafluorophenyl group causes formation of a hydrophobic environment around the catalytic center, so that dehydration techniques are required. Use of bulky ammonium groups together with arenesulfonyl anion results in highly efficient esterification. Dimesitylammonium pentafluorobenzenesulfonate is one of the most useful catalysts, effecting condensation between carboxylic acid and alcohol in a 1:1 ratio without use of Dean-Stark apparatus.

Polyaniline salts with HCl, HNO_3, H_2SO_4, H_3PO_4, *p*-tolSO_3H, etc. catalyze reactions between carboxylic acids and alcohols, and can be separated easily from the reaction mixture by filtration. Brønsted acidic ionic liquids function as dual solvents/catalysts for condensation between carboxylic acid and alcohol. Immobilized acidic ionic liquids can be recycled in catalysis for esterification. Acidic ionic liquids can catalyze reactions of carboxylic acids with alcohols in water.

2.6.2 Lewis acids

Lewis acids are another important class of acid catalyst. In general, they are milder than Brønsted acids and, more importantly, template effects are to be expected as they are sterically bulkier than a proton; the utilization of Lewis acids is therefore rapidly increasing. They are classified as follows, according to elements:

B	$BF_3 \cdot OEt_2$, BCl_3
Al	$AlCl_3$, $AlCl_3/ZnCl_2$
Zn	ZnO, $Zn(ClO_4)_2 \cdot 6H_2O$
Sn	$SnCl_2$, Bu_2SnO, Ph_2SnCl_2
Mn	$Mn(OAc)_3 \cdot 2H_2O$
Fe	$Fe(ClO_4)_3$, $Fe_2(SO_4)_3 \cdot H_2O$, $FeCl_3$
Ni	$NiCl_2 \cdot 6H_2O$, etc.

- $BF_3 \cdot OEt_2$ is the oldest Lewis acid to have been employed as an esterification catalyst, since the BF_3/CH_3OH complex had been known to be used for conversion of simple carboxylic acids to their methyl esters prior to GLC analysis.

- BCl_3 is also useful for esterification with primary alcohols, but yields are not so high with secondary and tertiary alcohols. The disadvantage of this method is the cleavage of coexisting methyl ether function. 3,4,5-Trifluorobenzeneboronic acid is claimed to be the most effective catalyst among boronic acids. Esterification takes place smoothly if heavy alcohols such as 1-butanol are employed. The reaction is presumed to proceed via a carboxylate intermediate.

- $AlCl_3$ is one of the most popular Lewis acids, but it is not employed in esterification because of its too strong acidity. However, polymer-supported $AlCl_3$ works as a milder catalyst for esterification although the yields are not always as high as those obtained by other methods. The advantage lies in the ease of separation of the catalyst by filtration. The Lewis acidity can be moderated in combination with a soft nucleophile, NaI, in CH_3CN. An equimolar mixture of acid and alcohol is smoothly converted into the desired ester under reflux, but the yield is not high in general (77 % at highest). Phenyl esters, which are otherwise rather difficult to prepare, can be obtained by reaction between aromatic or benzylic carboxylic acids with phenol in the presence of a catalytic amount of $AlCl_3$ and one equivalent of $ZnCl_2$. The strong acidity of $AlCl_3$ is responsible for efficient esterification, while $ZnCl_2$ serves for dehydration of the reaction mixture. Treatment of pentaerythritol with oleic acid in the presence of ZnO as catalyst provides a triester. Production of commercially important *p*-hydroxybenzoic acid ester (paraben) from *p*-hydroxybenzaldehyde and alcohol is catalyzed by $ZnCl_2$ under microwave irradiation conditions. The microwave irradiation is effective for esterification catalyzed by $Zn(OTf)_2$. An equimolar mixture of carboxylic acid and alcohol is esterified, but yields are less than 90 %. Smooth esterification is catalyzed by $Zn(ClO_4)_2 \cdot 6H_2O$ in the presence of $MgSO_4$ as a dehydrating agent.

Methyl esterification is feasible by heating a MeOH solution of carboxylic acid in the presence of $InCl_3$ (20 mol%). The reaction proceeds at room temperature under sonication as well.

- Another popular Lewis acid, $SnCl_4$, is also not usually employed in esterification, although the milder Lewis acid, $SnCl_2$, can catalyze reaction between carboxylic acids and solvent PrOH. Organotin compounds work quite well, however, because the acidity is moderated by the replacement of chlorine with electron-donating alkyl groups.

High-yielding ester synthesis from an equimolar mixture of carboxylic acid and alcohol is accessible by the use of $TiO(acac)_2$. The catalyst is water-tolerant and neutral to leave various functional groups intact. Alcohols are acetylated by heating at reflux with $Mn(OAc)_3 \cdot 2H_2O$ in acetic acid. Fe (III) salts are also effective. $Fe(ClO_4)_3 \cdot 9H_2O$ promotes esterification of carboxylic acids in alcohol. The reaction proceeds at room temperature, but a stoichiometric amount of the salt is needed. A catalytic version is available with $Fe_2(SO_4)_3 \cdot nH_2O$ and $FeCl_3$. Addition of a small amount of H_2SO_4 greatly increases the catalytic activity of $Fe_2(SO_4)_3 \cdot nH_2O$. Moreover, anhydrous $Fe_2(SO_4)_3$ is highly active for catalyzing acetylation of alcohols in acetic acid. $FeCl_3 \cdot 6H_2O$ effects esterification of an equimolar mixture of long-chain acids and alcohols in high yields. The reaction requires an excess amount of one reaction component in refluxing benzene or toluene. A similar outcome is obtained with $NiCl_2 \cdot 6H_2O$ catalyst.

- Cupric salts are another class of species that work as catalysts. $CuCl_2 \cdot nH_2O$ catalyzes conversion of carboxylic acids in methanol solvent at 130 ºC, while $Cu(NO_3)_2 \cdot 3H_2O$ effects acetylation of alcohols in refluxing acetic acid. $Cu(OTf)_2$ is used for acetylation of alcohols but to a somewhat limited extent. Cupric methanesulfonate ($Cu(OMs)_2$) is also effective. Treatment of carboxylic acid with alcohol (1.1 equiv.) in the presence of 1 mol% of the catalyst in refluxing cyclohexane affords the desired ester in excellent yield. $MoO(acac)_2$ also catalyzes transformation of propanoic acid into esters in refluxing alcohols.

- $Sc(OTf)_3$ can be employed as a catalyst for acylation of high-molecular weight polyethylene glycols. Polycondensation between aliphatic dicarboxylic acids and diols is also achievable with this catalyst to furnish polyesters.

- $HfCl_4 \cdot 2THF$ in the presence of 4A molecular sieves enables the use of equimolar amounts of alcohol and carboxylic acid to afford good to excellent yields of the desired esters. This commercially available catalyst is highly active (usually 0.1-0.2 mol% loading) and hydrolytically stable. Polycondensations of ω-hydroxy acids or between dicarboxylic acids and diols to furnish polyesters are also feasible. The selective esterification of primary alcohols in the presence of secondary alcohols or phenol can be achieved with this catalyst. Similar results are obtained with the zirconium analog. Unfortunately, however, these metal chlorides are moisture-sensitive. This drawback is overcome by the use of water-tolerant $ZrOCl_2 \cdot 8H_2O$ and $HfOCl_2 \cdot 8H_2O$. Combination of $Zr(O^1Pr)_4$ with $Fe(O^1Pr)_3$ exerts a synergistic effect, giving rise to increased catalytic activity as compared to the respective metal alkoxides alone. This combined catalyst is recovered by extraction with ionic liquid, so that recycling of the catalyst is feasible. Another method to recycle the catalyst is immobilization on *N*-(polystyrylbutyl)pyridinium triflylimide. The catalyst can be recycled at least 10 times with this technology. When a carboxylic acid is heated in alcohol with a catalytic amount of iodine, esterification takes place [27]. Primary, secondary, and even tertiary alcohols are employable, although the yields are rather low (56 %) in the last case. The reaction is tolerant of high amounts of water. It is claimed that the iodine works as a Lewis acid.

2.6.3 Solid acids

Various solid acids are utilized for esterification, although the substrates that can be employed suffer from considerable limitations due to the strong acidity. Nevertheless, solid acids have a great advantage in that they can be removed from the reaction mixture by filtration and thus applied to large - scale production.

- Nafion-H is the oldest solid acid to have been utilized as an esterification catalyst. When a mixture of carboxylic acid and alcohol is allowed to flow over this catalyst at 95-125 ºC, high yields of the corresponding esters are obtained with a contact time of 5 s. A batch reaction is also employable.
- Amberlyst 15; α-hydroxy esters and α-amino acids are successfully converted into the corresponding esters with this catalyst.
- Amberlite IR 120; various substrates with hydroxy and related functions, such as sugars, shikimic and quinic acids are esterified with this resin.
- Wolfatit KSP 200; esterification of chiral α-hydroxy carboxylic acids without racemization is feasible by heating in EtOH or MeOH/$CHCl_3$ in the presence of the ion-exchange resin Wolfatit KSP200. The products are useful intermediates for synthesis of the corresponding α-hydroxy aldehydes.
- Zeolite; the rare earth-exchanged RE H-Y zeolite is the best of the various zeolite catalysts. Heating of alcohol solutions of carboxylic acids in the presence of the freshly activated zeolite at 150 ºC provides good to excellent yields of esters. Zeolite catalysts for petroleum cracking are employable for synthesis of α-amino acid esters and phenyl benzoates.

- Mesoporous Silica has received extensive attention recently. Al-MCM-41 molecular sieves effect reactions between various acids and alcohols in the vapor phase: acetic acid/amyl alcohol, acetic acid/butyl alcohols, terephthalic acid/ methanol, butyric acid/1-pentanol, etc. Microporous titanosilicate ETS-10 molecular sieves are also effective for esterification of long-chain carboxylic acids with alcohols. Sulfonic acid-functionalized mesoporous silicas are utilized for esterification of fatty acids with methanol and glycerol. Mesoporous MCM-41 and SBA-15 functionalized with perfluoroalkanesulfonic acid are more active for esterification of long-chain fatty acids with alcohols than Nafion/silica composite. Comparison of commercial solid acid catalysts is now available in some reports.

- Modification of silica and alumina; treatment of silica or alumina with $ClSO_3H$ results in immobilization of sulfuric acid on the surface of silica or alumina, which catalyzes esterification of aryloxyacetic acid or aromatic carboxylic acid. Silica chloride obtained from silica and thionyl chloride effects esterification of amino acids. Sulfate-, phosphate-, and borate-modified silica, alumina and zirconia furnish benzyl acetate from acetic acid and benzyl alcohol concomitant with only a small amount of dibenzyl ether.

- $Nb_2O_5 \cdot nH_2O$; this catalyst is claimed to be more active than cation-exchange resin, $SiO_2 \cdot AlO_3$, and solid super acids. Interestingly, supermicroporous niobium oxide, synthesized using a nonionic block copolymer as a structural directing reagent, is employable for gas-phase esterification of acetic acid with ethanol.

- $ZrO_2 \cdot nH_2O$ and Mo-ZrO_2; hydrous ZrO_2, which catalyzes reactions between carboxylic acids and alcohols, exhibits the following advantages: (i) the catalyst is easily prepared and stable in air and (ii) the reaction does not require water-free conditions. The catalytic activity is further improved by use of Mo-ZrO_2 mixed oxide, because electron-deficient sites are formed by introduction of Mo cations into the lattice of the solid ZrO_2.

- Strongly Acidic Carbon Materials; Graphite bisulfate, which can be prepared by electrolysis of 98 % H_2SO_4 with a graphite anode, brings about reaction between alcohol and carboxylic acid in a 1:1 ratio at room temperature. The yields are usually over 90 %. Sulfonation of incompletely carbonized D-glucose results in amorphous carbon consisting of small polycyclic carbon sheets with high density of

SO_3H groups [36]. This carbon material exhibits remarkable catalytic performance for esterification of higher fatty acids. Poly(vinyl alcohol) membranes crosslinked with sulfosuccinic acid catalyze esterification of acetic acid with isoamyl alcohol.

- Natural Montmorillonite; another intercalation compound, natural montmorillonite, is useful for selective acylation of various functionalized primary and secondary alcohols.

- Metal-Exchanged Montmorillonite and Bentonite; montmorillonites enwrapped with various metal cations such as Na^+, Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Ti^{4+} are active catalysts for esterification. Acid-activated bentonite catalyzes reactions between various carboxylic acids and alcohols.

- Phosphorus Oxides; phosphorus pentoxide can be used for dehydration between carboxylic acid and alcohol. Heating a mixture of alcohol, carboxylic acid, and P_4O_{10} is the simplest treatment. In addition to intermolecular esterification, lactonization is also achievable. This procedure is modified by initial treatment of P_4O_{10} with alcohol to furnish an equimolar mixture of mono- and dialkylphosphates.

- Inorganic Sn- or Ti- Based Solid Acids; amorphous M (IV) tungstates (M = Sn, Ti) are useful for synthesis of dioctyl phthalate. Methyl ester synthesis from octanoic acid is feasible with a ceramic acid obtained by impregnating SnO_2H_2O and $(NH_4)_6(H_2W_{12}O_{40})$ followed by calcination. Solid superacid of sulfated tin oxide, SO_4^{2-}/SnO_2, is a highly active catalyst for condensation between acids and alcohols. Similarly, titanium superacid, SO_4^{2-}/SnO_2, is capable of esterifying chemically labile mandelic acid.

- Heteropolyacids; various bromoacetates are obtained by treatment of bromoacetic acids with alcohols in the presence of 12-tungstophosphoric acid, $H_3PO_{40}W_{12}\cdot H_2O$. Its partially substituted Cs and K salts are also useful catalysts for esterification. The corresponding ammonium salt catalyzes selective reactions between aliphatic carboxylic acids and alcohols in the presence of aromatic carboxylic acids. $H_{14}[NaP_5W_{30}O_{110}]$ can be employed for esterification of salicylic acid with aliphatic and benzylic alcohols. Cobalt-containing polyoxometalate, $K_5CoW_{12}O_{40}\cdot 3H_2O$, is suitable for esterification of mandelic acid.

- Acid Catalysts on Inorganic Solid Support; heteropoly acids often leak out of catalyst supports, because these acids are extraordinary soluble in water and several organic solvents. $H_3PW_{12}O_{40}$ can be immobilized onto hydrous zirconia, which catalyzes reactions between glacial acetic acid and cyclohexanol and between acetic acid and isoamyl alcohol. $H_4SiW_{12}O_{40}$ on hydrous zirconia brings about esterification of primary and secondary alcohols with C1-C3 carboxylic acids. Zirconia is also employable to support WO_3, which catalyzes esterification of palmitic acid with methanol. Porous zirconium phosphate is also employable to support WO_3. Silica gel is employable for supporting various acid catalysts: P_2O_5; $H_3PMo_{12}O_{40}$; $H_3PW_{12}O_{40}$. All of these supported catalysts are effective for esterification. Grinding $Fe(ClO_4)_3(ROH)_6/SiO_2$ with an equimolar amount of carboxylic acid provides esters. This protocol is operationally simple, but requires a stoichiometric amount of the promoter. Aliphatic carboxylic acids are esterified preferentially over aromatic ones at room temperature with the aid of $NaHSO_4$ supported on silica gel. $Hf[N(SO_2C_8F_{17})_4]$ supported on fluorous reverse-phase silica gel efficiently catalyzes esterification of methacrylic acid with methanol. Supporting $ZrOCl_2{\cdot}8H_2O$ on mesoporous silica MCM-41 enhances the catalytic activity for esterification of C10-C18 normal acid with alcohols. 12-Phosphotungstic acid and its cesium salts supported on a dealuminated Y zeolite catalyze reaction between 1-butanol and acetic acid in high yield. $H_3PW_{12}O_{40}$ can be supported on neutral alumina, catalyzing esterification of aliphatic carboxylic acids with primary and secondary alcohols. Activated carbon can tightly immobilize or entrap a certain amount of the acids. With $H_4SiW_{12}O_{40}$ entrapped in carbon, vapor-phase esterification of acetic acid with ethanol can be conducted efficiently. Zirconium sulfate supported on activated carbon exhibits higher activity for esterification of oleic acid with 1-butanol. Acid Catalysts on Organic Solid Support; heteropolyacids supported on ion-exchange resin accelerate the rates of reaction between lactic acid and ethanol. Polyaniline-supported acid catalysts are effective for esterification of carboxylic acids with alcohols. Triphenylphosphine ditriflate anchored onto cross-linked polystyrene is useful for ester synthesis from functionally substituted carboxylic acids and alcohols.

2.7 Porous molecular sieves

Molecular sieves are porous materials that exhibit selective adsorption properties which can be classified on the IUPAC definitions into three main types depending on their pore sizes that are microporous materials, mesoporous materials, and macroporous materials. Properties and examples of these materials are shown in Table 2.5.

Table 2.5 IUPAC classification of porous materials

Type of porous molecular sieve	**Pore size (Å)**	**Examples**
Microporous materials	< 20	Zeolites, Activated carbon
Mesoporous materials	20 – 500	M41s, SBA-15, Pillared clays
Macroporous materials	> 500	Glasses

2.8 Mesoporous materials

Two classes of materials that are extensively as heterogeneous catalyst and adsorption media are microporous and mesoporous materials. Well-known members of the microporous class are zeolites, which provide excellent catalytic properties by the virtue of their crystalline aluminosilicate framework. However, their applications are limited by the relatively small pore openings. Many attempts to synthesize zeolites with larger pores have been made, but they were unsuccessful. Larger pores are present in porous glasses and porous gels, which were known as mesoporous materials.

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosilicate mesoporous molecular sieves with exceptionally large uniform pore structures, which has resulted in a worldwide resurgence in this area. The template agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array as suggested initially. Three different mesophases in this family have been identified, i.e., lamellar, hexagonal, and cubic phase. MCM-41 [28] has a hexagonally packed array of cylindrical pores. The structure of MCM-48 [29] has a three-dimensional, cubic-ordered pore structure and MCM-50 [30] contains a lamellar structure as illustrated in Figure 2.8.

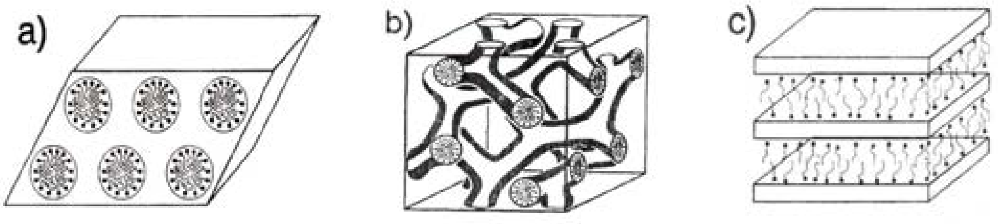


Figure 2.8 A schematic presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.

Recently there are many families of mesoporous materials. Especially, new mesoporous member with hexagonal structure was discovered, such as HMS (Hexagonal Mesoporous Silica) [31], FSM-16 (Folded Sheets Mesoporous Materials) [32] and SBA-15 [33] with straight hexagonal structure. Because different types of templates can be used for synthesizing hexagonal mesoporous materials at various pH of gel, the new hexagonal materials can be obtained. The interaction of various types of template with inorganic species for assembling these materials are different as summarized in Table 2.6, together with the condition typically employed for a synthesis.

Table 2.6 Various synthesis conditions of hexagonal mesoporous materials and the type of interaction between template and inorganic species.

Material	Template	Assembly	Media (pH)
MCM-41	Quaternary ammonium salt	Electrostatic	Basic or Acid
FSM-16	Quaternary ammonium salt	Electrostatic	Basic (pH = 8.5)
SBA-15	Amphiphilic triblock copolymer	Hydrogen bonding	Acid (pH = 1-2)
HMS	Primary amine	Hydrogen bonding	Neutral

MCM-41 and FSM-16 can be synthesized using quaternary ammonium salt as a template. In case of SBA-15, amphiphilic tribock copolymer can be modified as a template and must be synthesized in acid condition of hydrochloric acid. On the other hand, HMS can be prepared in neutral and environmentally benign condition using primary amine as a template. Although these materials have the same hexagonal structure, some properties are different as shown in Table 2.7.

Table 2.7 Properties of some hexagonal mesoporous materials [28, 31, 32, 33].

Material	Pore size (Å)	Wall thickness (nm)	BET specific surface area (m^2/g)	Framework structure
MCM-41	15-100	1	>1000	Honey comb
FSM-16	15-32	-	680-1000	Folded sheet
SBA-15	46-300	3-6	630-1000	Rope-like
HMS	29-41	1-2	640-1000	Wormhole

2.8.1 Mechanism of mesostructure formation

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for the various synthesis routes [33]. On the most common level, these models are predicted upon the presence of surfactants in a solution to direct the formation of inorganic mesostructure from stabilized inorganic precursors. The type of interaction between the surfactant and the inorganic species was significantly different depening on the various synthesis routes as shown in Table 2.8

Table 2.8 Example route for interaction between the surfactant and the inorganic soluble species.

Surfactant type	Inorganic type	Interaction type	example materials
Cationic (S^+)	I^-	S^+I^-	MCM-41, MCM-48
	I^+X^-	$S^+X^-I^+$	SBA-1, SBA-2, zinc phosphate
	I^0F^-	$S^+F^-I^0$	silica
Anionic (S^-)	I^+	S^-I^+	Al, Mg, Mn, Ga
	I^-M^+	$S^-M^+ I^-$	alumina, zinc oxide,
Neutral S^0 or N^0	I^0	S^0I^0 or N^0I^0	HMS, MSU-X, aluminum oxide
	I^+X^-	$S^0X^-I^+$	SBA-15

Where S^x or N^x : surfactant with charge of X
I^x : inorganic species with charge of X
X^- : halogenide anions
F^- : fluoride anion
M^{n+} : with charge of X

In case of MCM-41 and FSM-16, the interaction between template and inorganic species is electrostatic interaction while hydrogen bonding interaction occurs in HMS and SBA-15 synthesis [34]. The pore diameters of these materials were controlled by alkyl chain length of surfactant. Mechanisms of mesoporous formation were different depending on synthesis route for each material.

(a) Liquid crystal templating mechanism

A liquid crystal templating (LCT) mechanism was proposed by the Mobil researchers that firstly reported M41S material. The variation of surfactant concentration plays a significant role to control the structure. Figure 2.9 shows two possible for the LCT mechanism for hexagonal MCM-41.

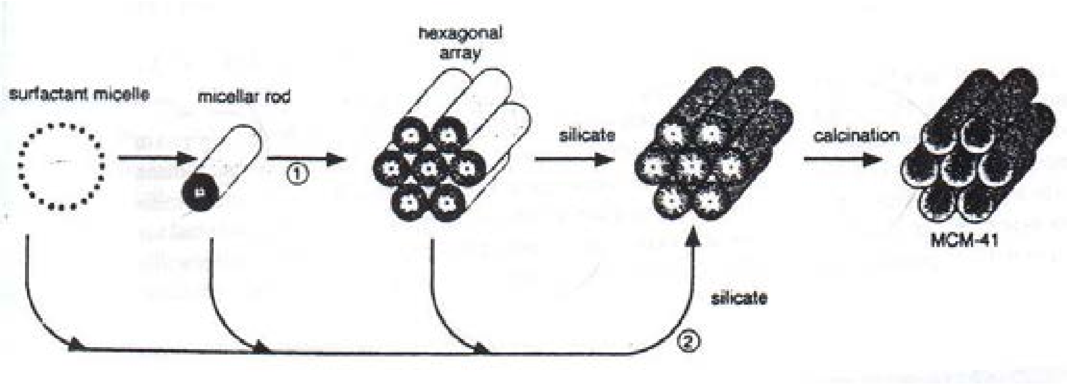


Figure 2.9 Two possible ways for the LCT mechanism.

There are two main pathways, in which either the liquid-crystal phase was intact before the silicate species were added (pathway 1), or the addition of the silicate results in the ordering of the subsequent silicate-encased surfactant micelles (pathway2).

(b) Folding sheet formation

The intercalation of ammonium surfactant into hydrated sodium silicate, which composed of singled-layered silica sheet call kanemite, produce the lamellar-to-hexagonal phase in FSM-16 material preparation. After the surfactants were ion-exchange into layered structure, the silicate sheets were thought to fold around the surfactants and condense into hexagonal mesostructure. The final product was claimed to be very similar to MCM-41. However, Vartuli *et al*. found that the layered structures were still retained in the kanemite-derived mesoporous materials [33]. Folding sheet formation is illustrated in Figure 2.10.

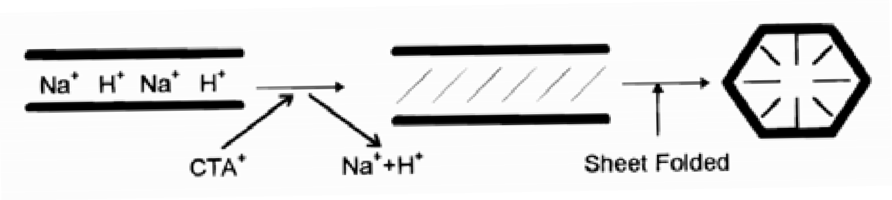


Figure 2.10 Schematic model representing “folding sheets” mechanism.

(c) Hydrogen bonding interaction

Tanev *et al.* [35] showed that mesoporous silica could be prepared by the hydrogen-bonding interaction of alkylamine (S^{o}) head group and hydroxylated tetraethyl orthosilicate (I^{o}) as shown in Figure 2.11 The materials lacked long-range order of pore, but had higher amounts of interparticle of mesoporosity, because the long-range effects of the electrostatic interaction that would normally control the packering of micellar rods were absent. This neutral templating synthesis route produced mesoporous silicates with thicker walls and higher thermal stability compared to the LCT-derived silicates. The silicate framework in the resulting mesophased was neutrally charged. From this reason, the surfactant can be easily removed by solvent extraction.

Using ionic surfactant (S^+ and S^-), the hydrophilic head mainly binds with inorganic species through electrostatic interactions. There are two possible formation routes. Firstly, direct pathway: surfactant and inorganic species of which charges are opposite interact together directly (S^+I^- and S^-I^+). Another is the indirect pathway, occurring when the charges of surfactant and inorganic species are the same, so the counter ions in solution get involved as charge compensating species for example the $S^+X^-I^+$ path takes place under acidic conditions, in the present of halogenide anions (X^- = Cl^- or Br^-) and the S^-M^+ I^- route is the characteristic of basic media, in the existence of alkaline cation (M^+ = Na^+ or K^+). Figure 2.8 shows the possible hybrid inorganic-organic interfaces.

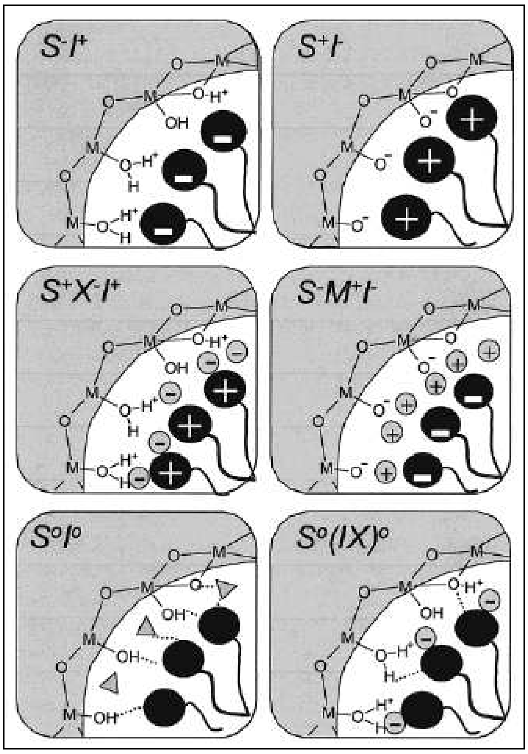


Figure 2.11 Schematic representation of the different types of silica-surfactant interfaces. Dashed line corresponded to H-bonding interactions [36].

In case of non-ionic surfactant (S^0 or N^0), the main interaction between template and inorganic species is hydrogen bonding or dipolar, which is called neutral path i.e. S^0I^0 and $S^0F^-I^+$. Nowadays, non-ionic surfactants give important commercial advantages in comparison to ionic surfactants because they are easily removable, nontoxic, biodegradable and relatively cheap.

2.8.2 Synthesis strategy of mesoporous material using block-copolymer as structure directing agent

In the synthesis of mesoporous materials such as MCM-41, FSM-16 ionic surfactant *i.e.* the cationic, alkyltrimethyl ammonium (C_nTA^+, $8<n<18$), and anionic surfactant, tertiary amine ($C_nH_{2n+1}N^+(CH_3)_3$) are used as template, respectively. These syntheses are done in extreme (alkaline) pH condition and the obtained materials have pore size in the range of 15 to 100 Å only. However, by this mean, two limitations occur:

(1) The lower stability of the obtained materials: due to the thinner pore wall of materials (8-13 Å).

(2) Difficult to expanding the pore size: the ionic surfactants give a limited pore size. The only way to expand the pore size is in employing swelling agents such as 1,3,5-trimethyl benzene, involving complicate synthesis.

Thus, the block copolymer has been used to solve these problems. Generally, amphiphilic block copolymer has been used in the field of surfactants, detergent manufacturing, emulsifying, coating, etc. The properties of block copolymer can be continuously tuned by adjusting solvent composition, molecular weight, or type of polymers. Figure 2.12 shows typical block copolymer used as templates.

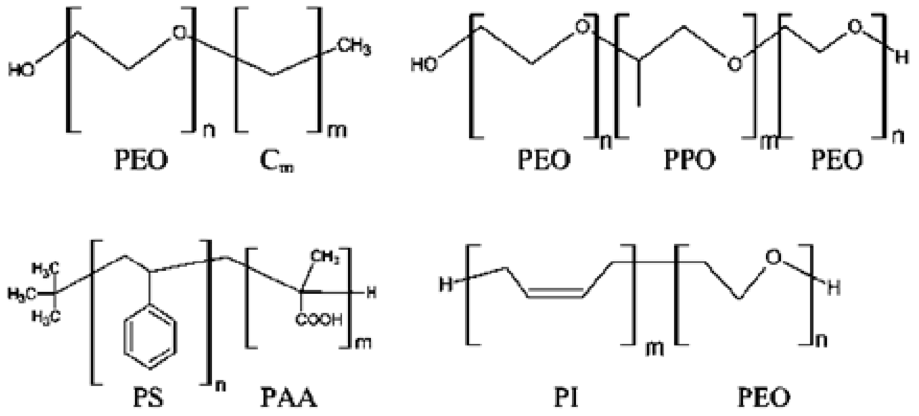


Figure 2.12 Block copolymer used in mesostructured generation [37].

Some advantages of using these block copolymer are:

(1) *The thicker wall thickness* (about 15-40 Å), enhancing hydrothermal and thermal stability of materials.

(2) *Pore diameter can be tuned easier* by varying type or concentration of polymer.

(3) *Easier to remove from mineral framework* by thermal treatment or solvent extraction. Due to the hydrogen bonding interaction between template and

inorganic framework, therefore, it should be easier to dissociate as compared to ionic templates (electrostatic interaction).

Interaction between block copolymer template and inorganic species, calls hybrid interphase (HI), is particularly important, especially in PEO-PPO based one. Different possible interactions take place at the HI are schematized in Figure 2.13. Most of the fine HI characterization has been performed on PEO-based (di or triblock) templates. Melosh *et al*. [38] determined that in F127-templated silica monoliths, organization arose for polymer weight fractions higher than 40%. For lower polymericsilica ratios, non-ordered gels were formed. This lack of order was due to a relatively strong interaction (probably of H-bonding type) of the (Si-–O–Si) polymers forming the inorganic skeleton with both PEO and PPO blocks.

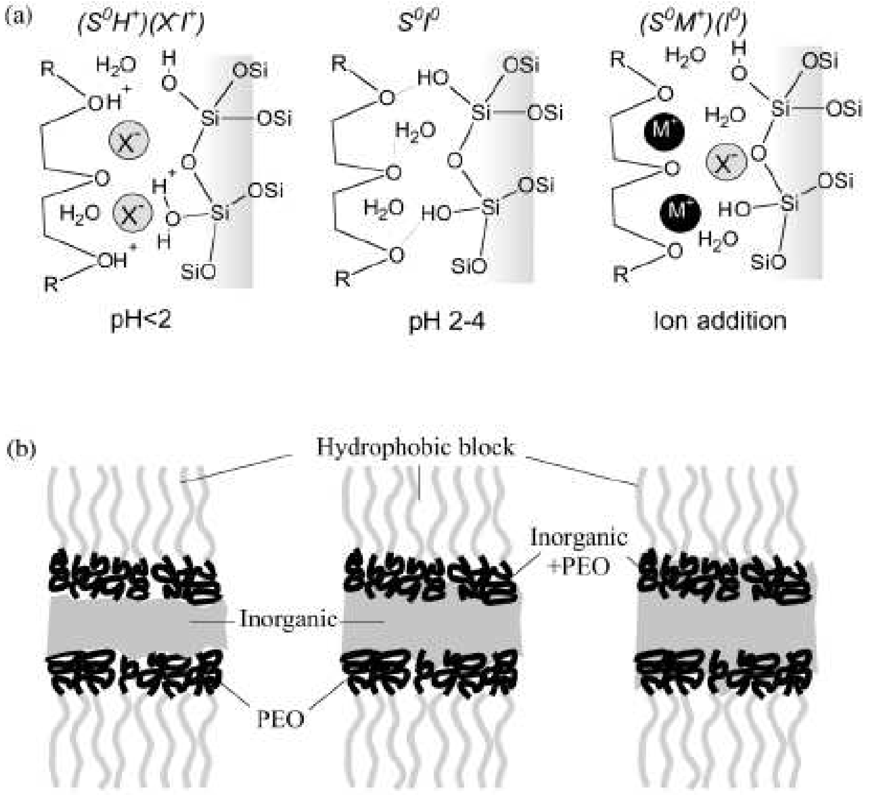
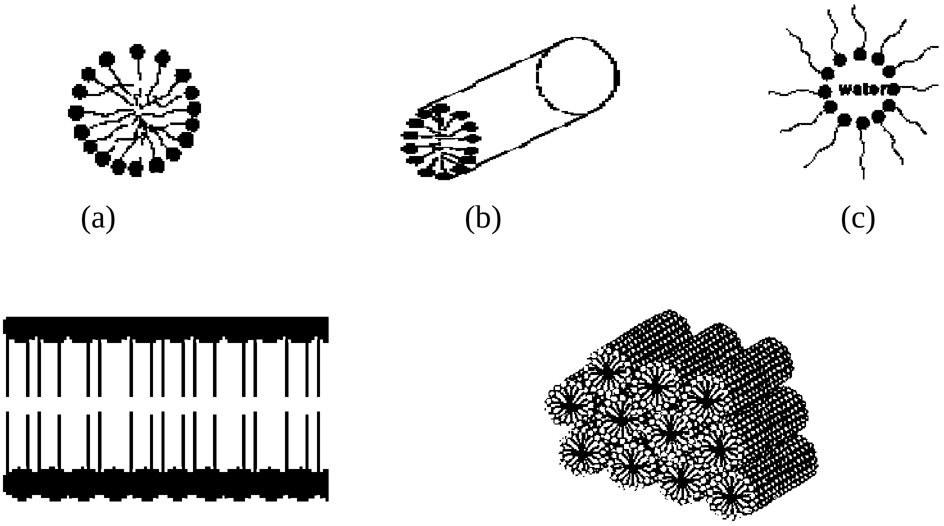


Figure 2.13 (a) Schematic view of the $(S^0H^+)(X^- I)$, S^0I^0 , and $(S^0 M^+)(X^-I^0)$ hybrid interphases (HIs) (b) Three possible structures of a HI composed by a nonionic polymer and an inorganic framework [38].

2.8.3 The behavior of surfactant molecules in an aqueous solution

In a simple binary system of water-surfactant, surfactant molecules, at a particular concentration can aggregate to form micelles in various types. The shapes of micelle strongly depend on the concentrations as shown in Figure 2.14.



(a) (b) (c)

(d) (e)

Figure 2.14 Phase sequence of the surfactant-water binary system (a) spherical micelle, (b) rod-shaped micelle, (c) reverse micelle, (d) lamellar phase, and (e) hexagonal phase.

At low concentration, they energetically exist as isolated molecules. With increasing concentration, surfactant aggregate together to form isotropic spherical and rod shaped micelles by directing the hydrophobic tails inside and turning the hydrophilic heads outside in order to decrease the system entropy. The initial concentration threshold at which those molecules aggregate to form isotropic micelle is called critical micelle concentration (CMC). The CMC determines thermodynamic stability of the micelles. When the concentration is continuously increased, the micellar shape changes from sphere or rod shape to hexagonal, lamellar, and inverse micelles. The particular phase present in a surfactant aqueous solution depends not only on the concentrations but also on the natural of surfactant molecules such as its length of the hydrophobic carbon chain, hydrophilic head group, and counter ion. Moreover the ionic strength, pH value, and temperature including other additives are the factors determining the shape of micelles.

2.9 SBA-15

2.9.1 Structure and properties of SBA-15

Recently, SBA-15 mesoporous material has been synthesized under acidic condition using triblock copolymer as a structure directing agent. This novel mesoporous material has shown higher hydrothermal stability as compared to MCM-41 due to its thicker pore walls (3.1-6.4 nm). They also posses uniform and hexagonal-structured channel similar to MCM-41 as shown in Figure 2.15 with larger pore size which make them more desirable to deal with bulky molecule. Some properties of MCM-41 and SBA-15, two well-known materials, are compared as described in Table 2.9. According to the properties listed in Table 2.6 SBA-15 show a better performance than MCM-41 in almost of properties.

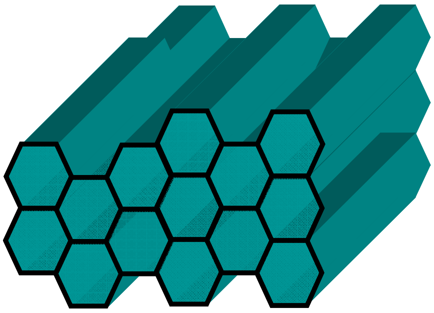


Figure 2.15 Hexagonal mesoporous structure.

Table 2.9 Comparison of two well-known mesoporous materials, MCM-41 and SBA-15 in their characteristic properties [39,40]

Properties	MCM-41	SBA-15
Pore size (Å)	20-100	46-300
Pore volume (mL/g)	>0.7	0.8-1.23
Surface area (m^2/g)	>1000	690-1040
Wall thickness (Å)	10-15	31-64

2.9.2 Synthesis of SBA-15 and formation mechanism

For SBA-15 materials, aging time and temperature are particularly important. Some research found that mesoporous SBA-15 prepared from calcination of an ‘as-prepared’ hybrid precursor contained a significant fraction of microporosity; further aging of the precursor in the mother liquors leads to an improvement on the pore size distribution (Figure 2.16), in agreement with the first work by Stucky [11].

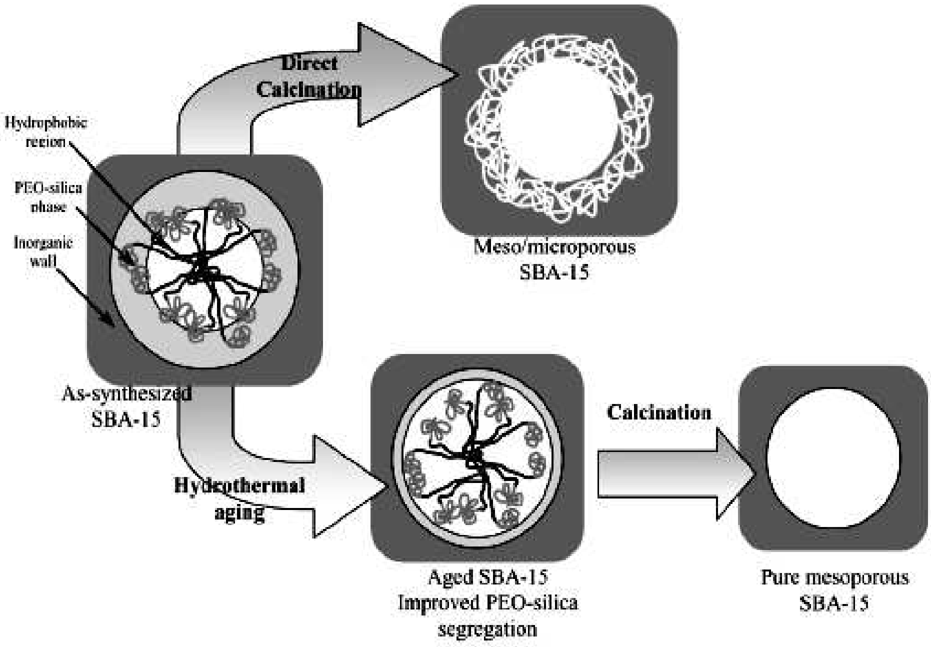


Figure 2.16 Pore evolution upon thermal treatment, depending on pre-treatment and aging [37].

Aging of an as-prepared precipitate at 80–100°C seems to help segregation of the PEO blocks and the inorganic framework, by promoting condensation of the latter. High temperatures also change the polymer behavior. It is known that for $T > 60°C$, PEO blocks become less hydrophilic and expel water similar to PPO blocks when the temperature is higher than 40°C [42]. For a mechanism, firstly alkoxysilane species (TMOS or TEOS) are hydrolyzed as:

$$\mathrm{Si(OEt)_4} + n\mathrm{H_3O^+} \xrightarrow[\mathrm{pH<2}]{\mathrm{hydrolysis}} \mathrm{Si(OEt)}_{4-n}\,(\mathrm{H_2O^+})_n + n\ \mathrm{EtOH}$$

This is followed by partial oligomerization at the silica. Furthermore, at this condition, the PEO parts of surfactant associate with hydronium ions as followed:

$$\text{-PEO}_m\text{-} + y\text{HX} \xrightarrow{H_2O} \text{-PEO}_{m-y}[(\text{EO})\cdot 3\text{H}_2\text{O}^+]_y \text{ ---X}_y^-$$

Next, coordination sphere expansion around the silicon atom by anion coordination of the form $X^-SiO_2^+$ may play an important role. The hydrophilic PEO blocks are expected to interact with the protonated silica and thus be closely associated with the inorganic wall. During the hydrolysis and condensation of the silica species, intermediate mesophase is sometimes observed and further condensation of silica species and organization of the surfactant and inorganic species result in the formation of the lowest energy silica-surfactant mesophase structure allowed by solidifying network.

2.10 Modification of catalysts

Nowadays, the attachment of organic functionalities such as sulfonic acid groups to the surface of siliceous SBA-15 mesoporous material is an interesting research area in heterogeneous catalysis and green chemistry. Basically, two strategies have been generally used to anchor organic groups onto a mesostructured silica surface.

2.10.1 Direct synthesis

Direct synthesis consists of the co-condensation of siloxane and organosiloxane precursors in the presence of the corresponding structure-directing agent.

The preparation of sulfonic-acid modified mesostructured materials is illustrated in Figure 2.17. This method is simplicity, because the incorporation of the organic precursor and the formation of the mesoporous material occur in a single synthetic step. To have a useful catalyst after synthesis, one must be able to extract the template from within the pores to create porosity. Calcination the synthetic material will destroy the incorporated organic functional groups. Extraction technique can be most effectively accomplished by ethanol solution [43-45].

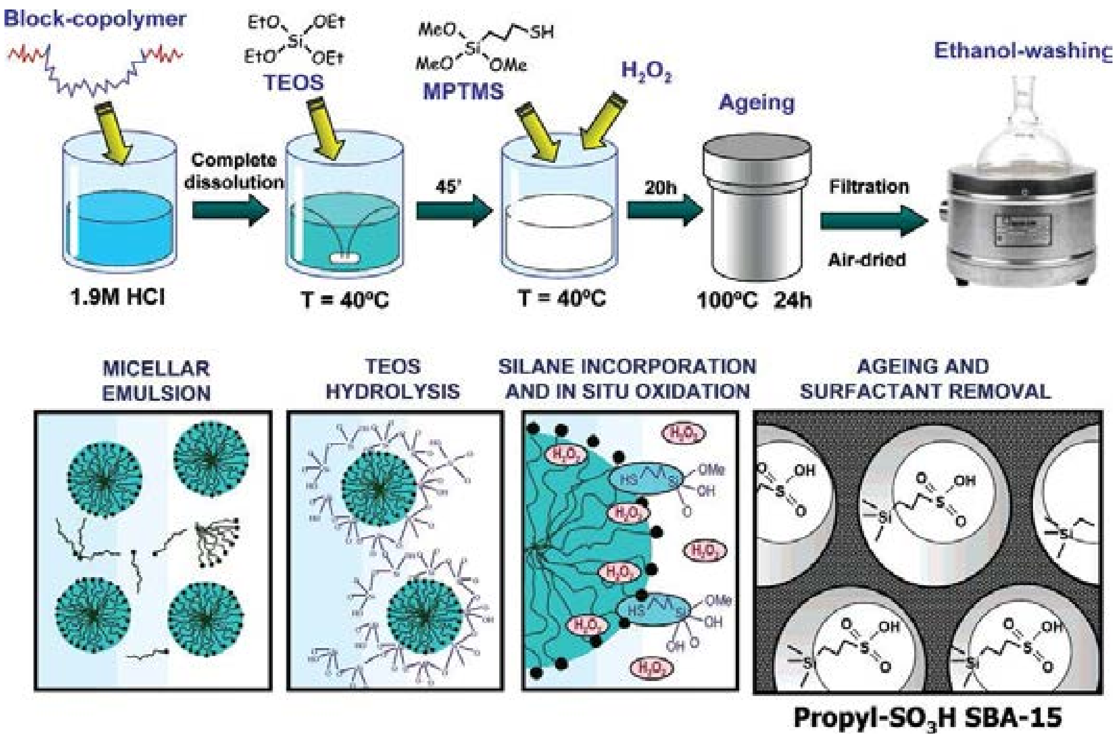


Figure 2.17 In-situ oxidation synthesis strategy for the preparation of sulfonic-acid-modified mesostructured materials [44].

2.10.2 Post synthesis (Grafting method)

Grafting procedure based on modification of the silica surface with organic groups through silylation reaction occurring on isolated (≡Si-OH) and germinal (=Si(OH)$_2$) silanol groups using trichloro- or trialkoxyorganosilane and silylamines as organic precursors [44].

Synthesis of sulfonic functionalized SBA-15 by post synthesis is shown in Figure 2.18. In typical procedure, calcined SBA-15 is treated with a silating agent like 3-mercaptopropyltrimethoxysilane (MPTMS) in nonpolar solvent (commonly toluene) to immobilize thiol groups on the surface. These thiol functionalities are then oxidized, normally using hydrogen peroxide. The most apparent advantage of this procedure is good preservation of the mesostructure after post-modification.

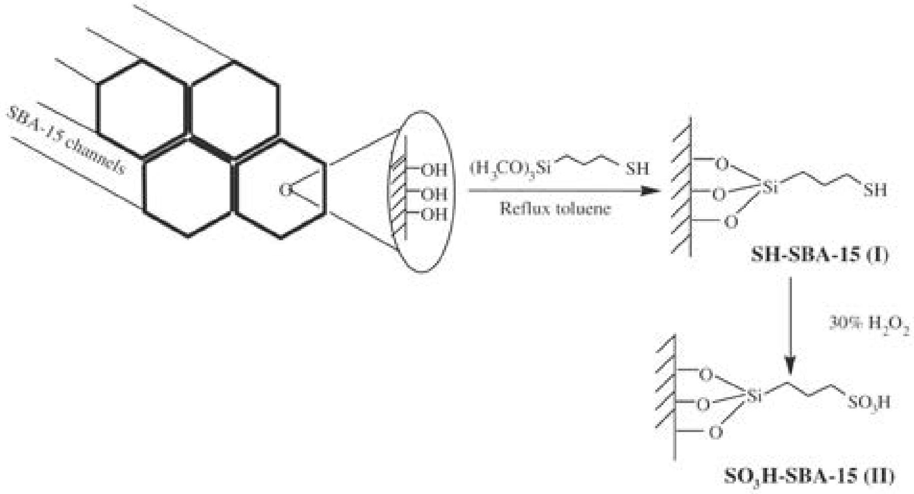


Figure 2.18 Post synthesis procedure for the preparation of sulfonic-acid-modified mesostructured materials [46].

2.11 Characterization of materials

2.11.1 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is an instrumental technique used for identification of minerals, as well as other crystalline materials. XRD is a technique in which a collimated beams of nearly monochromatic. X-rays is directed onto the flat surface of a relatively thin layer of finely ground material. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Other obtained information can include the degree of crystallinity of the minerals present, possible deviations of the minerals from their ideal compositions, the structural state of the minerals and the degree of hydration for minerals that contain water in their structure.

XRD is a reliable technique that can be used to identify mesoporous structure. Typically, the XRD pattern of hexagonal symmetry shows five well-resolved peaks corresponding to lattice planes of Miller indices (100), (110), (200), (210), and (300) [36]. These XRD peaks appear at low angle (2θ angle between 0.5 and 3 degree) because the materials are not crystalline at atomic level, diffraction at higher angles are not observed.

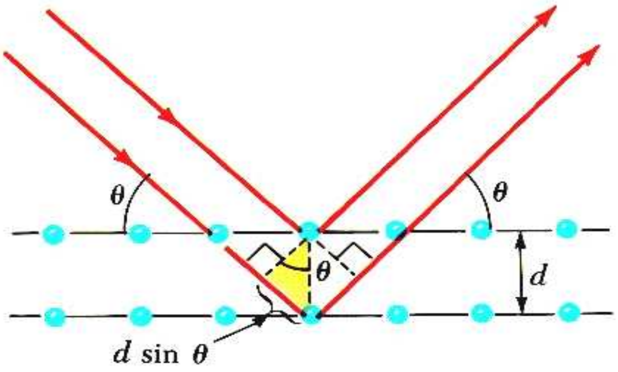


Figure 2.19 Diffraction of X-ray by regular planes of atoms [47].

Figure 2.19 shows a monochromatic beam of X-ray incident on the surface of crystal at an angle θ. The scattered intensity can be measured as a function of scattering angle 2θ. The resulting XRD pattern efficiently determines the different phases present in the sample. Using this method, Braggs' law is able to determine the interplanar spacing of the samples, from diffraction peak according to Bragg's angle.

$$n\lambda = 2\, d \sin\theta$$

Where the integer *n* is the order of the diffracted beam, λ is the wavelength; *d* is the distance between adjacent planes of the crystal (the *d*-spacings) and θ is the angle between the incident beam and these planes.

2.11.2 Nitrogen adsorption-desorption technique

The N_2 adsorption-desorption technique is used to classify the porous materials and its physical properties such as surface area, pore volume, pore diameter and pore-size distribution of solid catalysts. Adsorption of gas by a porous material is described by an adsorption isotherm, the amount of adsorbed gas by the material at a fixed temperature as a function of pressure. Porous materials are frequently characterized in terms of pore sizes derived from gas sorption data [48-49]. The IUPAC classification of adsorption isotherms is illustrated in Figure 2.20.

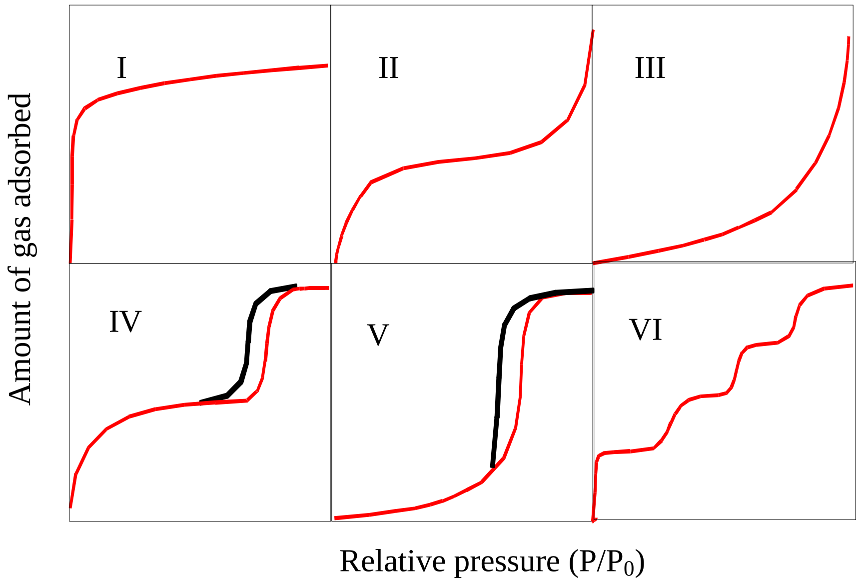


Figure 2.20 The IUPAC classification of adsorption isotherm [48].

As shown in Table 2.10, adsorption isotherms base on the strength of the interaction between the sample surface and adsorptive. Pore size distribution is measured by the use of nitrogen adsorption/desorption isotherm at liquid nitrogen temperature and relative pressures (P/P_o) ranging from 0.05-0.1. The large uptake of nitrogen at low P/P_o indicates filling of the micropores (<20 Å) in the adsorbent. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface of the sample, and the concave upward portion of the curve represents filling of mesoporous and macropores. The multipoint Brunauer, Emmett and Teller (BET) method is commonly used to measure total surface area.

$$\frac{1}{W[(P_o/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}(P/P_o)$$

Where W is the weight of nitrogen adsorbed at a given P/P_o, W_m is the weight of gas to give monolayer coverage, and C is a constant that is related to the heat of adsorption. A slope and intercept are used to determine the quantity of nitrogen adsorbed in the monolayer and calculate the surface area. For a single point method, the intercept is taken as zero or a small positive value, and the slope from the BET plot is used to calculate the surface area. The surface area depends upon the method used, as well as the partial pressures at which the data are collected.

Table 2.10 Features of adsorption isotherms

Type	Interaction between sample surface and gas adsorbate	Porosity	Example of sample-adsorbate
I	relatively strong	Micropores	activated carbon-N_2
II	relatively strong	Nonporous	oxide-N_2
III	weak	Nonporous	carbon-water vapor
IV	relatively strong	Mesopore	silica-N_2
V	weak	Micropores	
		Mesopore	activated carbon-water vapor
VI	relatively strong sample surface has an even distribution of energy	Nonporous	graphite-Kr

2.11.3 Scanning electron microscope (SEM)

The scanning electron microscope (SEM) has unique capabilities for analyzing surfaces and morphology of materials. It is analogous to the reflected light microscope, although different radiation sources serve to produce the required illumination. Whereas the reflected light microscope forms an image from light reflected from a sample surface, the SEM uses electrons for image formation. The different wavelength of these radiation sources result in different resolution levels: electron have much shorter wavelength than light photons, and shorter wavelength are capable of generating the higher resolution information. Enhanced resolution in turn permits higher magnification without loss of detail. The maximum magnification of the light microscope is about 2,000 times; beyond this level is “empty magnification”, or the point where increased magnification does not provide additional information.

This upper magnification limit is a function of the wavelength of visible light, 2000 Å, which equal the theoretical maximum resolution of conventional light microscope. In comparison, the wavelength of electron is less than 0.5 Å, and theoretically the maximum magnification of electron beam instrument is beyond 800,000 times. Because of instrumental parameters, practical magnification and resolution limits are about 75,000 times and 40 Å in a conventional SEM [50]. The SEM consists basically of four systems:

1. The *illuminating/imaging system* produces the electron beam and directs it onto the sample.

2. The *information system* includes the data released by the sample during electron bombardment and detectors which discriminate among analyze these information signals.

3. The *display system* consists of one or two cathode-ray tubes for observing and photographing the surface of interest.

4. The *vacuum system* removes gases from the microscope column which increase the mean free path of electron, hence the better image quality.

CHAPTER III

EXPERIMENTALS

3.1 Instruments and apparatus

3.1.1 Oven and furnace

SBA-15 was crystallized at 100^{o}C for 48 hours in static condition using UM-500 oven. The synthesized catalyst was calcined in air using a Carbolite RHF 1600 muffle furnace. The calcination of SBA-15 was employed to remove moisture and organic template from the catalyst. The calcination temperature program for SBA-15 was shown in Figure 3.1.

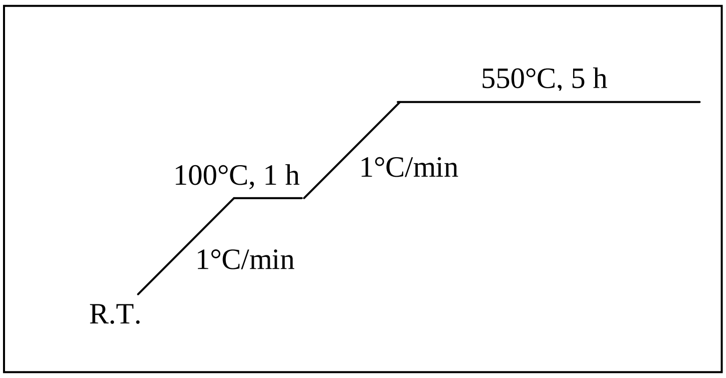


Figure 3.1 The calcination temperature program for the of SBA-15

3.1.2 X-ray powder diffractometer (XRD)

Rigaku D/MAX-2200 Ultima^{+} X-ray diffractometer was used to identify the characteristic of XRD patterns of synthesized materials. The instrument used a Cu target X-ray tube and applied high voltage at 40 kV to generate at Cu K_{α} x-rays. The characterization method was using 2-theta angle between 0.5 and 3.00 degree with a scan speed and sampling width at 1.00 degree/min and 0.02 degree, respectively. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, and 0.15 mm, respectively. The diffractograms were measured using MDI software (Jade 6.5) to estimate the relative intensity of each crystallographic plane.

3.1.3 Nitrogen adsorption-desorption technique

A BEL Japan, BELSORP-mini instrument was employed to analyze the catalysts N_2 adsorption-desorption isotherms, BET specific surface area, and pore size distribution. The materials weights were approximately weighted at 40 mg and then weighted exactly after 3 hours pretreatment which the materials were carried out at different temperature at 400 ^{o}C and 150 ^{o}C for the non-functionalized materials and the functionalized materials, respectively.

3.1.4 Scanning electron microscope (SEM)

The observation of morphology and particle sizes of the catalysts were using scanning electron microscope model JEOL JSM-6480 LV. All specimens were coated with spluttering gold under vacuum and applied voltage at 15 kV during investigations.

3.1.5 Gas chromatograph (GC)

The obtained reaction mixtures were analyzed using a Varian CP 3800 model gas chromatography equipped with a MXT-5 capillary metal column, the equivalent stationary phase to DB-5 and HP-5 column, in length of 30 m and 0.25 mm inner diameter. The flame ionization detector (FID) was used as a detector. The injection volumes were 1 μL. The experiments were injected to column with the same temperature program which was illustrated in Figure 3.2.

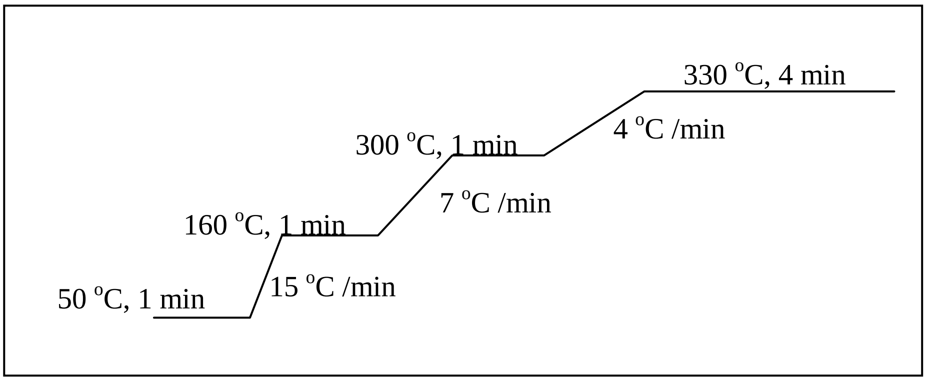


Figure 3.2 The GC temperature progarm for reaction analysis.

3.1.6 Gas chromatograph-mass spectrometer (GC-MS)

GC-MS was used to identify the reaction products. This qualitative analysis used GC system network of Agilent 68090 N equipped with HP-5 column with a 30 m length × 0.25 mm inner diameter. In addition, Mass selective detector network of Agilent 5973 and injector of Agilent 7683 Series were also used. The temperature program was slightly changed from the GC program which was shown in Figure 3.3.

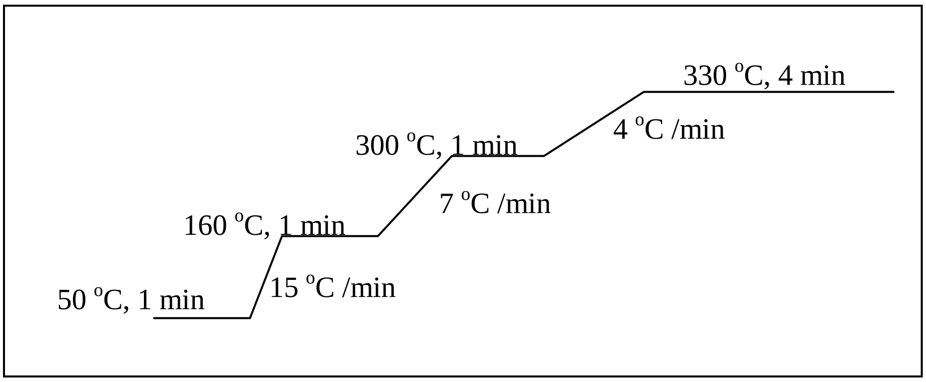


Figure 3.3 The temperature progarm of GC-MS analysis.

3.1.7 Nuclear magnetic resonance spectrometer (NMR)

NMR spectra were obtained from a Varian Mercury$^+$ 400 NMR spectrometer operated at 400 MHz for ^{1}H. The chemical shift was reported in δ (ppm) which assigned the residual protons in deuterated $CDCl_3$ solvents to reference signal.

3.1.8 Parr reactor

The esterifications of polyols with monocarboxylic acid experiments were carried out in 100 ml stainless steel batch reactor (PARR reactor). The temperature was programed between 60-130 °C to optimize the reaction. The progam was illustrated in Figure 3.4.

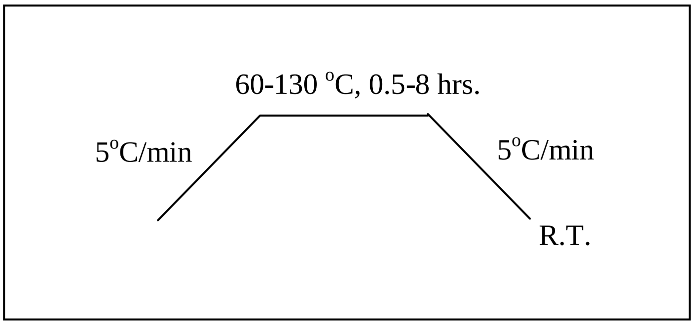


Figure 3.4 The temperature program of esterification

3.2 Chemicals

3.2.1 Chemicals for synthesis catalysts

1. Triblock copolymer pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}, average molecular weight = 5800) (Aldrich)
2. Tetraethyl orthosilicate, TEOS (Fluka, 98 %)
3. Hydrochloric acid, HCl (Fluka, 37 %)
4. (3-Mercaptopropyl)trimethoxysilane, MPTMS (Aldrich, 95 %)
5. Hydrogen peroxide (Merck, 30 %)
6. Toluene (CARLO ERBA, 99.5%)
7. Sulfuric acid, H_2SO_4 (Merck, 95-97%)
8. Deionized Water

3.2.2 Chemicals for esterification

1. Neopentyl glycol ($C_5H_{12}O_2$) (Merck, 99%)
2. Trimethylol propane ($C_5H_{12}O_3$) (Merck, 99%)
3. Butyric acid ($C_4H_8O_2$) (Sigma Aldrich, 98%)
4. Octanoic acid ($C_8H_{16}O_2$) (Sigma Aldrich, 99%)
5. Lauric acid ($C_{12}H_{24}O_2$) (Sigma Aldrich, 99.6%)

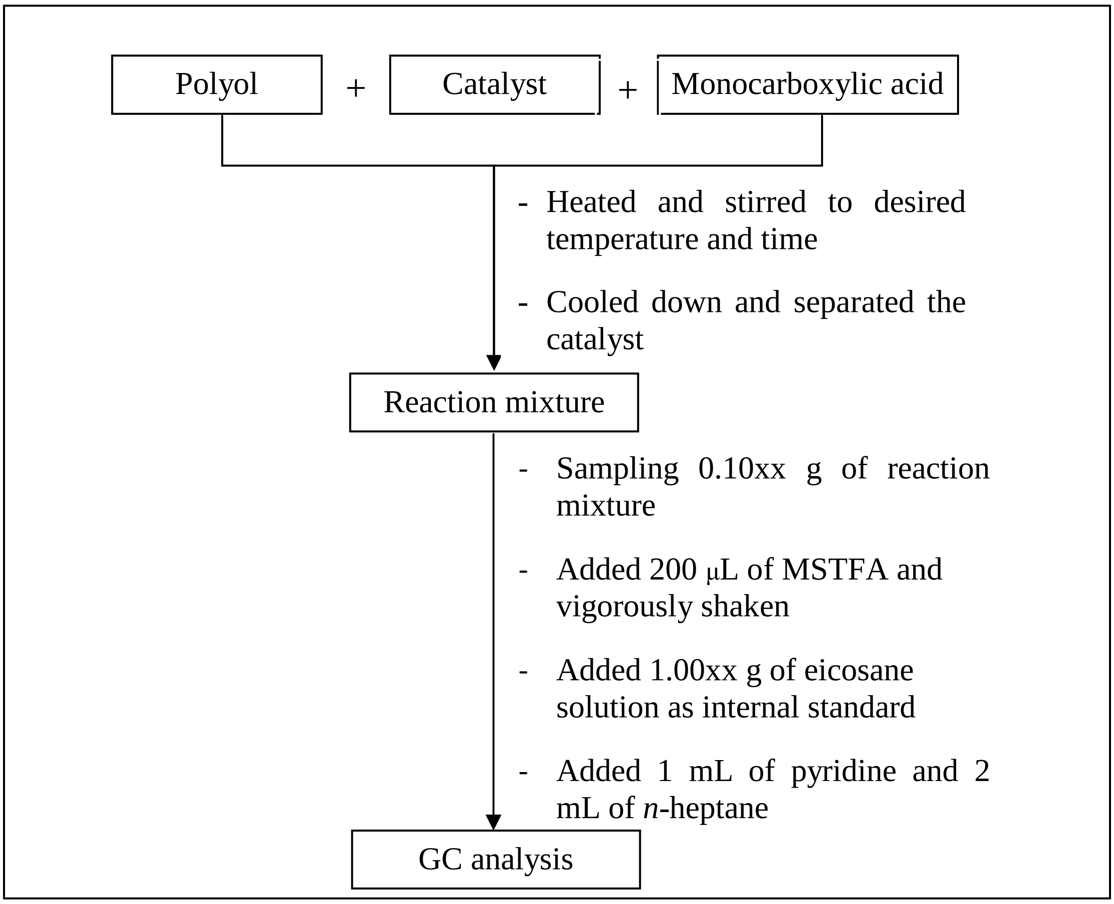
3.1.3 Chemicals for reaction product analysis

1. *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide, $C_6H_{12}F_3NOSi$ (Derivatization grade, Sigma Aldrich)

2. Eicosane ($C_{20}H_{42}$) (Sigma Aldrich, 99%)
3. Heptane (C_7H_{16}) (MERCK, 99%)
4. Pyridine

3.3 Model Esterification Procedure

The synthesis of polyolester was performed over stainless steel batch reactor. The experiment was beginning with reactants, 5 g of neopently glycol (NPG) mixed with octanoic acid and then, added the catalyst together in PARR reactor (Scheme 3.1). Next, a heater was applied to the reaction. After the reaction completed, the reaction mixture was cooled down and then the catalyst was separated from the reaction mixture by using centrifuge. The resulted products were separated by column chromatography to obtain authentic samples. The separated samples were using NMR and GC technique to confirm the structure and purity. Likewise, the reaction mixture was quantitatively analyzed by gas chromatography compared with calibration curve.



Scheme 3.1 Method for preparing esterification

3.4 Parameters affecting lubricant preparation

The study of parameter effecting on esterification was usually fixed substrate mole ratio between acid and alcohol as 2 for theoretical investigation.

3.4.1 Effect of reaction temperature

The reaction was variously operated different temperature in the range 60-130°C. Whereas, the others parameter such as time, stirring speed and catalytic amount at 5 hours, 200 rpm and 5% wt, respectively.

3.4.2 Effect of reaction time

The obtained reaction temperature was using in these experiments with the same other parameters and various times at 0.5-8 hours.

3.4.3 Effect of catalytic amount

The investigation of catalytic amount was varied as 0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, 5 wt.% and 10 wt.% based on total weight of substrate. In addition, the experiments were also used the optimal reaction temperature and time.

3.4.4 Effect of stirring speed

The optimum reaction tempearature, time and catalytic amount were used in this study while stirring speed was varied to 100, 150, 250 and 300 rpm.

3.4.5 Effect of various catalysts

The study of catalytic activities was employed to various catalysts such as sulfuric acid, *p*-toluene sulfonic, Amberlyst-15, Amberlyst-131, Nafion SAC-13, H-ZSM-5, H-MCM-22, H-beta, SBA-15-Pr-SO_3H, FSM-16-Pr-SO_3H and clay treated sulfuric acid with previous optimal condition.

3.4.6 Effect of octanoic acid to NPG mole ratio

The substrate mole ratios were varied from 2-5 mol/mol to investigate the condition which gave highest expected product.

3.4.7 Kinetic study of acid site

The amount of acid, which used in the reaction, were compared Amberlyst-15 with synthesized material, SBA-15-Pr-SO_3H. The experiment performed over optimal condition except reaction time which investigated at 0.5 hour.

3.4.8 Effect of structure of monocarboxylic acid

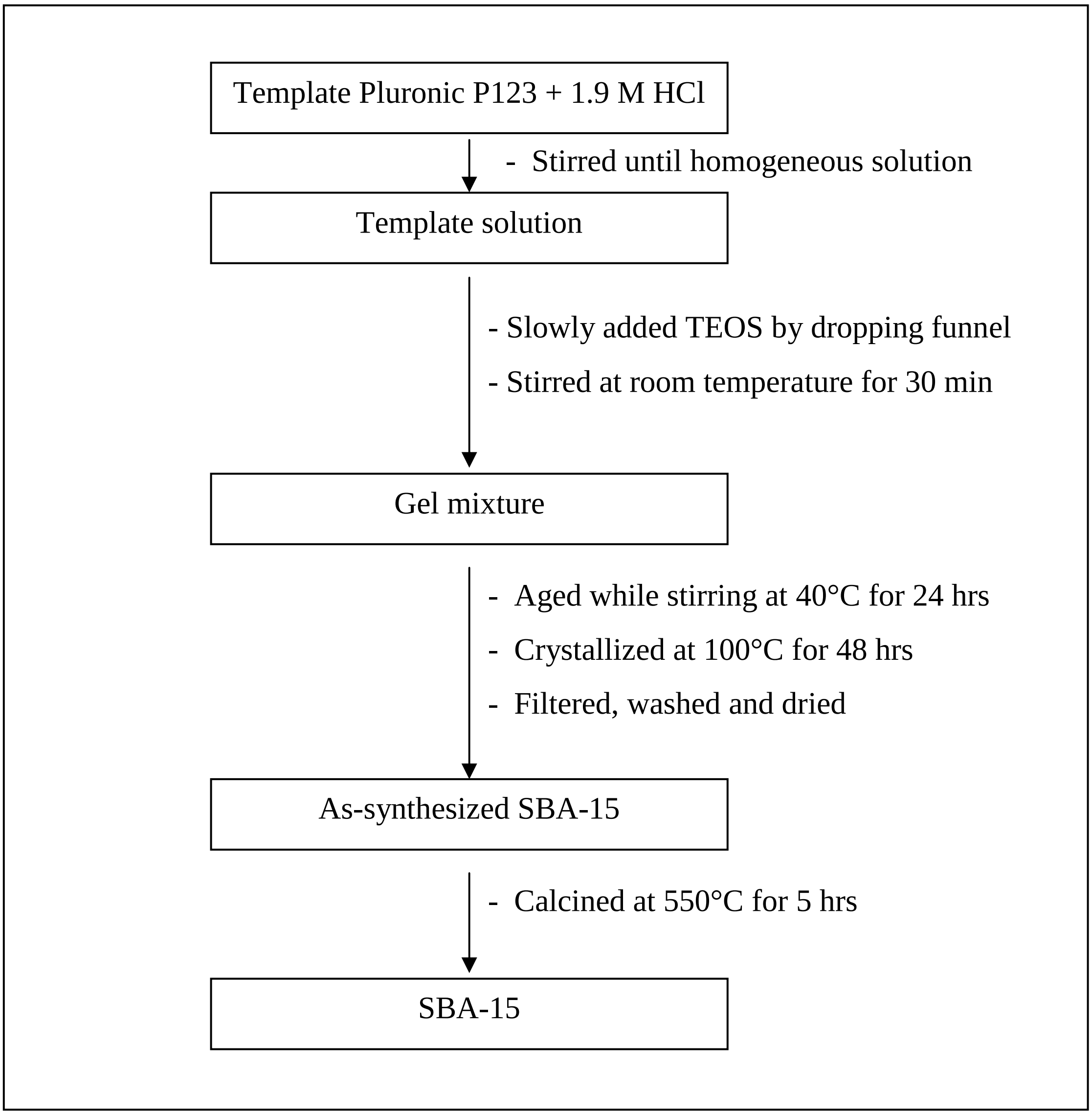
Esterification of neopentyl glycol with various monocarboxylic acids was carried out using the optimal condition of neopentyl glycol with octanoic acid esterification.

3.4.9 Effect of structure of alcohol

The investigation was studied the effect of alcohol structure using the optimal condition of neopentyl glycol with octanoic acid esterification. The alcohol was changed from neopentyl glycol to trimethylol propane.

3.5 Synthesis of SBA-15 by hydrothermal method

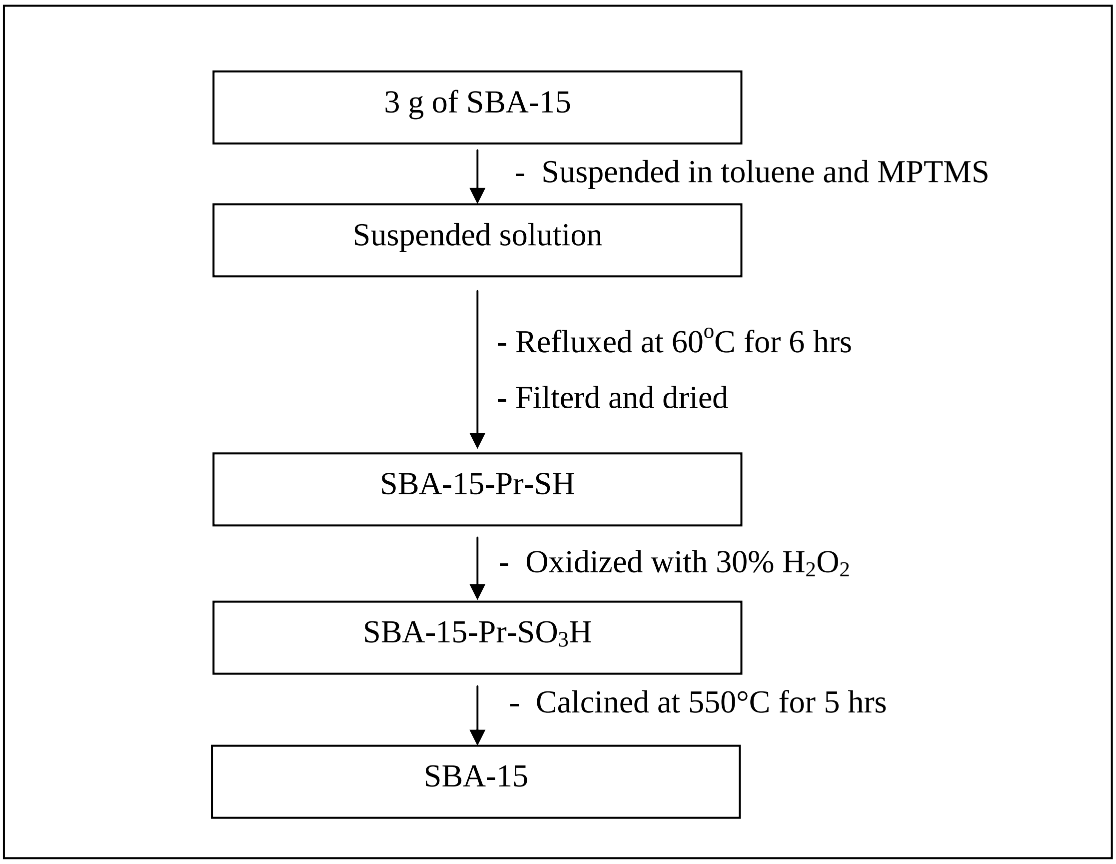
SBA-15 was synthesized using Stucky *et al* method[11]. The gel mole composition was 1.0TEOS: 0.0165 P123: 6.95 HCl: 140 H_2O. In a typical procedure, a template, triblock copolymer Pluronic P123, was dissolved in 1.9 M HCl solution at room temperature under stirring. Subsequently, TEOS was slowly dropwised and then, stirred for 30 min. Afetrwards, the gel was aged at 40^oC for 24 hrs under stirring at 200 rpm. The resulted gel was transferred to a Teflon-lined covered with stainless steel autoclaves and hydrothermal crystallized at 100^oC for 48 hrs. The obtained gel was separated by filtration, washed with deionized water for several times, and dried overnight which designated as As-synthesized SBA-15. Then, the obtained material was calcined to remove template at 550^{o}C for 5 hrs. The procedure for SBA-15 synthesis was illustrated in Scheme 3.2.



Scheme 3.2 Synthesis diagram for SBA-15 by hydrothermal method.

3.6 Sulfonic functionalized mesoporous materials

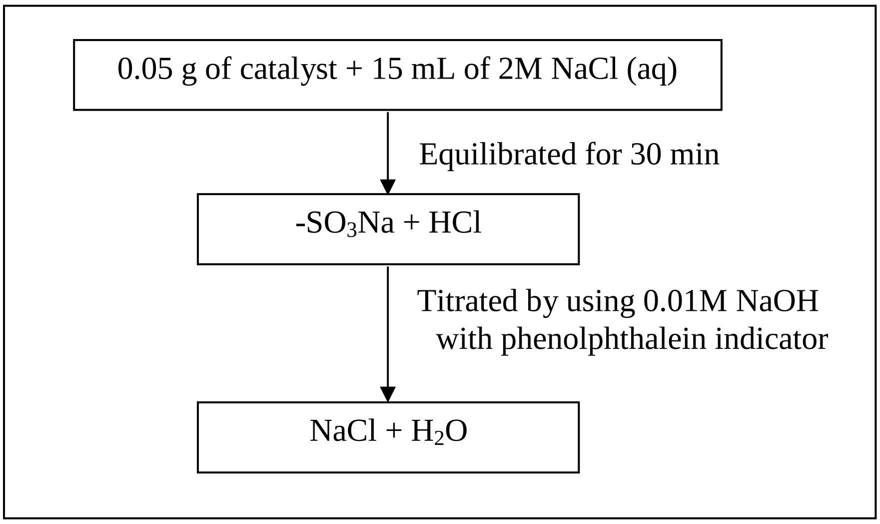
To grafting propyl sulfonic group, 3 g of mesoporous materials was suspended in toluene with (3-mercaptopropyl) tri-methoxysilane (MPTMS). Then, the suspended solution was refluxed at 60^{o}C for 6 hrs to give propyl thiol groups. The resulted materials were oxidized by 30% H_2O_2 to obtain sulfonic groups. Afterwards, The wet material was acidified in 0.2 M H_2SO_4 and stirred for 2 hrs [58]. Finally, the obtained product was filtered and dried in oven for overnight at 60°C. The functionalization procedure was presented in Scheme 3.3.



Scheme 3.3 Acid functionalization diagram of SBA-15.

3.7 Acid-base titration

The functionalized mesoporous materials were analyzed to quantify acid capacities of sulfonic acid groups by the procedure in Scheme 3.4. Firstly, Approximately 0.05xx g of the catalysts was exchanged with 15 ml of 2M NaCl solution for 30 min under constant stirring agitation at room temperature. Then, the solution was titrated by using 0.01 M NaOH as tritrant with phenolphthalein indicator [51].



Scheme 3.4 Acid-base titration diagram.

3.8 Recycle of catalysts

After the completion of reaction, the used catalyst was separated from reaction mixture and washed several times with various solvents such as hexane and acetone. The obtained catalyst was dried at 80°C overnight, so the catalyst was designated as 1st used catalyst. The difference solvent washed catalyst was tested again over the same reaction to compare the highest catalytic activity. The best catalyst was performed once again to test its catalytic activity. The resulted catalyst was designated as 2nd used catalyst. The 2nd used catalyst was regenerated by grafting the catalyst with MPMTS in toluene, H_2O_2 and H_2SO_4, respectively as the same procedure as Scheme 3.3. The catalyst was denoted as regenerated catalyst. Afterwards, catalyst was characterized by XRD and surface area analysis before testing in subsequently experiment. The reaction was performed in the same way as described in Section 3.7.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Model of polyol esterification

To investigate the optimum condition, a commercial cationic exchange resin, Amberlyst-15, was used as a catalyst in esterification due to their high catalytic activity [52] and easy to separate from the reaction mixture. Moreover, the obtained optimal condition was considered to be a model reaction for adjusting other parameters.

4.1.1 Effect of reaction temperature

The effect of reaction temperature was firstly investigated. The product yield and selectivity were performed in Table 4.1. The experiments were carried out using various temperatures with fixed other parameters such as time, stirring speed, substrate mole ratio and catalytic amount. The temperatures were applied in the range of 60 to 130°C.

Table 4.1 Effect of reaction temperature on product yield and selectivity

Temperature (°C)	% yield[a]		Total ester yield	% selectivity	
	mono	di		mono	di
60	46.1	23.6	69.7	66.2	33.8
70	33.7	40.9	74.6	45.2	54.8
80	21.8	53.8	75.6	28.8	71.2
90	15.7	56.4	72.1	21.8	78.3
100	14.0	56.5	70.5	19.9	80.2
110	11.8	49.2	61.0	19.3	80.7
120	7.4	40.9	48.3	15.3	84.7
130	5.3	44.5	49.7	10.6	89.4

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction time 5 hrs.; 5wt.%Amberlyst-15 based on total reaction weight; and stirring speed 200 rpm.
[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

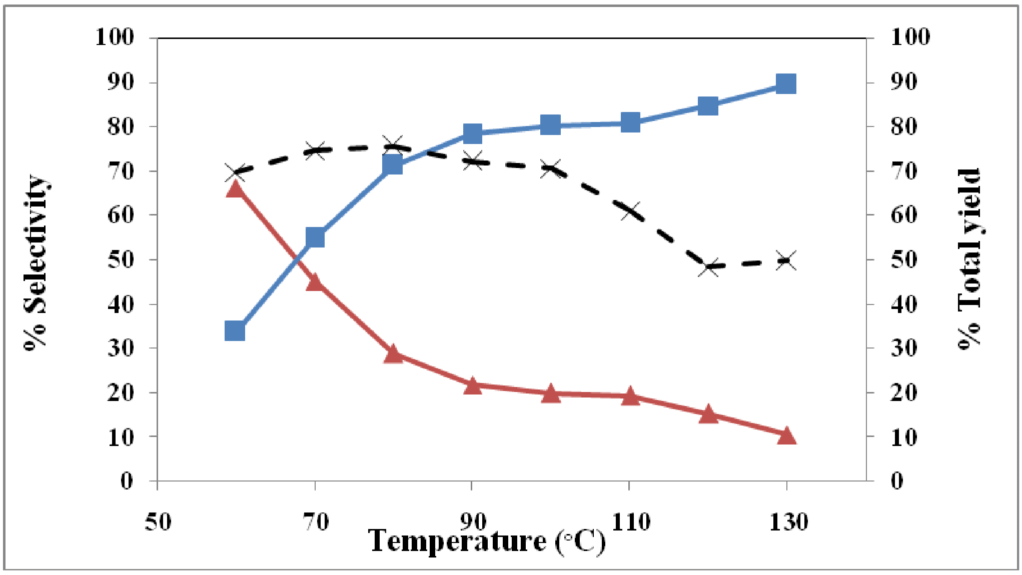


Figure 4.1 Influence of reaction temperature on the product yield and selectivity over Amberlyst-15.(Symbols: (▲) NPG monooctanoateselectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

As a result, the effect of reaction temperature was performed that the highest total ester yield was obtained at 80°C as 75.6 %. Although the NPG dioctanoate selectivity had been extended with increasing temperature but total yield was decreased. This effect might be explained by the disproportionation reaction [5] of NPG monooctanoate which conversed to NPG dioctanoate and NPG at higher temperature. Thus, the temperature at 80°C was used in the subsequent experiments.

4.1.2 Effect of reaction time

After the reaction temperature was investigated. Then, the effect of reaction time was studied in the range of 0.5-10 hrs to optimize time for the subsequent reaction. The result was shown in Table 4.2

Table 4.2 Effect of reaction time on product yield and selectivity

Time (h)	% yield[a] mono	% yield[a] di	Total ester yield	% selectivity mono	% selectivity di
0.5	49.3	13.8	63.1	78.1	21.9
1	39.6	27.1	66.7	59.4	40.6
2	29.7	37.9	67.7	44.0	56.0
3	27.3	46.0	73.4	37.2	62.8
4	19.8	54.3	74.0	26.7	73.3
5	19.8	54.9	74.7	26.6	73.4
6	20.1	55.2	75.3	26.7	73.3
7	18.9	56.9	75.8	25.0	75.0
10	19.1	60.5	79.6	23.9	76.1

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; 5wt.%Amberlyst-15 based on total reaction weight; and stirring speed 200 rpm.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

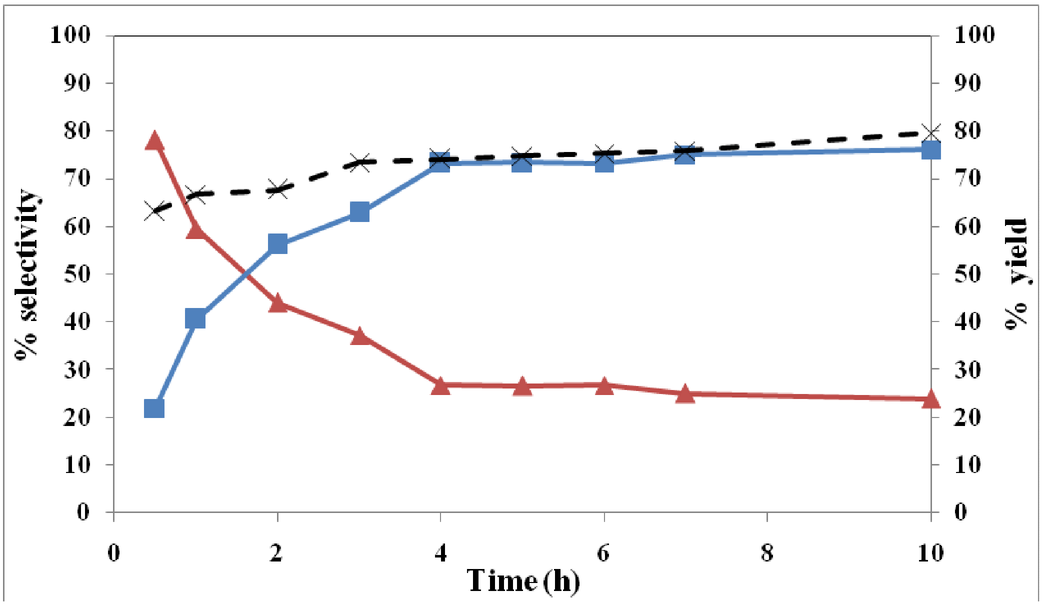


Figure 4.2 Influence of reaction time on the product yield and selectivity over Amberlyst-15. (Symbols: (▲) NPG monooctanoate selectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

The influences of reaction time on the product yield and selectivity exhibited that the total ester yield slightly increased with longer reaction time with constantly after 3 hrs as about 74 %, whereas the NPG dioctanoate selectivity was rapidly increased from 0.5 to 4 hrs and kept constant after 4 hrs. Thus, the reaction promoted high NPG dioctanoate selectivity as 73.3 % while the time at 10 hrs allowed no significantly difference between 4 and 10 hrs which exhibited the selectivity as 76.0 %. As a result, the reaction time at 4 hrs was selected due to energy saving.

4.1.3 Effect of catalytic amount

As a similar way to the previous reaction, this effect was studied using the optimum reaction temperature and time which were obtained from prior experiments. Catalytic weights were varied in the range of 0 to 10 wt% based on total substrate quantity. This study investigated the influence of catalytic amount on product yield and selectivity which could be seen in Table 4.3

Table 4.3 Effect of catalytic amount on product yield and selectivity

Catalyst amount (wt%)	**%yield[a]**		**Total ester yield**	**%selectivity**	
	mono	**di**		**mono**	**di**
non-catalyst	29.6	8.2	37.8	78.3	21.7
1	38.8	25.1	63.9	60.7	39.3
2	31.9	43.1	75.0	42.5	57.5
3	19.8	54.3	74.0	26.7	73.3
5	18.2	56.6	74.8	24.4	75.6
10	15.3	48.7	64.1	23.9	76.1

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; reaction time 4 hrs. and stirring speed 200 rpm.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

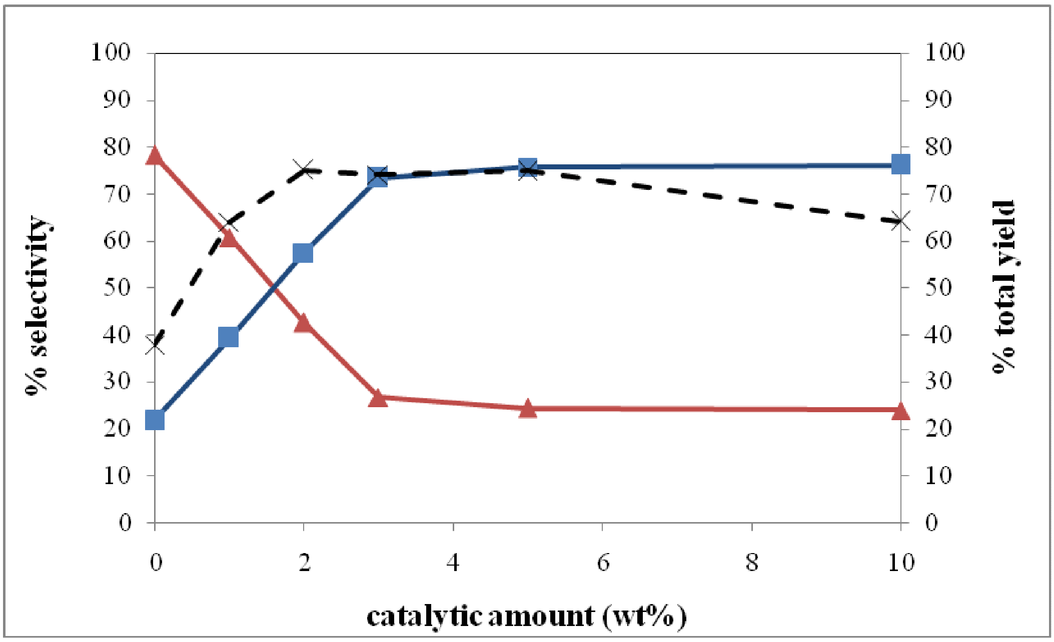
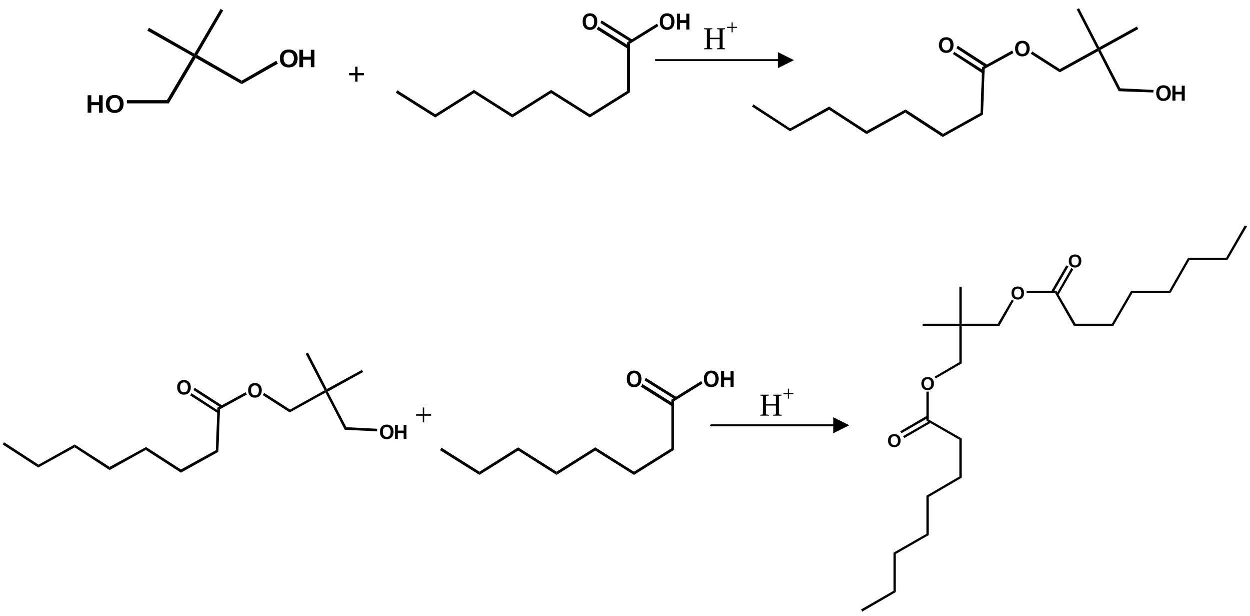


Figure 4.3 Influence of catalytic amount on the product yield and selectivity over Amberlyst-15.(Symbols: (▲) NPG monooctanoate selectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

According to the result, it was found that the spontaneous reaction at 80°C preferred NPG monooctanoate product which contained high monoester selectivity as 78.3%. Although, the reaction with no catalyst, accelerated the monoester product but it provided total ester yield only 37.8%. When catalyst was used in the reaction, the NPG dioctanoate selectivity surprisingly shoot from 21.7 to 39.3 and 57.5% by catalyzed with catalyst 1 and 2 wt%, respectively. Similarly, the obtained reaction mixture also gained more total ester yield when catalytic amount was increased until 2 wt%. After increasing of catalyst to 3 wt%, the experiment kept constantly total ester yield while the diester selectivity could be raised more. This effect might be explained by amount of catalytic site in the reaction. The esterification of polyol and monocarboxylic acid is well known that the reaction was proposed to occur by two step esterification [52] as shown in Scheme 4.1 which meant using low amount of catalyst could accelerated more monoester than diester. With higher amount of catalyst at 3 wt%, there are more acidic sites to catalyze the second step of reaction which gave higher diester selectivity. In addition, an uncommon trend of the total ester yield was also observed when the reaction performed with 10 wt% of catalyst. The extraordinary tend could be explained by phase disturbance of catalyst in which the large amount of heterogeneous catalyst might induce the adsorption on catalyst surface. Thus, the use of catalyst at 3wt% of total substrates was selected due to cost saving and their high product yield 74.0 % with NPG dioctanoate selectivity as 73.3 %.



Scheme 4.1 Two-step esterification of neopentyl glycol and octanoic acid

4.1.4 Effect of stirring speed

The distribution of product yield and selectivity which were affected by stirring speed in the reaction was shown in Table 4.4. The stirring speed was varied in the range of 100 to 300 rpm in which other conditions obtaining from the previous experiments were fixed.

Table 4.4 Effect of stirring speed on product yield and selectivity

Stirringspeed (rpm)	%yield[a] mono	%yield[a] di	Total ester yield	%selectivity mono	%selectivity di
100	26.8	49.3	76.1	35.2	64.8
150	21.6	51.7	73.3	29.5	70.5
200	19.8	54.3	74.0	26.7	73.3
250	27.1	47.3	74.3	36.4	63.6
300	25.7	50.2	75.9	33.9	66.1

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; reaction time 4 hrs. and 3wt.%Amberlyst-15 based on total reaction weight.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

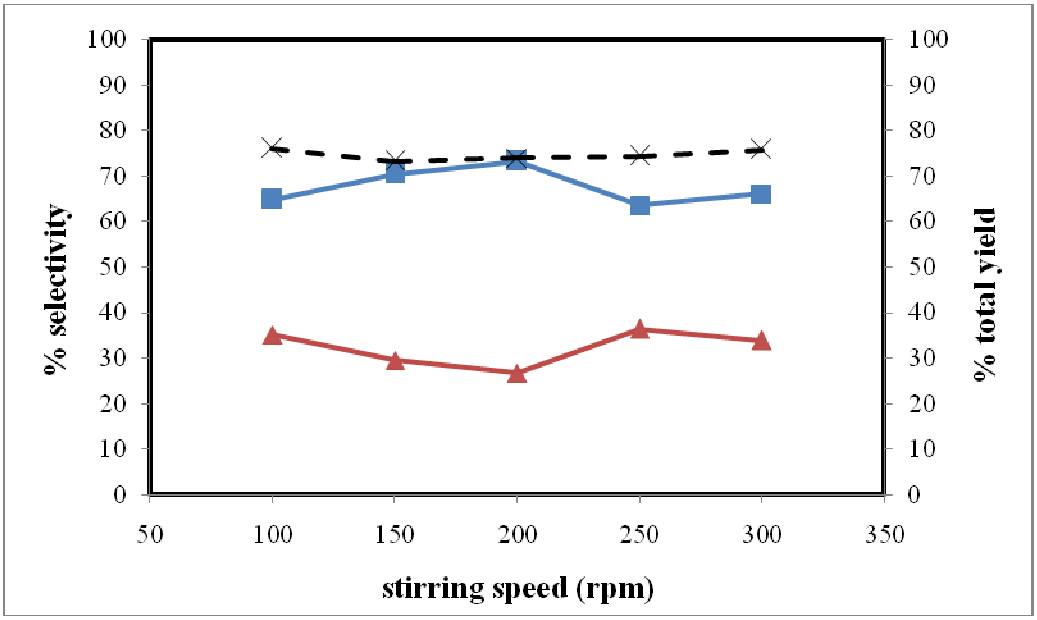


Figure 4.4 Influence of stirring speed on the product yield and selectivity over Amberlyst-15. (Symbols: (▲) NPG monooctanoate selectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

According to the result, there was no significantly difference on the total ester yield. However, the stirring speed in this reaction had an impact on the product selectivity. The stirring speed between 100 to 200 rpm tended to increase the NPG dioctanoate selectivity owing to the compatibility of substrate and catalyst. In case of the stirring speed higher than 200 rpm, the Amberlyst-15, rounded grain shape catalyst had been destroyed from particle to powder which might decrease their catalytic efficiencies.

4.1.5 Effects of substrates mole ratio

This experiment focused on the mole ratio of octanoic acid to neopentyl glycol on the esterification over Amberlyst-15 which gave the highest total ester product and diester selectivity. The reactions performed by varying mole ratio of octanoic acid to neopentyl glycol in the range of 2 to 6. The result was shown in Table 4.5.

Table 4.5 Effect of substrates mole ratio on product yield and selectivity

mole ratio of octanoic acid to neopentyl glycol	**%yield**[a]		**Total ester yield**	**%selectivity**	
	mono	**di**		**mono**	**di**
2	19.8	54.3	74.0	26.7	73.3
3	14.4	63.2	77.6	18.6	81.4
4	7.6	69.5	77.1	9.9	90.1
5	10.6	66.9	77.5	13.7	86.3
6	9.0	68.1	77.1	11.7	88.3

Esterification conditions: reaction temperature 80^{o}C; reaction time 4hrs.; 3wt.%Amberlyst-15 based on total reaction weight and stirring speed 200 rpm.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

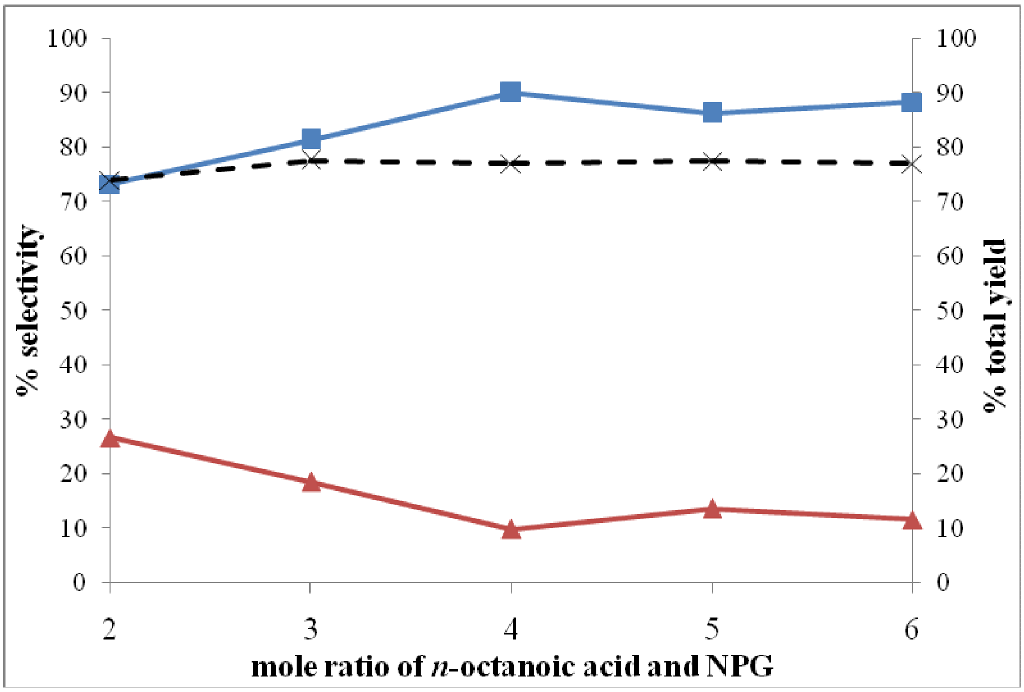


Figure 4.5 Influence of substrate mole ratio on the product yield and selectivity over Amberlyst-15. (Symbols: (▲) NPG monooctanoate selectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

The result from table 4.5 indicated an increasing of the NPG dioctanoate selectivity at mole ratio as 2-4 which this effect theoretical depended on ratio of substrates. The reaction which contained more amount of acid probably promoted higher diester product whereas the increasing higher ratio than 4, performed constantly selectivity. The highest yield was obtained since mole ratio of octanoic acid to neopentyl glycol as 3 was used in the reaction. So, the optimal condition which gave highest diester selectivity was performed at substrate mole ratio as 4.

4.1.6 Effects of catalytic types

The catalytic usages had an impact on the total ester yield and selectivity. The reactions were carried out with various types of catalyst. The catalysts, which were used in the experiments, could be divided to two major groups as homogeneous and heterogeneous catalysts. For heterogeneous catalyst, the catalytic types were firstly parted using substances which they had made from as a consideration. The catalysts consist of two types such as polymeric organic based catalyst and inorganic based catalyst. The polymeric organic based catalysts, which were used in this research, were commercial catalyst *e.g.* Amberlyst-15 and Amberlyst-131. Moreover, the inorganic based catalysts were also studied. Mostly inorganic based catalysts in this research consisted of silica in their structures. The using catalysts were classified into two groups as aluminosilicate material and siliceous material. Thus, the microporous aluminosilicate material, for example ZSM-5, MCM-22 zeolite and Beta zeolite, was investigated. In addition, the siliceous material which used in this research was further classified to other three catalytic types. Firstly, Nafion SAC-13 is the fluorosulfonic acid polymer on amorphous silica. Secondly, the organic functionalized mesoporous materials as SBA-15-$PrSO_3H$ and FSM-16-$PrSO_3H$ were used in the experiment which the difference of two materials is pore size. Lastly, the low cost material bentonite clay was also used this reaction. The clay was initially treated with H_2SO_4 to increase its acidity and dried in the air. Then, it was readily for applying to the reaction. The result of effect on catalytic types was shown in the following Table.

Table 4.6 Effect of catalysts on product yield and selectivity

catalytic type	**% yield**[a] **mono**	**di**	**Total ester yield**	**%selectivity mono**	**di**
Blank	29.6	8.2	37.8	78.3	21.7
H_2SO_4	18.7	63.1	81.8	22.9	77.1
p-Toluene-SO_3H	19.0	58.5	77.5	24.5	75.5
Amberlyst-15	19.8	54.3	74.0	26.7	73.3
Amberlyst-131	40.8	12.3	53.1	76.8	23.2
H-ZSM-5	19.7	3.6	23.3	84.6	15.4
H-MCM-22	18.4	3.2	21.6	85.1	14.9
H-beta	22.1	3.3	25.4	87.1	12.9
Nafion SAC-13	42.1	7.3	49.3	85.2	14.8
SBA-15-$PrSO_3H$	19.8	51.5	71.3	27.8	72.2
FSM-16-$PrSO_3H$	17.6	53.6	71.2	24.7	75.3
H_2SO_4-treated Clay	16.7	53.8	70.5	23.7	76.3

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; reaction time 4hrs.; 3wt.%Amberlyst-15 based on total reaction weight and stirring speed 200 rpm.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

According to Table 4.6, it was shown that homogeneous catalysts, sulfuric acid and para-toluene sulfonic acid, provided highest total yield and diester selectivity. This result could be caused by the homogenity between substrates and catalyst which easiler facilitated catalyst to substrate.

In case of heterogeneous catalysts, the result could be explained by each type. Firstly, the polymeric organic based catalysts, Amberlyst-15 and Amberlyst-131, were investigated due to their commercially usage in many industries. The catalytic performance of Amberlyst-15 obtained high total ester yield and NPG dioctanoate selecitivity. Conversely, the Amberlyst-131 performance exhibited lower total ester yield and promoted more NPG monooctanoate ester. This result might be caused by higher moisture in Amberlyst-131 which introduced hydrolysis process to the reaction. The catalyst characterizations, which were provided by Rohm & Hass co. Ltd., were given in Table 4.7

Table 4.7 Physicochemical and textural properties of ion-exchange resins[a]

Catalyst	**BET area ($m^2 \cdot g^{-1}$)**	**Pore size (Å)**	**Pore volume ($cm^3 \cdot g^{-1}$)**	**Moisture (%)**	**Acid capacity**[b]	**Temp. limit (°C)**
Amberlyst-15 (dry)	53	300	0.4	≤1.5	3.32[c]	120
Amberlyst-131 (wet)	-	-	-	65	4.8	130

[a] Properties provided by the suppliers,
[b] Millimoles of acid centers per gram of catalyst
[c] Analyzed by acid-base titration

Next, the result was focused on inorganic based catalysts, the catalysts could be divided to other two mainly parts as zeolite (aluminosilicate material) and organic supported on siliceous material. In zeolite part, The experiment performed very low total ester yield with no significantly difference as about 21-25% due to diffusion problem. Contrastingly, the NPG monooctanoate selectivity held highest as 87.1%. To give the reason for interpreting this appearance, the physicochemical and textural properties of zeolite would have been firstly renowned. The zeolites, commercial H-ZSM-5, H-MCM-22 and commercial H-Beta, which were used in the reaction, contained SiO_2/Al_2O_3 ratios around 30 that meant the catalyst owned nearly amount of acid capacity. Thus, the properties, which were proposing to be involved with this effect, might be concerned with the zeolite structure and their pore size. So, the physicochemical and textural properties including, zeolite pore structure were shown in Table 4.8 and Figure 4.6, respectively. Moreover, the obtained result had to be discussed together with the molecular size as shown in Table 4.9 which accomplished using Hyper Chem computer program for easier understanding.

Table 4.8 Physicochemical and textural properties of zeolites

Catalyst	**Total specific surface area^{a}($m^2 \cdot g^{-1}$)**	**Micropore distribution, d_p^{b}(nm)**	**External surface area, S_{ext}^{c}($m^2 \cdot g^{-1}$)**	**Micropore volume, V_p^{c}($cm^3 \cdot g^{-1}$)**
H-ZSM-5 (SiO_2/Al_2O_3 = 28.2)	321.98	0.6	40.070	0.1181
H-MCM-22 (SiO_2/Al_2O_3 = 30)	417.86	0.6	64.463	0.1593
H-beta (SiO_2/Al_2O_3 = 30.3)	487.07	0.6	179.71	0.1334

[a] Calculated using the BET plot method,
[b] Calculated using the MP plot method,
[c] Calculated using the t-plot method.

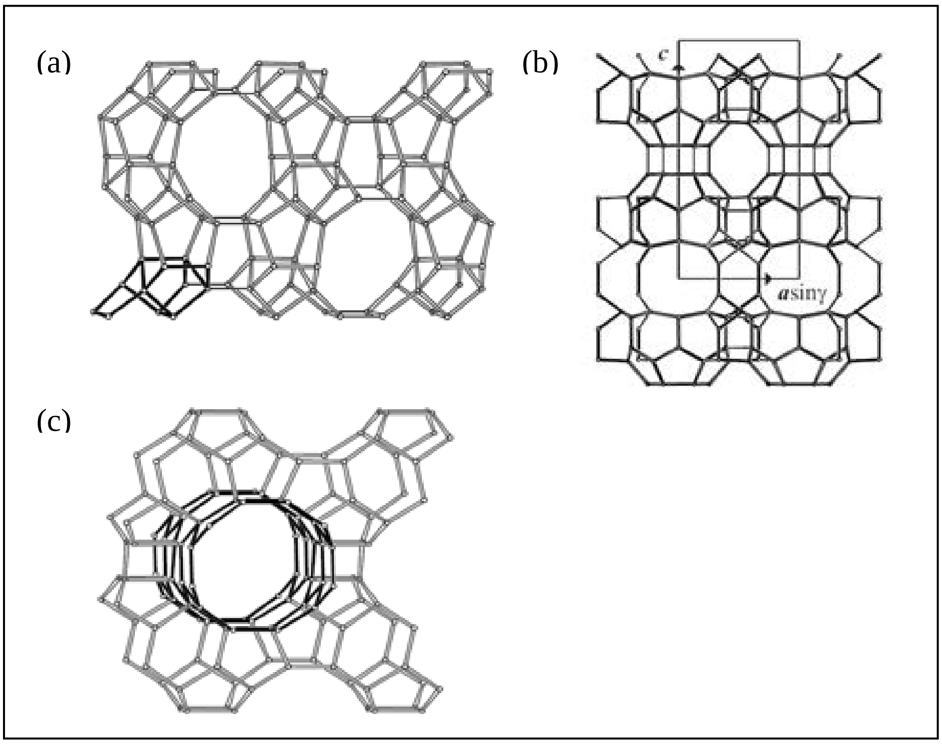


Figure 4.6 Structures of zeolites (a) ZSM-5, (b) MCM-22 and (c) Beta zeolite [53-55].

Table 4.9 Molecular width and length from Hyper Chem

Molecules	Width(nm)	Length (nm)
Neopentyl glycol	0.433	0.489
Octanoic acid	0.532	1.021
NPG monooctanoate	0.479	1.466
NPG dioctanoate	1.328	2.187

The zeolitic physicochemical and textural properties from the Table 4.8 showed theoretical tend according to their pore structure which was defined as 10, 10 and 12 membered rings for H-ZSM-5, H-MCM-22 and H-Beta, respectively. However, the catalysts exhibited the similar pore size distribution as 0.6 nm which were extremely small to perform the reaction in their pore. It seemed like the reaction possibly occurred by entering ability of substrates but the reaction processed by randomly substrate side attacking which caused the reaction gained low yield. For the selectivity, could be explained using similar reason as total ester yield. The extremely small pore size was selective to give NPG monooctanoate ester which had seen from Table 4.9. Both molecular width and length of NPG dioctanoate ester exhibited larger size than the catalytic pore size. So the obtained product would be stuck in the pore and could not leach out. On the other hand, the obtained monoester contained smaller size than the catalyst pore. So, the selectivity of NPG monooctanoate hit the highest value in the experiments.

Lastly, the experiments were investigated another class of catalyst which had effects on the neopentyl glycol and octanoic acid esterification. The catalysts were classified as organic supported on siliceous material which had already descriped in the former paragraph. For these experiments, the commercial Nafion SAC-13 catalyst was obtained from sigma-aldrich, the SBA-15-PrSO$_3$H, FSM-16-PrSO$_3$H and acid treated clay was prepared in laboratory which clay sample was provided from Mr. Somyod Kedpokasiri, a member of laboratory group. According to the result in Table 4.6 exhibited that this catalytic type enhanced high total ester yield as same as the product which was obtained from the catalyzed reaction by Amberlyst-15 except the Nafion SAC-13 performed low total ester yield as 49.3 %. This effect could be explained by amount of its acid strength which would be presented in Table 4.10.

Table 4.10 Acid value of catalysts

Catalysts	Acid strength (mmol/g)
Nafion SAC-13[a]	0.12
Amberlyst-15[b]	3.32
SBA-15-Pr-SO_3H[b]	1.48
FSM-16-Pr-SO_3H[b]	1.18
Treated Clay[b]	7.00

[a] Acid strength provided by DuPont.
[b] Acid strength determined by acid-base titration.

As a result from Table 4.10, the acid strength of Nafion SAC-13 provided the lowest value comparing with other catalysts. The low acidity of catalyst theoretical appeared low total ester yield because there was not enough acidity to accelerate forward reaction to give higher yield. Moreover, it was interested that this catalyst exhibited high NPG monooctanoate selectivity. So, this effect might be caused by the same reason as the effect of total yield which the obtained acidity on catalyst mostly accelerated the first step esterification reaction and gave high monoester selectivity as shown in the result.

The result of other three catalysts conducted to interpret more in explanation. The result performed high total ester yield and NPG dioctanoate selectivity as same result as Amberlyst-15. Although, there were lower acidity on the SBA-15-PrSO_3H and FSM-16-PrSO_3H comparing to Amberlyst-15 but they obtained contained surface area than Amberlyst-15. The surface area of SBA-15-PrSO_3H and FSM-16-PrSO_3H were higher than that Amberlyst-15 as about 6 times or more. This property might be the main reason which was significant for explanation. Because of their high surface area, the catalyst might act the similar behavior to homogeneous catalyst which the substrates could be approached to the acid site easier than the low surface area catalyst. So, The SBA-15-PrSO_3H and FSM-16-PrSO_3H resulted high total ester yield as about 71% and high NPG diester selectivity as 72.2 % for SBA-15-

$PrSO_3H$ and 75.3 % for FSM-16-$PrSO_3H$ whereas, the acid treated clay exhibited the similar result to both previous catalysts. The reason for this effect also might be more acid site than the other catalysts. Thus, the acid treated clay exhibited the total ester yield and NPG dioctanate selectivity as 70.5 and 76.3 %, respectively.

Since the synthetic SBA-15-$PrSO_3H$, FSM-16-$PrSO_3H$ and acid treated clay performances reached the similar result as Amberlyst-15. The kinetic studies of these three catalysts were investigated to optimize the reaction condition for energy saving and catalytic development.

4.1.7 Kinetic study on the esterification over sulfonic functionalized materials.

For the completely comparable on the activity, this study focused on the catalytic performance of the catalysts which were functionalized grafted sulfonic group in their material. So, the treated clay was not investigated in this study due to their supporting only sulfuric acid and unclearly well-known.

This study performed using exactly the same as the optimal condition which was obtained from varying effects over Amberlyst-15 except the reaction time. The reaction time as 30 min was used in this experiment in order to avoid other effects which might be involving in the reaction and disturbing the study. Thus, the result was shown in Table 4.11

Table 4.11 The study on product yield, product selectivity, initial rate, TON and TOF

Catalyst type	**Total ester yield**	**%selectivity**		**TON**	**TOF**	**initial rate[a]**		
		mono	**di**		**(min^{-1})**	**r_m**	**r_d**	**r_p**
Amberlyst-15	63.1	78.1	21.9	25.38	0.85	0.36	0.06	0.42
SBA-15-$PrSO_3H$	60.3	32.7	67.3	44.89	1.50	0.14	0.19	0.33
FSM-16-$PrSO_3H$	58.2	53.9	46.1	59.77	1.99	0.23	0.12	0.35

[a] unit as mmol min^{-1}

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; reaction time 0.5 hr.; 3wt.% Amberlyst-15 based on total reaction weight and stirring speed 200 rpm.

TON=Turnover number,

TOF=Turnover frequency,

r_m, r_d, r_p amount of occurring product per minute.

Table 4.11 showed the total ester yield and selectivity of NPG monooctanoate and dioctanoate, including TON, TOF and product initial rates. For this experiment, TON and TOF were calculated using total ester yield instead of conversion because it appeared only product in the analysis. The result exhibited that FSM-16-PrSO$_3$H ranked highest TON and followed by SBA-15-PrSO$_3$H which Amberlyst-15 stood at the last place. So, the result referred that the synthesized FSM-16-PrSO$_3$H accelerated highest amount of esters product to an acid site comparing with other two catalysts. Although, FSM-16-PrSO$_3$H gained highest kinetic activity per acid site but the SBA-15-PrSO$_3$H gave highest an expected product (NPG dioctanoate). The synthesized SBA-15-PrSO$_3$H performed the most selective catalyst because it was activated to give diester product higher than Amberlyst-15 and FSM-16-PrSO$_3$H about 3 and 1 time, respectively. The possibly reasons were explained by the catalytic surface area and their pore size. The characteristic details of catalysts, which involved in the experiment discussion, were shown in Table 4.12.

Table 4.12 Physicochemical and textural properties of Amberlyst-15 and synthesized materials

Catalyst	**BET area ($m^2 \cdot g^{-1}$)**	**Pore size (Å)**	**Pore volume ($cm^3 \cdot g^{-1}$)**	**Acid strenght (mmol/g)^c**
Amberlyst-15 (dry)	53	300	0.4	3.32
SBA-15-PrSO$_3$H	295.89^a	86.0^b	0.6^b	1.48
FSM-16-PrSO$_3$H	569.55^a	24.3^b	0.7^b	1.18

^{a}Calculated using the BET plot method,
^{b}Calculated using the BJH method,
^{c}Acid strength determined by acid-base titration.

In case of FSM-16-PrSO$_3$H which promoted highest TON and TOF, the surface area played an important role to cause this effect. The observation was found that higher surface area would prolong higher amount of total esters product. As seen in the Table 4.12, the surface area of FSM-16-PrSO$_3$H run the first place and followed by SBA-15-PrSO$_3$H and Amberlyst-15, respectively which this rank tended the same pattern as the obtained TON as 59.77, 44.89 and 25.38.

On the other hand, the selectivity of NPG dioctanoate did not behave the same trend as TON, it was surprising that the synthesized SBA-15-PrSO$_3$H acted as the best catalyst which was selective to promote this diester product. The reason might be given using catalytic pore size as an explanation which it was concerned with the NPG dioctanoate width as 2.187 nm. Comparing between SBA-15-PrSO$_3$H and FSM-16-PrSO$_3$H, the pore size of SBA-15-PrSO$_3$H exhibited about 3.6 times larger than another catalyst pore size but it was not significant as well as the 2.43 nm pore size of FSM-16-PrSO$_3$H which comprised equally small as the product width. Owing to this reason, it performed difficult accessibility of product leaching out which meant the FSM-16-PrSO$_3$H revealing lower NPG dioctanoate selectivity. In the event of Amberlyst-15, which performed lowest diester selectivity, it might be explained by its shape and surface area. Firstly, The Amberlyst-15 shape is a rounded particle and quite bigger than the other two catalysts particle, which gave more difficulty for substrate accessibility, even though they contained larger pore size than other catalysts. Lastly, the low catalytic surface was the essential reason which Amberlyst-15 spent more time to accelerated the reaction. The low catalytic surface area exhibited the low amount of substrate which contacted tothe acid site.

As a result, SBA-15-PrSO$_3$H was selected as a catalyst in this esterification due to its selective to NPG dioctanoate ability. Moreover, it exhibited high total ester yield. Thus, this research would focus on the synthesis of SBA-15-PrSO$_3$H and adjust the reaction to obtain the optimal condition.

4.2 Synthesis and Functionalization of SBA-15

4.2.1 The physico-chemical properties of synthesized materials

4.2.1.1 XRD results

The diffractograms, which were measured at low angle X-ray powder diffraction of the synthesized mesoporous materials, were shown in Figure 4.7. After the template triblock copolymer was removed from the material pores, the synthesized SBA-15 showed hexagonal characteristic as one very intense peak and two weak peaks which were indexed the miler plane to (100), (110) and (200) diffractions, respectively. The intense peak indicated that the prepared materials contained well-ordered hexagonal structure [41]. In case of SBA-15-PrSO_3H., Its diffractogram exhibited the similar characteristic pattern as SBA-15. The functionalized SBA-15 diffractogram was compared to pure synthesized material SBA-15, the SBA-15-PrSO_3H diffraction peaks exhibited the lower intensity which this appearance might be explained due to the increasing of organic group in its structure that occurred a few distortion of plane. Moreover, the functionalized SBA-15 would have passed the oxidation and acidify step which might decrease its crystallinity. Additionally, the result found that the sulfonic functionalized SBA-15 diffractogram was slightly shifted to higher 2 theta values, which indicated the presence of bulky functional group on the SBA-15 surface would decrease its pore volume.

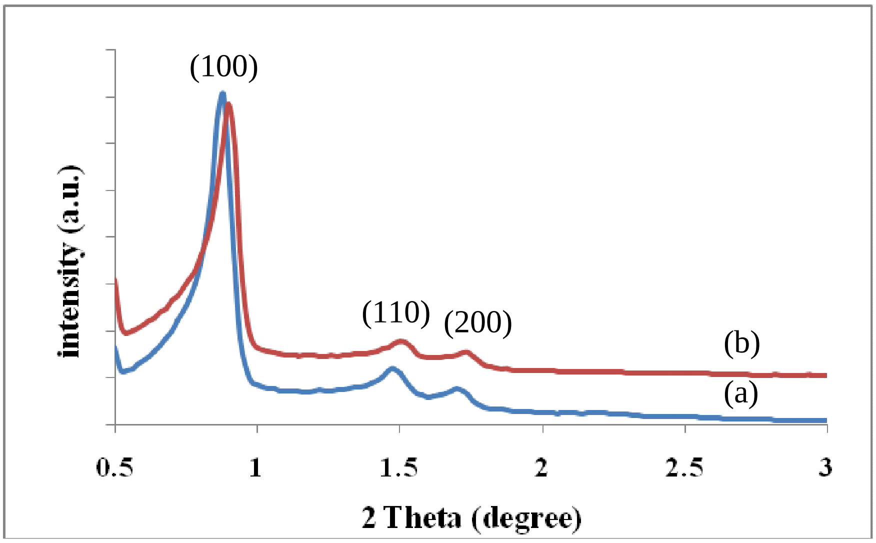


Figure 4.7 X-ray diffractograms of (a) SBA-15, (b) SBA-15-PrSO_3H

4.2.1.2 Sorption properties of synthesized materials

Figure 4.8 showed the N_2 adsorption-desorption isotherm and pore size distribution of synthesized SBA-15 and sulfonic functionalized SBA-15. The materials exhibited hysteresis loop H1-type from type IV adsorption isotherm of IUPAC classification which were a characteristic pattern of mesoporous material [56]. Some physical properties, which was derived from the Brunauer, Emmett and Teller

(BET) equation of SBA-15 and sulfonic functionalized specimens, were revealed in Table 4.13. The total specific surface area of materials was calculated using BET method, which was reported as 696 $m^2.g^{-1}$ and 296 $m^2.g^{-1}$, respectively. The pore size distribution of the synthesized materials was evaluated using Barrett-Joiner-Halenda (BJH) method which exhibited values as 9.23 and 8.06, respectively. The SBA-15-$PrSO_3H$ exhibited lower surface area and mesopore volume comparing with the pure SBA-15 which it caused by transferring of the organo sulfonic functional into pore structure. So, the result was corresponding with their intensities of XRD pattern in previous results. The organic group did not decrease only mesopore volume, it also induced decreasing of surface area and pore size.

Table 4.13 Textural properties of SBA-15 and sulfonic functionalized SBA-15.

Catalyst	Total specific surface area[a]($m^2 \cdot g^{-1}$)	Pore size distribution[b] (nm)	Mesopore volume[b]($cm^3 \cdot g^{-1}$)	d_{100}[c] (nm)	Wall thickness[d] (nm)
SBA-15	696	9.23	1.0013	10.07	2.3978
SBA-15-$PrSO_3H$	296	8.06	0.6543	9.84	3.3022

[a] Calculated using the BET plot method,
[b] Calculated using the BJH method,
[c] Calculated using XRD, Jade 5.6,
[d] Calculated as: a_0-pore size ($a_0 = 2 \times d_{(100)} / \sqrt{3}$)

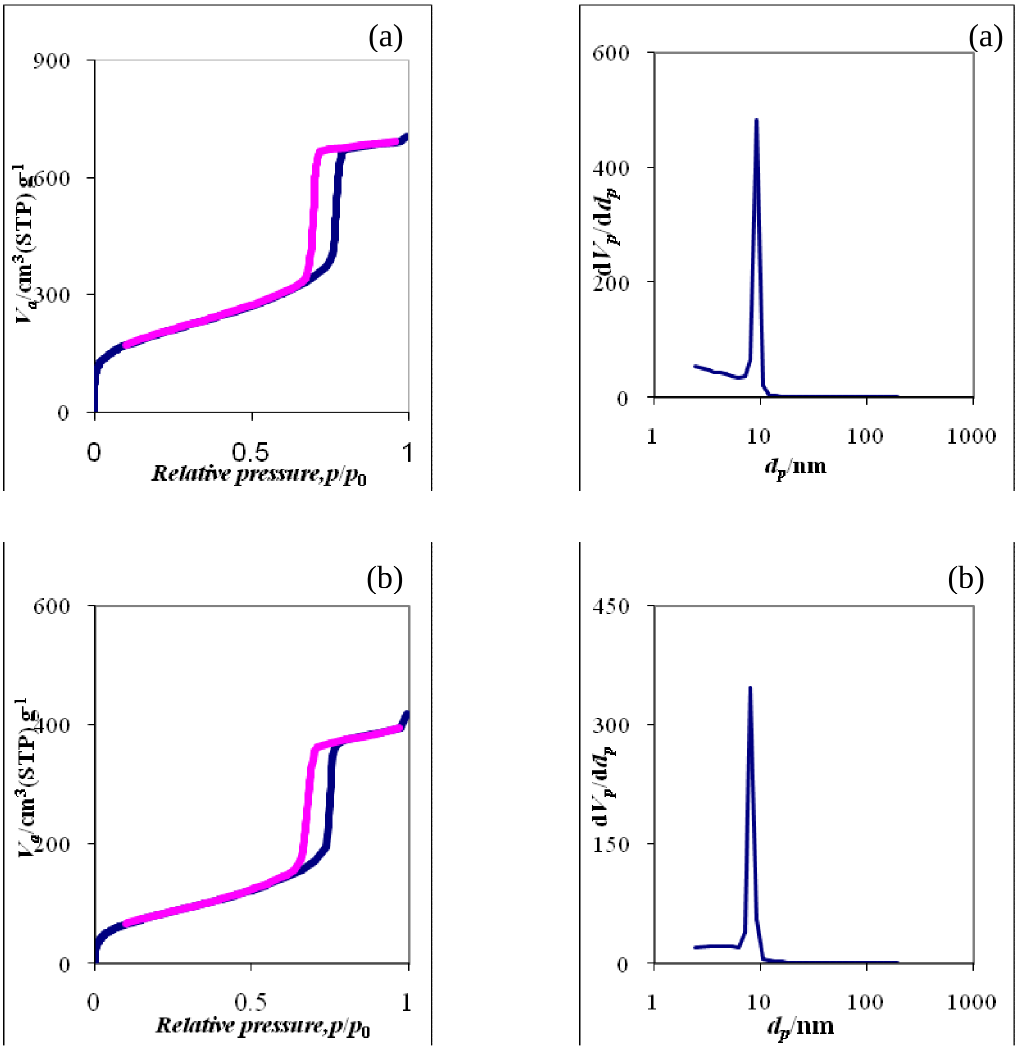


Figure 4.8 N_2 adsorption-desorption isotherm and pore size distribution of (a) SBA-15 and (b) SBA-15-$PrSO_3H$

4.2.1.3 SEM images

The SEM images of SBA-15 and its sulfonic functionalized SBA-15-$PrSO_3H$ were displayed in Figure 4.9. The morphology of SBA-15 was uniform rope-like clearly edge particle shape aggregation. In addition, the particle was scaled and averaged their size as 0.8 × 0.6 μm. In case of SBA-15-$PrSO_3H$, the specimen particles aggregated the similar rope-like structure to SBA-15 with the average particle size performed as 0.9× 0.7 μm. However, The SBA-15-$PrSO_3H$ image exhibited slightly non-uniform particle and unclearly edge as pure SBA-15 because functionalization step via oxidation and acidification which might destruct some structure of SBA-15. Thus, this observation was involving in XRD result which obtained lower intensity in diffractogram of SBA-15-$PrSO_3H$.

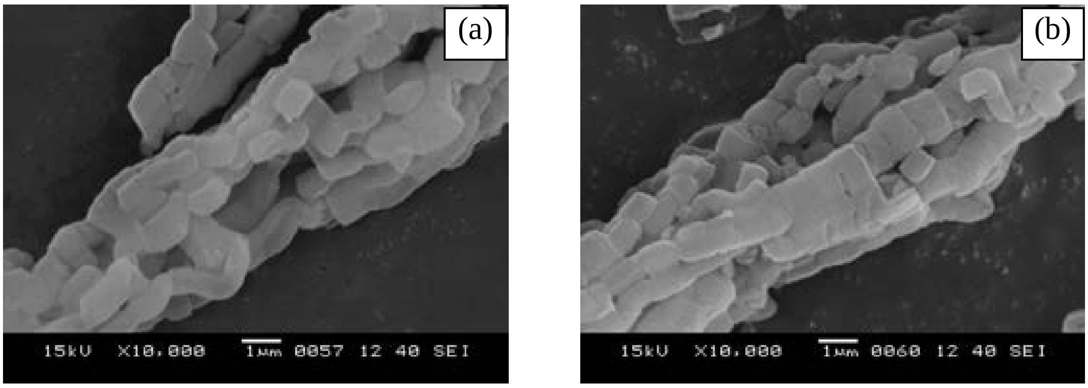


Figure 4.9 SEM images of (a) SBA-15 and (b) SBA-15-$PrSO_3H$

4.3 The esterification over SBA-15-$PrSO_3H$

4.3.1 Condition optimization of neopentyl glycol and octanoic acid esterification over SBA-15-$PrSO_3H$

From 4.1.6 the result exhibited that the synthesized SBA-15-$PrSO_3H$ performed excellent activity which gave highest NPG dioctanoate selectivity. So the synthesized catalyst was detected in the reactions to optimize condition. The experiments were adjusted using the previous optimal condition which obtained by Amberlyst-15 catalyst. The reaction time was varied to compare with Amberlyst-15. The result was shown in Table 4.14.

Table 4.14 Effect of reaction time on product yield and selectivity using SBA-15-$PrSO_3H$

Time	% yield[a] mono	% yield[a] di	Total ester yield	% selectivity mono	% selectivity di
15 mins	31.1	35.9	67.1	46.4	53.6
30 mins	23.9	45.6	69.4	34.4	65.6
45 mins	21.8	48.8	70.6	30.8	69.2
1 hrs.	21.2	52.8	74.0	28.7	71.3
2 hrs.	17.5	56.7	74.1	23.6	76.4
3 hrs.	18.4	57.4	75.8	24.3	75.7

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80 °C; 3wt.% SBA-15-$PrSO_3H$ based on total reaction weight and stirring speed 200 rpm.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

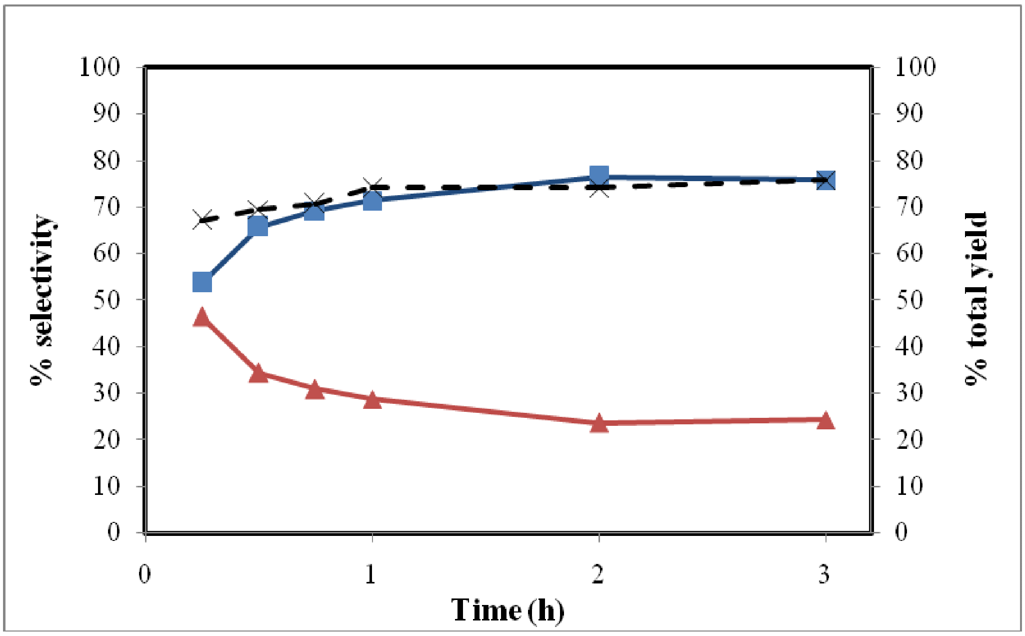


Figure 4.10 Influence of reaction time on the product yield and selectivity over SBA-15-$PrSO_3H$. (Symbols: (▲) NPG monooctanoate selectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

The experimental result revealed the influences of reaction time on the product yield were slightly increased with longer reaction time until it was kept constant after 1 hrs as about 74%. Moreover, the NPG dioctanoate selectivity was rapidly increased within 30 mins. Then, it was slightly increased until the time was at

2 hrs. and finally, stayed constantly from 2-3 hrs around 76%. However, the reaction exhibited similar activity as Amberlyst-15 at 2 hrs. Whereas the Amberlyst- 15 catalyzed reaction spent a long time as 4 hrs. The synthesized SBA-15-PrSO_3H took a time shorter than Amberlyst-15 catalyzed reaction. Thus, the optimal condition would be performed at 2 hrs. over 3wt% of SBA-15-PrSO_3H based on the total reaction weight which promoted high NPG dioctanoate selectivity as 76.4%.

4.3.2 Effect of substrates mole ratio

This experiment focused on the mole ratio of octanoic acid to neopentyl glycol on the esterification over SBA-15PrSO_3H to study ratio which gave the highest total ester product and diester selectivity. The reactions performed by varying mole ratio of octanoic acid to neopentyl glycol in the range of 2 to 6. The result was shown in Table 4.5.

Table 4.15 Effect of substrates mole ratio on product yield and selectivity

mole ratio of octanoic acid to neopentyl glycol	**%yield[a]**		**Total ester yield**	**%selectivity**	
	mono	**di**		**mono**	**di**
2	17.5	56.7	74.1	23.6	76.4
3	16.0	62.6	78.6	20.4	79.6
4	8.5	69.6	78.1	10.9	89.1
5	10.0	68.7	78.7	12.7	87.3
6	9.2	69.3	78.5	11.7	88.3

Esterification conditions: reaction temperature 80°C; reaction time 4 hrs.; 3wt.% SBA-15PrSO_3H based on total reaction weight and stirring speed 200 rpm.
[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

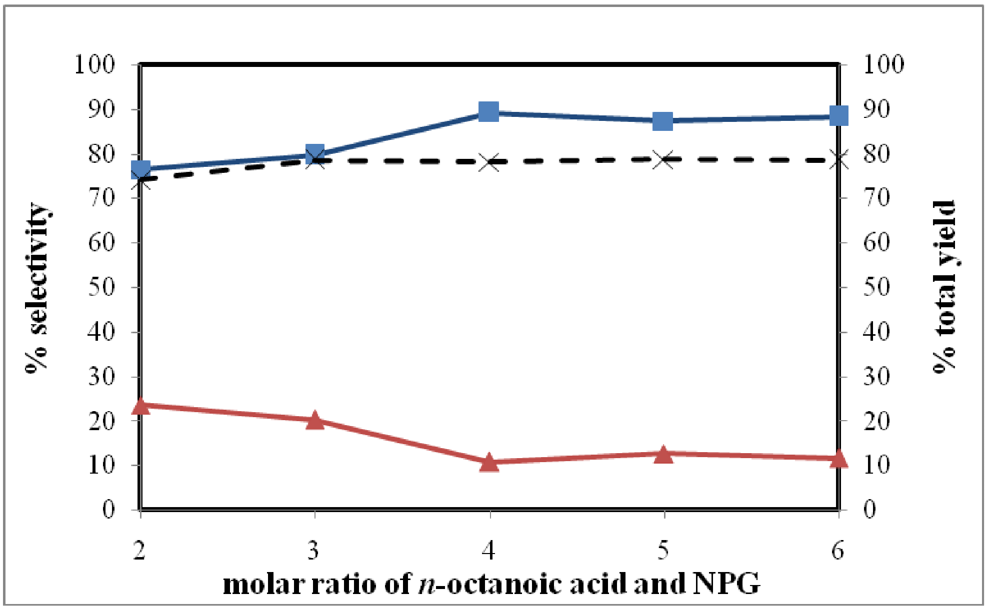


Figure 4.11 Influence of substrate mole ratio on the product yield and selectivity over SBA-15-PrSO$_3$H. (Symbols: (▲) NPG monooctanoate selectivity, (■) NPG dioctanoate selectivity and (×) total ester yield)

According to table 4.15, the result indicated an increasing mole ratio of octanoic acid to neopentyl glycol as 2-4 conducted higher the NPG dioctanoate selectivity. The reaction which contained high amount of acid probably promoted more diester product whereas the increasing higher ratio than 4, performed constant selectivity. Although the total product yield exhibited the similar way as the selectivity but the highest yield was obtained as 78.6% since mole ratio of octanoic acid to neopentyl glycol as 3 was carried on the reaction. However, this result was very similar to this kind of effect on the reaction over Amberlyst-15. Thus, the optimal condition which performed at substrate mole ratio as 4, hit highest diester selectivity as 89.1%.

4.3.3 Effects of monocarboxylic acid chain length

The effects of carbon chain length of various monocarboxylic acids esterification with neopentyl glycol were studied using butyric acid, octanoic acid and lauric acid with the number of carbon atom of 4, 8 and 12, respectively. The reactions were performed in similar condition to study intensively in the effect. The result was shown in Table 4.16.

Table 4.16 Effect of monocarboxylic acid chain length on product yield and selectivity

carboxylic acid	% ester yield		total ester yield	% selectivity	
	mono	**di**		**mono**	**di**
Butyric acid ($C_4H_8O_2$)	14.0	56.4	70.4	19.9	80.1
Octanoic acid ($C_8H_{12}O_2$)	17.5	56.7	74.1	23.6	76.4
Lauric acid ($C_{12}H_{24}O_2$)	22.1	50.4	72.5	30.5	69.5

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80 °C; reaction time 2 hrs.; 3wt.% SBA-15PrSO$_3$H based on total reaction weight and stirring speed 200 rpm.
[a]*Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

According to Table 4.16, the selectivity of diester product tended to slightly decrease with higher number of carbon atom in acid molecule. This effect might cause by the molecule size which needed more activation energy to perform the esterification in case high molecular size [5]. Thus, the selectivity of diester of butyrate, octanoate and laurate ester decreased as 80.1, 76.4 and 69.5 %, respectively. Conversely, the total ester yield exhibited uncertainty trend which could split the reason comparing with the esters yield from esterification of neopentyl glycol and octanoic acid. Hence, the total ester yield of butyrate and octanoate esters was firstly discussed. The result found that the ester yield did not tend theoretically because the excess energy, which perfomed in the neopentyl glycol and butyic acid esterification, induced the occurring of disproportionation as discussed in topic 4.1.1. On the other hand, comparison between esterification of octanoic acid and lauric acid with neopentyl glycol was secondly focused on. It was theoretically going on with the result. The smaller amount of ester yield, which obtained from lauric acid esterification, might cause by deficiency of energy to promote diester product.

4.3.4 Effects of structure of alcohol

Two kinds of alcohols with different structure, neopentyl glycol (NPG) and trimethylol propane (TMP), were investigated in esterification with octanoic acid using the optimal condition catalyzed by SBA-15-PrSO$_3$H at 80°C for 2 hrs and stirring speed 200 rpm. The mole ratio of starting material in experiment depended on amount of hydroxyl group in molecule. For the experiments, the dihydric alcohol (NPG) was performed using theoretical octanoic acid to NPG ratio as 2 whereas the trihydric alcohol (TMP) was also carried out using theoretical octanoic acid to TMP ratio as 3. The result was seen in Table 4.17.

Table 4.17 Effect of structure of alcohol on product yield and selectivity

Alcohol	**% ester yield**			**total ester yield**	**% ester selectivity**		
	mono	**di**	**tri**		**mono**	**di**	**tri**
NPG	17.5	56.7	-	74.1	23.6	76.4	-
TMP	32.4[a]	27.5[b]	1.1[c]	61.0	53.1	48.1	1.8

[a] estimate by using NPG monoocanoate calibration curve
[b] estimate by using NPG diocanoate calibration curve
[c] calculation by separated yield from column chromatography

In case of the product from esterification of octanoic acid with TMP, the obtained products were quantified based on TMP mono- and dioctanoate peak area of GC. Anyway, the product structures, TMP monooctanoate and TMP dioctanoate, were identified using GC-MS, the spectra was shown in appendix A-9-A-10. In order to the TMP trioctanoate can be separated, the triester product was identified using ^{1}H-NMR and ^{13}C-NMR. Therefore, the result from table 4.17 obtained total ester yield and its selectivity. The experiment exhibited that the optimal condition was perfectly suitable for the esterification of octanoic acid with NPG whereas the other reaction found lower ester yield. This effect might be explained by energy applying for the reaction because TMP consists of three hydroxyl group which performed more hydrogen bond strength. The deficiency of applying energy might cause the lower yield. In order to the ester selectivity of TMP esterification, it indicated that the monoester product was mostly promoted because they owned higher probability for accessed by octanoic acid. So, the monoester hit the highest selectivity for this reaction. Conversely, the triester product was rarely obtained in this reaction. The effect could be also described by the applying energy explanation. Moreover, it could be explained by its steric molecule.

4.4 Catalyst reusability

The mainly advantage of heterogeneous catalysts usage is easy to separate and can be reused in the successive catalytic cycles. In this research, SBA-15-PrSO_3H was the best catalyst for the esterification of octanoic acid and neopentyl glycol. The catalyst was tested its reusability by using several times in the optimal condition for esterification. After the reaction completed, the catalyst was filtered, washed with two solvents (hexane and acetone) to remove substances, products and other by-products which were adhering on the surface and catalytic active site. Then, the washed catalyst was dried at 100 ºC overnight and reused. Moreover, the used and regenerated catalysts were characterized before testing in the subsequence reactions.

4.4.1 Characterization of used catalysts

4.4.1.1 XRD result

The XRD diffractograms of fresh and used SBA-15-PrSO_3H catalysts which had been already washed with two solvents were shown in Figure 4.11. The diffractograms exhibited similar three characteristic peaks of hexagonal phase to the fresh SBA-15-PrSO_3H catalyst. Moreover, it was found a few lower intensity of the one very intense peak (100) and the two weak peaks indexed to (110) and (200) diffractions of reused catalysts comparing with fresh catalyst. This effect might be caused by the adhering of organic substances on the catalyst surface.

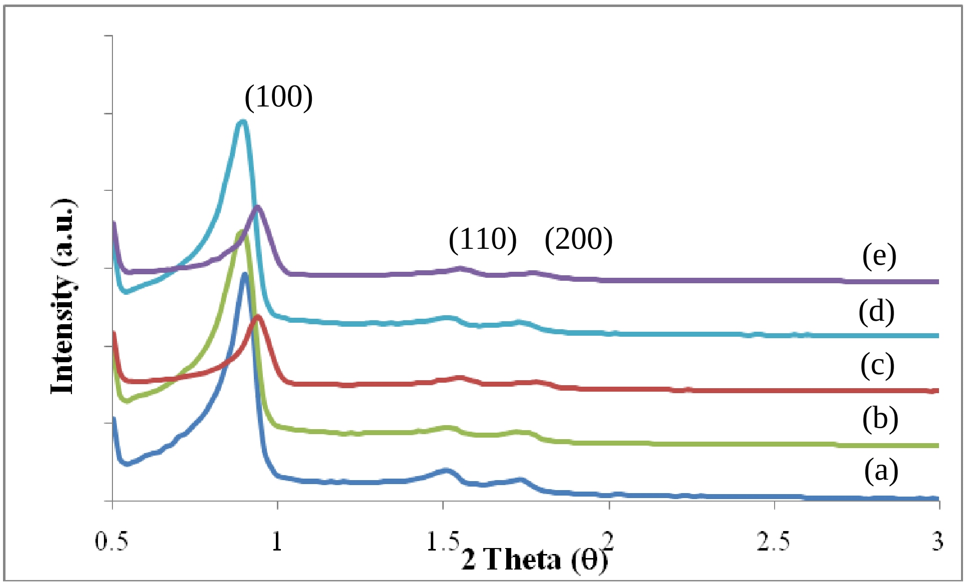


Figure 4.12 X-ray diffractograms of (a) SBA-15 $PrSO_3H$, (b) 1st used SBA-15-$PrSO_3H$ washed with hexane, (c) 2nd used SBA-15-$PrSO_3H$ washed with hexane, (d) 1st used SBA-15-$PrSO_3H$ washed with acetone, (e) 2nd used SBA-15-$PrSO_3H$ washed with acetone

4.4.1.2 Sorption properties of used catalysts

The result showed the similar characteristic adsorption-desorption isotherms of all used catalysts as mesoporous materials. The physical properties and acid strength of the catalysts were exhibited in Table 4.18. It was found that the catalysts which were washed by hexane contained higher surface area and pore volume than the acetone washed catalysts. The decreasing of surface area and pore volume might cause by the blockage of remaining organic molecules inside the mesoporous pore. Although, the hexane washed catalysts performed nearly surface area as fresh catalyst but they were showing the decreasing of pore volume. Additionally, the blockage of organic substances could be also observed by the decreasing of mesopore volume.

Table 4.18 Textural properties of fresh and used SBA-15-PrSO_3H.

Catalyst	Total specific surface area[a]($m^2 \cdot g^{-1}$)	Pore size distribution[b] (nm)	Mesopore volume[b] ($cm^3 \cdot g^{-1}$)	Acid strength (mmol/g)
Fresh	296	8.06	0.654	1.48
Hexane				
1st used	296	7.05	0.610	1.02
2nd used	294	7.05	0.556	0.83
Acetone				
1st used	268	7.05	0.576	0.99
2nd used	267	7.05	0.525	0.68

[a]Calculated using the BET plot method,
[b]Calculated using the BJH method

4.4.2 The performance of reused SBA-15-PrSO_3H

The catalytic performances of reused catalyst were shown in Table 4.19. The experiments were carried out using various catalysts with difference washing solvent. The reactions were performed using optimal condition from previous investigation.

Table 4.19 The catalytic performance of reused SBA-15-PrSO_3H

-Catalyst	%yield[a]		Total ester yield	%selectivity	
	mono	di		mono	di
Fresh	17.7	56.8	74.5	23.8	76.2
Hexane					
1st used	19.7	52.8	72.5	27.2	72.8
2nd used	18.0	49.5	67.5	26.6	73.4
Acetone					
1st used	21.3	50.2	71.5	29.8	70.2
2nd used	19.6	47.8	67.4	29.0	71.0

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; reaction time 2 hrs.; 3wt.% SBA-15PrSO_3H based on total reaction weight and stirring speed 200 rpm.
[a]*Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

The result exhibited that the hexane washed catalyst observed higher diester selectivity than the acetone washed catalyst. The effect could be explained by the polarity of solvent which used for washing. It was well-known that hexane is non-polar solvent whereas the product and substrate held low polarity which could be better dissolved than acetone. As a result in Table 4.18, it was found the lower pore volume which the product might be stuck in catalyst pore. On the other hand, the acetone is an intermediate solvent which was not suitable for washing the catalyst in the reaction. Moreover, Acetone might cause the lower acid strength which might not be performed well in the reaction. Thus, the reaction result exhibited the lower total ester yield and diester selectivity. The hexane was selected to use for washing the catalyst in subsequent reaction.

4.4.3Characterization of regenerated catalysts

4.4.3.1 XRD result

The result from Figure 4.13 showed three characteristic peaks of hexagonal phase like the fresh catalyst. Additionally, the one very intense peak (100) and the two weak peaks indexed to (110) and (200). However, regenerated catalyst showed lower intensity than the pure catalyst in order to the blockage of organic substances in the mesoporoe structure.

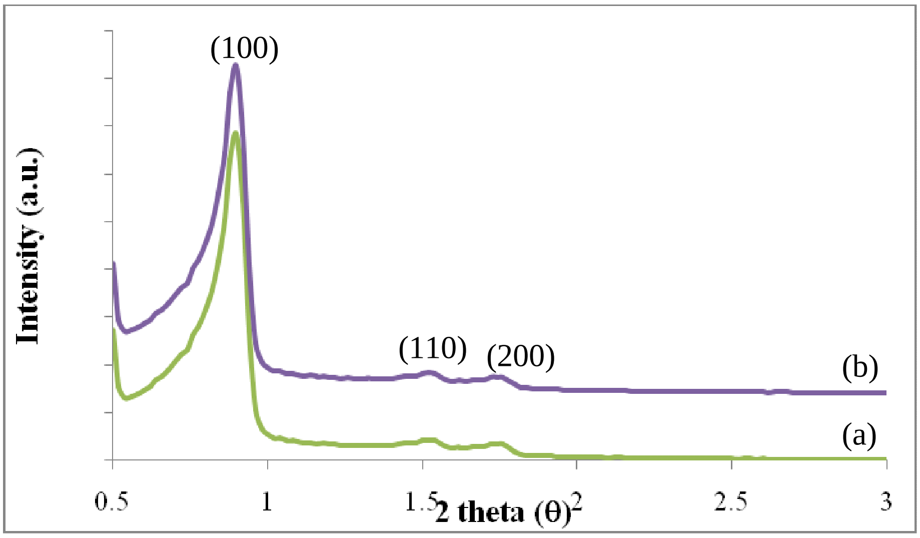


Figure 4.13 X-ray diffractograms of (a) fresh (b) regenerated SBA-15-PrSO_3H.

4.4.3.2 Sorption properties of regenerated SBA-15-PrSO$_3$H

The adsorption-desorption isotherms of all catalysts showed the characteristic isotherm of mesoporous materials. The regenerated catalyst contained lower surface area comparing with the fresh one (295.89 m^3/g). However, the fresh catalyst exhibited the higher acid strength than the used catalyst which might facilitate the esterification to be higher activity than the used catalyst.

Table 4.20 Textural properties of regenerated SBA-15-PrSO$_3$H.

Catalyst	**Total specific surface area^a(m^2·g^{-1})**	**Pore size distribution^b (nm)**	**Mesopore volume^b (cm^3·g^{-1})**	**Acid strength (mmol/g)**
Fresh	296	8.06	0.654	1.48
Hexane				
1st used	296	7.05	0.610	1.02
2nd used	294	7.05	0.556	0.83
Regenerated	265	7.05	0.524	1.39

^{a}Calculated using the BET plot method,
^{b}Calculated using the BJH method.

4.4.3.3 The performance of reused SBA-15-PrSO$_3$H

The regeneration step was developed in order to improve its catalytic performance. As seen in Table 4.21, the result exhibited 7% decreasing of total ester yield after the catalyst was used in the second time. However, the regenerated catalyst could increase the total ester yield due to its higher acid strength. Thus, the catalytic performance performed nearly the same as the fresh catalyst. Additionally, the result was observed the lower total ester yield and diester selectivity which could be explained due to the destructive of the catalyst structure by the regeneration step.

Table 4.21 The catalytic performance of regenerated SBA-15-PrSO_3H

Catalyst	%yield[a]		Total ester	%selectivity	
	mono	di	yield	mono	di
Fresh	17.7	56.8	74.5	23.8	76.2
Hexane					
1st used	19.7	52.8	72.5	27.2	72.8
2nd used	18.0	49.5	67.5	26.6	73.4
Regenerated	19.0	52.1	71.1	26.8	73.2

Esterification conditions: octanoic acid / neopentyl glycol mole ratio as 2; reaction temperature 80°C; reaction time 2 hrs.; 3wt.% SBA-15PrSO_3H based on total reaction weight and stirring speed 200 rpm.

[a] *Deviation within 0.6% (experiments) and 0.7% (GC analysis)*

CHAPTER V

CONCLUSIONS

The resulted optimal condition in the esterification of neopentyl glycol and octanoic acid catalyzed by Amberlyst-15 was obtained successfully from this research. The reaction could be excellently performed at 80 ^{o}C for 4 hours with stirring speed 200 rpm using 3 wt. % of Amberlyst-15 based on total reaction weight in stainless steel batch reactor which gave high total ester yield as 74.0% and 73.3% of NPG dioctanoate ester selectivity using the octanoic acid to neopentyl glycol mole ratio as 2. Whereas the highest ester yield and diester selectivity could be perceived over the similar parameters as in the optimal condition except the octanoic acid to neopentyl glycol mole ratio which were changed to 4. On the other hand, the synthesized catalysts, SBA-15-PrSO_3H and FSM-16-PrSO_3H, performed almost the same performance as Amberlyst-15. So, the study of initial rate, TON and TOF indicated that SBA-15-PrSO_3H showed the highest initial rate of NPG dioctanoate amount as 0.19 within 30 minutes.

The SBA-15-PrSO_3H was successfully prepared via hydrothermal method and post synthesis with propyl sulfonic grafting method. The resulted catalyst was confirmed by following characterization: The X-ray diffractograms, showed the characteristic hexagonal structure, the N_2 adsorption-desorption, exhibited type IV isotherms which meant the mesoporous structure was obtained and the SEM image, displayed aggregated particles with rope-like structure. Moreover, the synthesized catalyst contained the highest acid strength as 1.48 mmol/g.

In order to their high surface area, acid strength and initial rate of occurring diester product, The SBA15-PrSO_3H was applied to the reaction and adjusted the optimal condition. Finally, the optimal condition was performed at 80 ^{o}C with stirring speed 200 rpm using 3 wt. % of SBA15-PrSO_3H based on total reaction weight which the reaction time was reduced time as only 2 hours to give nearly the same catalytic activity as Amberlyst-15. So, the result showed 74.1% total ester yield and 76.9% of diester selectivity. Additionally, the esterification with difference molecular size of monocarboxylic acid and alcohol type significantly affected to the total ester yield and diester selectivity due to the different requirement of energy in each reaction.

The activity of reused catalysts indicated the catalytic performance gradually decreased after performing in the reaction. Although, the total ester yield decreased but the diester selectivity still kept nearly constant around 73-76% in case the catalysts were washed with hexane. So, the hexane washed catalyst was found higher performance than acetone washed catalyst which this SBA15-$PrSO_3H$ could be reused for two cycles. After the catalyst was regenerated, the activity gained higher total product yield.

The suggestion for future work

1. Modify the SBA-15-$PrSO_3H$ to give its higher stability and more cycle in reuse process.
2. Optimize the reaction conditions for NPG dilaurate synthesis.
3. Study on acidic modification of porous material with other alkyl sulfonic acid groups to improve the activity of catalyst.

REFERENCES

[1] M.Sc. Suwanwuttiwat, C. “Synthesis of polyol ester lubricating base oil” Program of Petrochemical and Polymer science, Chulalongkorn University, 1997.

[2] M.Sc. Panchoowong, K. “Synthesis of synthetic diester lubricating agent from fatty acid” Program of Petrochemical and Polymer science, Chulalongkorn University, 1999.

[3] S.J. Miller, S.A. Elomari (2008) *WO2008/100822A2*.

[4] S.J. Miller, S.A. Elomari (2008) *US2008/0248982A1*.

[5] Vahteristo, K.; Laari, A.; Haario, H. and Solonen, A.; Estiamtion of kinetic parameters in neopenyl glycol esterifcation with propionic acid. *Chem. Eng. Sci.* **2008**, 63, 587-589.

[6] Yunus, R.; Fakhru’l-Razi, A.; Ooi, T.L.; Omar, R. and A. Idris. Preparation and characterization of trimethylol propane esters from plam kernel oil esters. *J. Oil Plam. Res.* **2003**, 15(2), 42-49.

[7] Viswanadham, N.; Singh, M.; Kamble, R.; and Saxena, S. K. A comparative study of the esterification activity of nanosized H-ZSM-5 with commercial H-ZSM-5 and H-beta zeolite. *Pet. Sci. Technol.* **2010**, 28, 219–224.

[8] Pandurangan, A.; Palani, A.; and Palanichamy, M. Vapour phase esterification of butyric acid with 1-pentanol over Al-MCM-41 mesoporous molecular sieves. *Catal. Lett.* **2007**, 115(2), 40-45.

[9] Ali, S.H.; Tarakmah, A.; Merchant, S.Q.; and Al-Sahhaf, T. Synthesis of esters: Development of the rate expression for the Dowex 50 Wx8-400 catalyzed esterification of propionic acid with 1-propanol. *Chem. Eng. Sci.* **2007**, 62, 3197– 3217.

[10] Bhorodwaj, S.K.; and Dutta, D.K. Heteropoly acid supported modified Montmorillonite clay: An effective catalyst for the esterification of

acetic acid with sec-butanol. *Appl. Cat. A: General.* **2010**, 378, 221–226.

[11] William, A.G. Theory of lubrication. *United States: Stanford University Press*, **1962**, 250-254.

[12] Asseff, P.A. *Lubrication theory and practice.* Ohio: The Lubrizol Co., Press, **1988**, 1-8.

[13] Will, J.G. *Lubrication fundamentals.* New York: Marcel Dekker, Inc., **1980**, 34-40, 75-87.

[14] **Sarin, R.; Tuli, D.K.; Sureshbabu, A.V.; Misra, A.K.; Rai, M.M. and Bhatnagar, A.K.** Molybdenum dialkylphosphorodithioates: synthesis and performance evaluation as multifunctional additives for lubricants. *Tribology International*. **1994**, 27, 379-386.

[15] Bannister, K.E. *Lubrication for industry. 1st edition.* New York : Industrail Press Inc., **1996**, 204.

[16] Rudnick, L.R. and Shubkin, R.L. *Synthetic lubricants and high-performance functional fluids. 2nd edition.* New York : Marcel Dekker, Inc., **1999**.

[17] Mortier, R.M.; Fox, M.F. and Orszulik, S.T. *Chemistry and Technology of Lubricants*. New York : Springer Science, **2010**.

[18] ASTM International. Standrad Test Method for kinetic viscosity of transparent and opaque Liqiud. *An American National Standard.* **2006**, 71.

[19] ASTM International. Calculating viscosity Index from Kinetic viscosity at 40 and 100 ^{o}C. *An American National Standard.* **2004**, 226/91.

[20] ASTM International. Standrad Test Method for Pour Point of Petroleum products. *An American National Standard.* **2006**, 15-95.

[21] BOND, G. C. *Heterogeneous Catalysis: Principles and Applications*, Clarendon, Oxford, **1974**.

[22] Lepage, J. F.; Cosyns, J.; Courty, P. *Applied Heterogeneous catalysis: Design Manufacture and Use of solid catalysts*, Technip, Paris, **1987**.

[23] Hagen, J. *Industrial Catalysis*. New York: Weinheim Wiley, **1999**.

[24] Otera, J. and Nishikido, J. *Esterification: Methods, Reactions, and Applications*. *2nd edition*. Germany : WILEY – VCH, 2010.

[25] Carey F.A. and Giuliano R.M, *Organic Chemistry, 8th Edition.* USA : McGraw-Hill, **2011.**

[26] Wakasugi, K.; Misaki, T.; Yamada, K. and Tanabe, Y. Diphenylammonium triflate (DPAT): efficient catalyst for esterification of carboxylic acids and for transesterification of carboxylic esters with nearly equimolar amounts of alcohols. *Tetrahedron Lett*. **2000**, 41, 5249 – 5252.

[27] Ramalinga, K.; Vijayalakshmi, P. and Kaimal, T.N.B. A mild and efficient method for esterification and transesterification catalyzed by iodine. *Tetrahedron Lett*. **2002**, 43, 879 – 882.

[28] Kresge, C.T.; Leonowicz, M.E.; Roth, W.J.; Vartuli, J.C. and Beck, J.S. Ordered mesoporous molecular sieves synthesized by a liquid crystal template mechanism. *Nature*. **1992**, 359, 710.

[29] Campelo, J.M.; Luna, D.; Luque, R. and Marinas, J.M. Synthesis of acidic Al-MCM-48: influence of the Si/Al ratio, degree of the surfactant hydroxyl exchange, and post-treatment in NH_4F solution. *J. Catal.* **2005**, 203, 327.

[30] Dubois, M.; Gulik-Krzywicki, Th. and Cabane, B. Growth of silica polymer in a lamellar mesophases. *Langmuir*. **1993**, 9, 673.

[31] Chiranjeevi, T.; Muthu Kumaran, G. and Gupta, J.K. Synthesis and characterization of acidic properties of Al-HMS materials of varying Si/Al ratios. *Thermochemica Acta*. **2006**, 443, 87.

[32] Inagaki, S. and Fukushima, Y. Adsorption of water vapor hydrophobicity of ordered mesoporous silica, FSM-16. *Micropor. Mesopor. Mater.* **1998**, 21, 667.

[33] Ying, J.Y.; Mehnert, C.P. and Wong, M.S. Synthesis and Application of Supramolecular-Templated Mesoporous Materials. *Anger. Chem. Int. Ed.* **1999**, 38, 56-77.

[34] Charanjeevi, T.; Kmar, P.; Maity, S.K.; Rana, M.s.; Murali Dhar, G. And Prasada Rao, T.S.R. Characterization and Hydrodesulfurization Catalysis on WS_2 Supported on Mesoporous Al-HMS Materials. *Micropor. Mesopor. Mater.* **2001**, 444, 547-556.

[35] Tanev, P.T. and Pinnavavia, T. J. A Neutral Templating Route to Mesoporous Molecular Sieve. *Science.* **1995**, 267, 865-867.

[36] Soler-Illia, G. J. A. A. ; Sanchez, C. ; Lebeau, B. and Patarin**,** J. Chemical strategies to design textured materials: from microporous and mesoporous oxides to nanonetworks and hierarchical structures**.** *Chem. Rev*. **2002**, 102, 4093-4138.

[37] Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Grosso, D. and Sanchez, C. Block copolymer-templated mesoporous oxides. *Curr. Opin. Colloid Interface Sci*. 2003, 8, 109-126.

[38] Melosh, N.A.; Lipic, P.; Bates, F.A. and Stucky, G.D. Molecular and mesoscopic structure of transparent block copolymer silica monoliths. *Macromolecules*. **1999**, 32, 4332-4342.

[39] Yanik, J.; Uddin, M. A.; Ikeuchi, K. and Sakata, Y. The catalytic effect of red mud on the degradation of poly (vinyl chloride) containing polymer mixture into fuel oil *Polym. Degrad. Stab.*, **2001**, *73*, 335.

[40] Luo, Q.; Deng, F.; Yuan, Z.; Yang, J.; Zhang, M.; Yue, Y. and Ye, C. Using trimethylphosphine as probe molecule to study the acid sites in Al-

MCM-41 materials by solid state NMR spectroscopy *J. Phys. Chem. B*, **2003**, *107*, 2435.

[41] Stucky, G.D.; Zhao D.; Feng J.; Huo Q.; Melosh N.; Fredrickson G. H. and Chmelka B. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstorm pores. *Science*. **1998**, 279, 548-552.

[42] Activation energy [online]. Available from: http://en.wikipedia.org/wiki/Activation_energy [2011, June 12]

[43] Athens, G. L.; Shayib, R. M. and Chmelka, B. F. Functionalization of mesostructured inorganic-organic and porous inorganic materials. *Curr. Opin. Colloid Interface Sci.* **2009**, 14, 281-292.

[44] Melero, J. A.; Grieken, R. V. and Morales, G. Advances in the synthesis and catalytic applications of organosulfonic-functionalized mesostructured materials. *Chem. Rev.* **2006**, 106, 3790-3812.

[45] Wight, A. P. and Dais, M. E. Design and preparation of organic-inorganic hybrid catalysts. *Chem. Rev.* **2002**, 102, 3589-3614.

[46] Kureshy, R. I. et al. Sulfonic acid functionalized mesoporous SBA-15 as an efficient and recyclable catalysyt for the chromenes from chromanols. *Catal. Commun.* **2009**, 10, 572-575.

[47] Skoog, D. A. *Principles of Instrumental Analysis*. New York, Harcourt Brace College Publishers, **1997**.

[48] BET [online]. Available from: Basic operating principles of the sorptomatic, http://saf.chem.ox.ac.uk./Instruments/BET/sorpoptprin [2011, June 7].

[49] Analysis software user's manual, Belsorp, Bel Japan, Inc.

[50] Gabriel, B. L. *SEM: A User's Manual for Material Science*, Ohio: American Society for Metal, **1985**.

[51] Mbaraka, I. K., Radu, D. R., Lin, V. S. Y., and Shanks, B. H. Organosulfonic acid-functionalized mesoporous silicas for the esterification of fatty acid. *J. Catal.* **2003**, 219, 329-336.

[52] Vahteristo, K.; Maury, S.; Laari, A. and Solonen, A.; Haario, H. and Kinetics of neopentyl glycol esterification with different carboxylic acids. *Ind. Eng. Chem. Res.* **2009**, 48, 6237-6247.

[53] MFI Framework type [online]. Available from: http://www.iza-structure.org/databases/ ModelBuilding/MFI.pdf [2011, June 24].

[54] MWW Framework type [online]. Available from: http://www.iza-structure.org/databases/ ModelBuilding/MWW.pdf [2011, June 24]

[55] BEA Framework type [online]. Available from: http://www.iza-structure.org/databases/ModelBuilding/BEA.pdf [2011, June 24].

[56] Stucky, G.D.; Zhao D.; Feng J.; Huo Q.and Chmelka B. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *J. Chem. Soc.* **1998**,120, 6024-6036.

APPENDIX

1. Standard solution and calibration solution

1.1 NPG monooctanoate standard solution

1.1.1 Stock standard solution 2.5 x 10^{-1} M

A 0.2877 g of NPG monooctanoate was accurately weighed in a 5 mL volumetric flask and made up to the mark with *n*-heptane.

1.1.2 Working standard solution (0.125, 0.075, 0.0375 and 0.01875, 0.0075 M)

The working standard solutions were prepared by dilution of the stock standard solution using a pipette and then made up to the mark with *n*-heptane.

1.2 NPG dioctanoate standard solution

1.2.1 Stock standard solution 1.0 x 10^{-1} M

A 0.4476 g of NPG dioctanoate was accurately weighed in a 5 mL volumetric flask and made up to the mark with *n*-heptane.

1.2.2 Working standard solution (0.125, 0.075, 0.0375 and 0.01875, 0.0075 M)

The working standard solutions were prepared by dilution of the stock standard solution using a pipette and then made up to the mark with *n*-heptane.

1.3 Standard calibration solution

Five calibration solutions were prepared into a series of vials. The weight 2.5 g of stock and working NPG monooctanoate and NPG dioctanoate solutions were transferred into the five vials and added 0.5 g of internal standard 1.2 x 10^{-1} M eicosane stock solution to the five standard solutions. Then, a 1 μL of each reaction mixture was analyzed by GC technique under the condition described in Section 3.1.5 Preparation of calibration solution were listed in Table A-1 and A-2

Remark: The preparation of stock standard solution for other esters were performed in the similar calculation to described in Section 1.1, 1.2 and 1.3.

Table A-1 Preparation of standard NPG monooctanoate calibration solution.

NPG monooctanoate calibration solution	1	2	3	4	5	6
2.50 x 10^{-1}M (g)	2.50					
1.25 x 10^{-1}M (g)		2.50				
7.50 x 10^{-2}M (g)			2.50			
3.75 x 10^{-2}M (g)				2.50		
1.875 x 10^{-2}M (g)					2.50	
7.50 x 10^{-2}M (g)						2.50
Internal standard solution 1.2 x 10^{-1} M (g)	0.50	0.50	0.50	0.50	0.50	0.50

Table A-2 Preparation of standard NPG dioctanoate calibration solution.

NPG dioctanoate calibration solution	1	2	3	4	5	6
2.50 x 10^{-1}M (g)	2.50					
1.25 x 10^{-1}M (g)		2.50				
7.50 x 10^{-2}M (g)			2.50			
3.75 x 10^{-2}M (g)				2.50		
1.875 x 10^{-2}M (g)					2.50	
7.50 x 10^{-2}M (g)						2.50
Internal standard solution 1.2 x 10^{-1} M (g)	0.50	0.50	0.50	0.50	0.50	0.50

2. Calibration function

The calibration function was given by the following expression, obtained from the experimental data using the linear regression method.

Linear regression equation: $Y = aX + b$

2.1 NPG monooctanoate calibration function

$$M_{mono}/M_{eicosane} = a(A_{mono}/A_{eicosane}) + b$$

M_{mono} = the mass of NPG monooctanoate (g)
$M_{eicosane}$ = the mass of internal standard (eicosane, g)
A_{mono} = the peak area of NPG monooctanoate
$A_{eicosane}$ = the peak area of eicosane

In regression function X was represented by the term of $A_{mono}/A_{eicosane}$ while Y was $M_{mono}/M_{eicosane}$.

2.2 NPG dioctanoate calibration function

$$M_{di}/M_{eicosane} = a(A_{di}/A_{eicosane}) + b$$

M_{di} = the mass of NPG dioctanoate (g)
$M_{eicosane}$ = the mass of internal standard (eicosane, g)
A_{di} = the peak area of NPG dioctanoate
$A_{eicosane}$ = the peak area of eicosane

In regression function X was represented by the term of $A_{di}/A_{eicosane}$ while Y was $M_{di}/M_{eicosane}$.

Remark: Calibration function for other esters were performed in the similar caculation to described in Section 2.1 and 2.2.

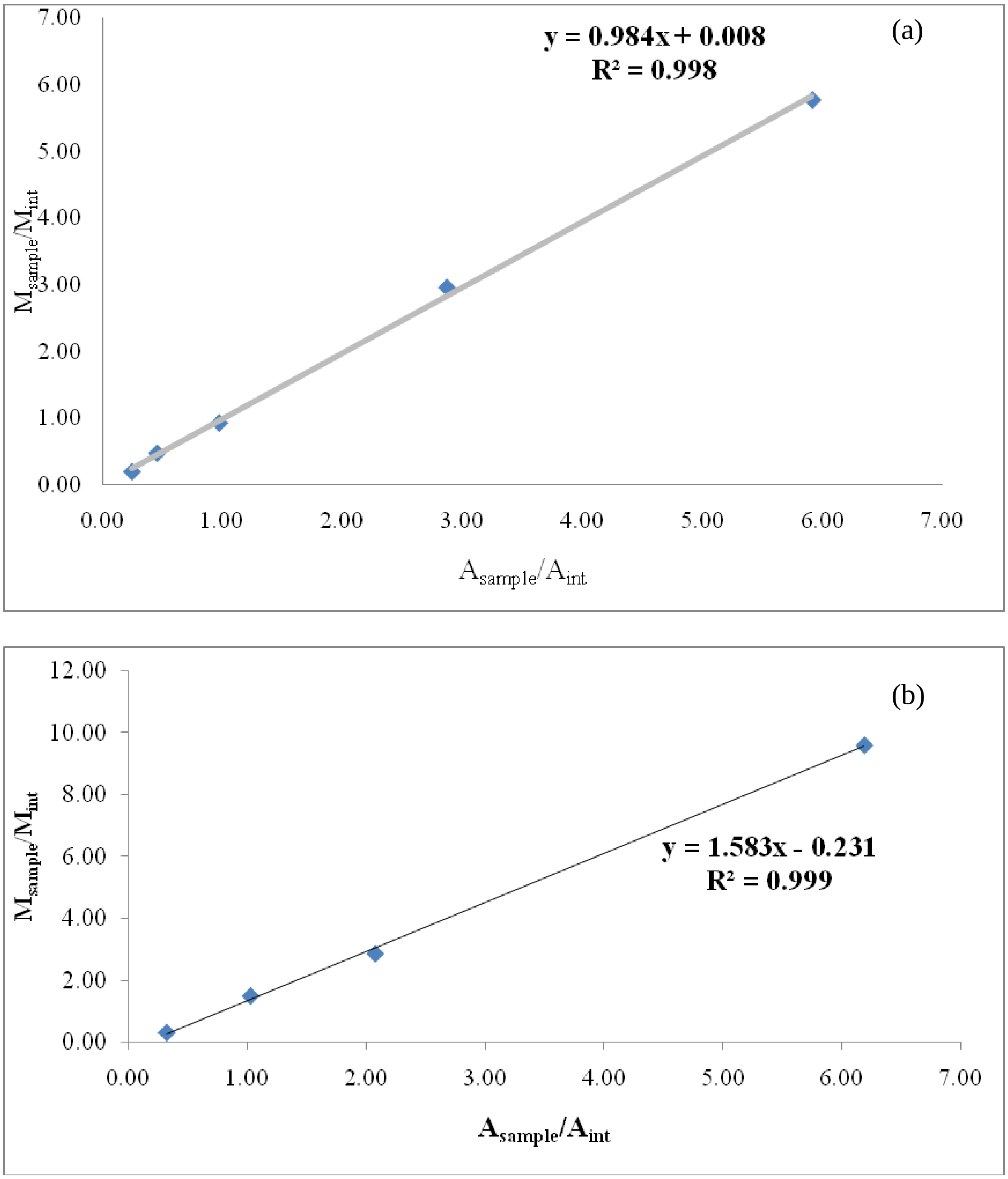
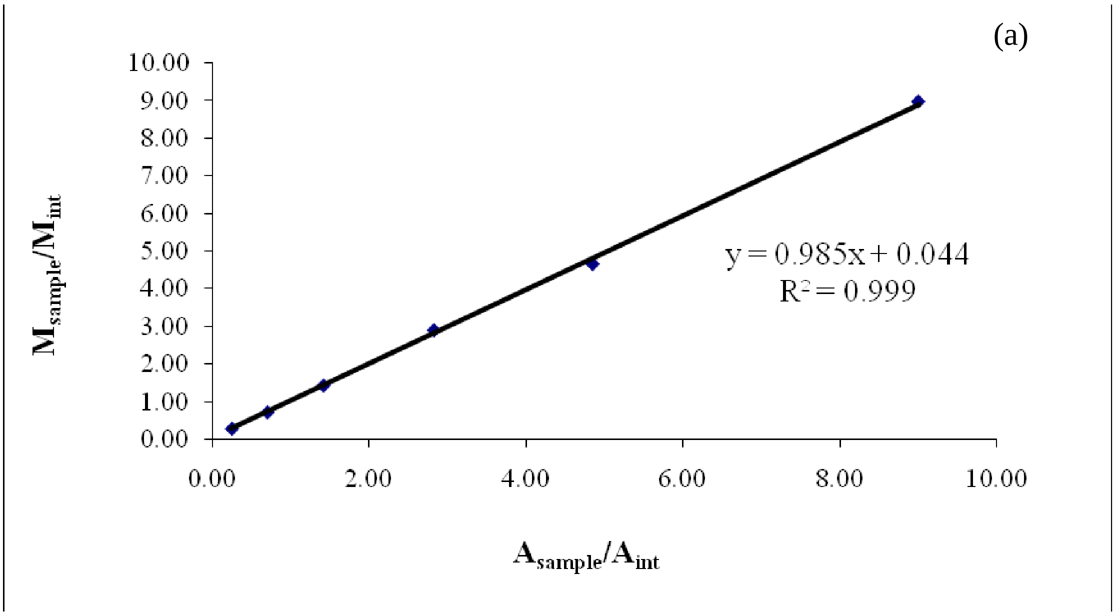


Figure A-1 Calibration curve of (a) NPG monobutyrate and (b) NPG dibutyrate.



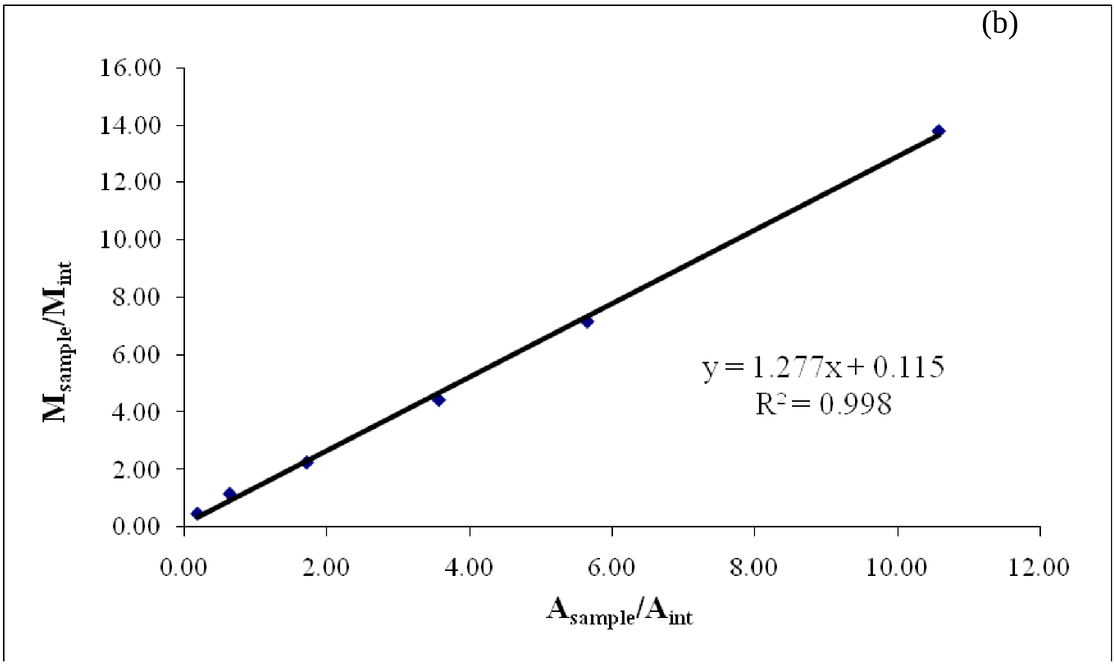


Figure A-2 Calibration curve of (a) NPG monooctanoate and (b) NPG dioctanoate.

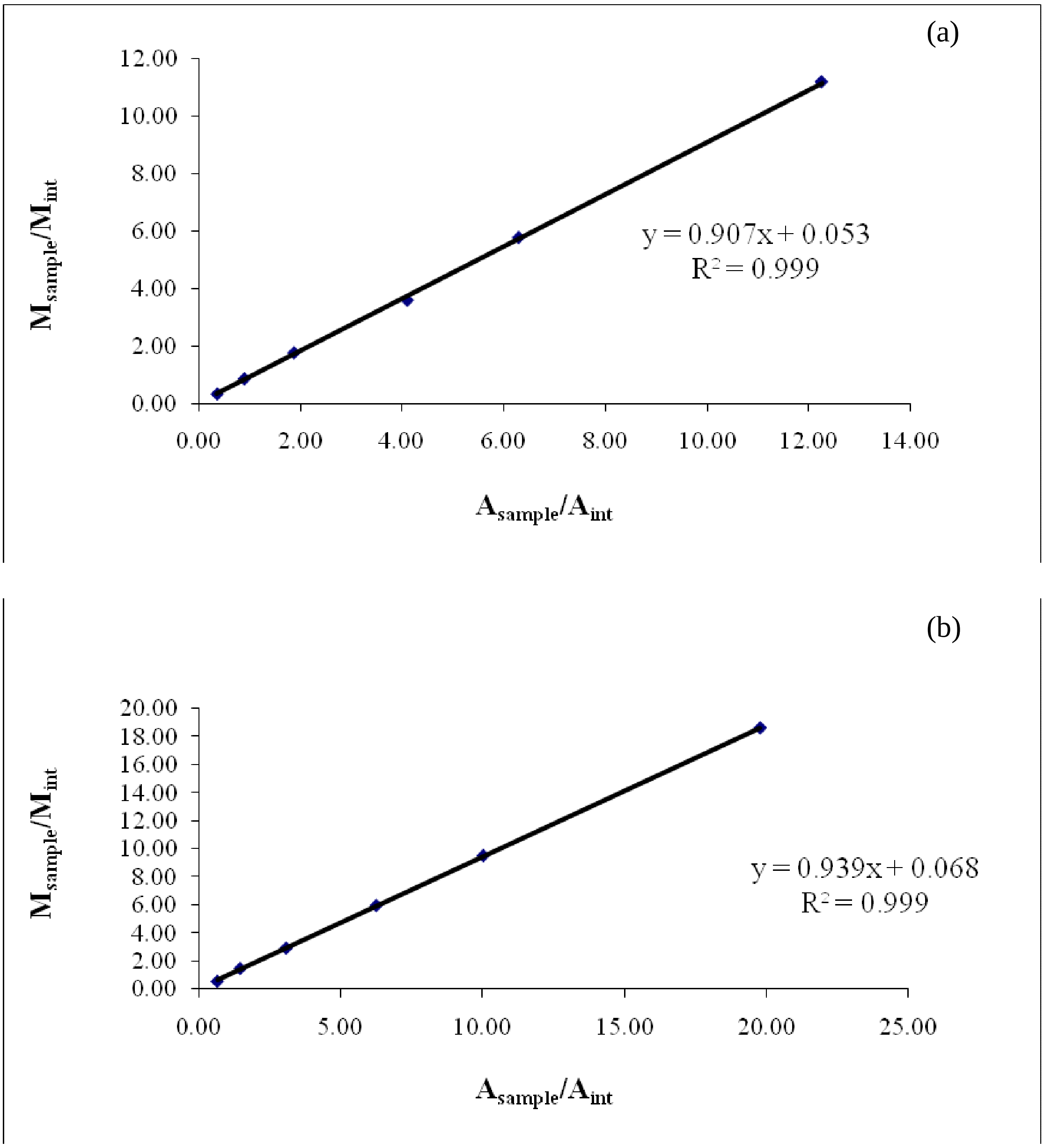


Figure A-3 Calibration curve of (a) NPG monolaurate and (b) NPG dilaurate.

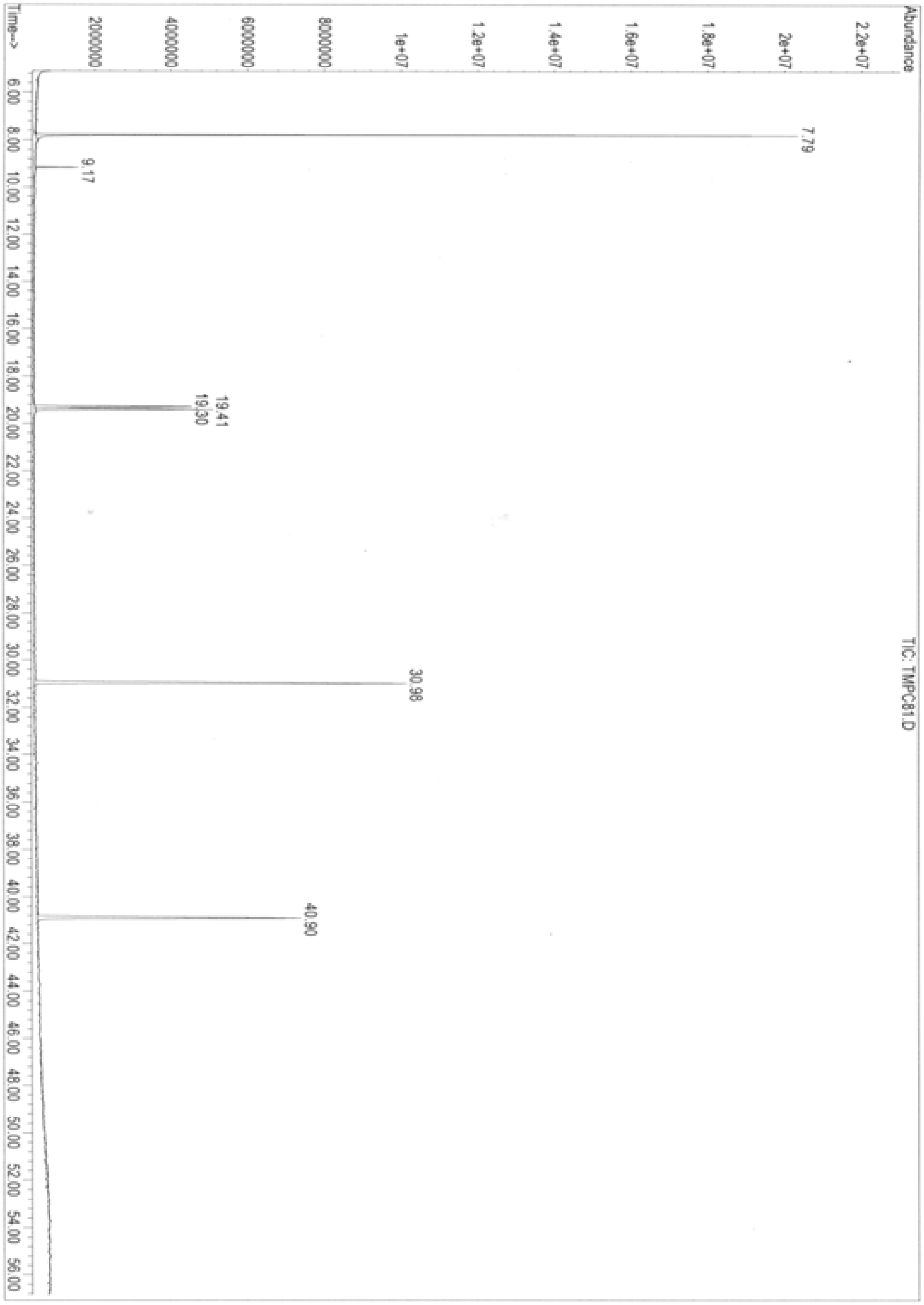


Figure A-4 Chromatogram of esterification TMP and octanoic acid.

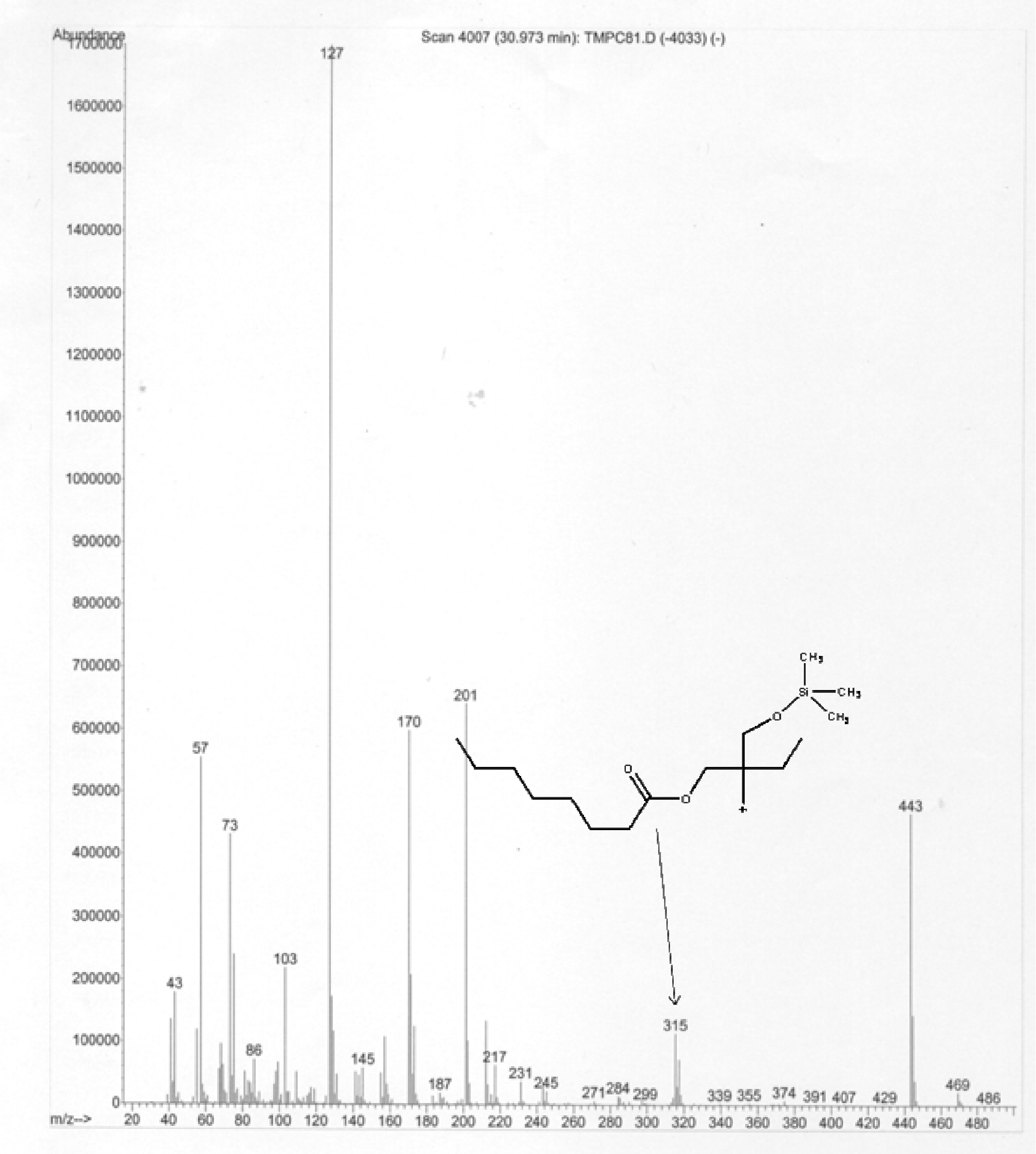


Figure A-5 Mass spectrum of TMP monooctanoic

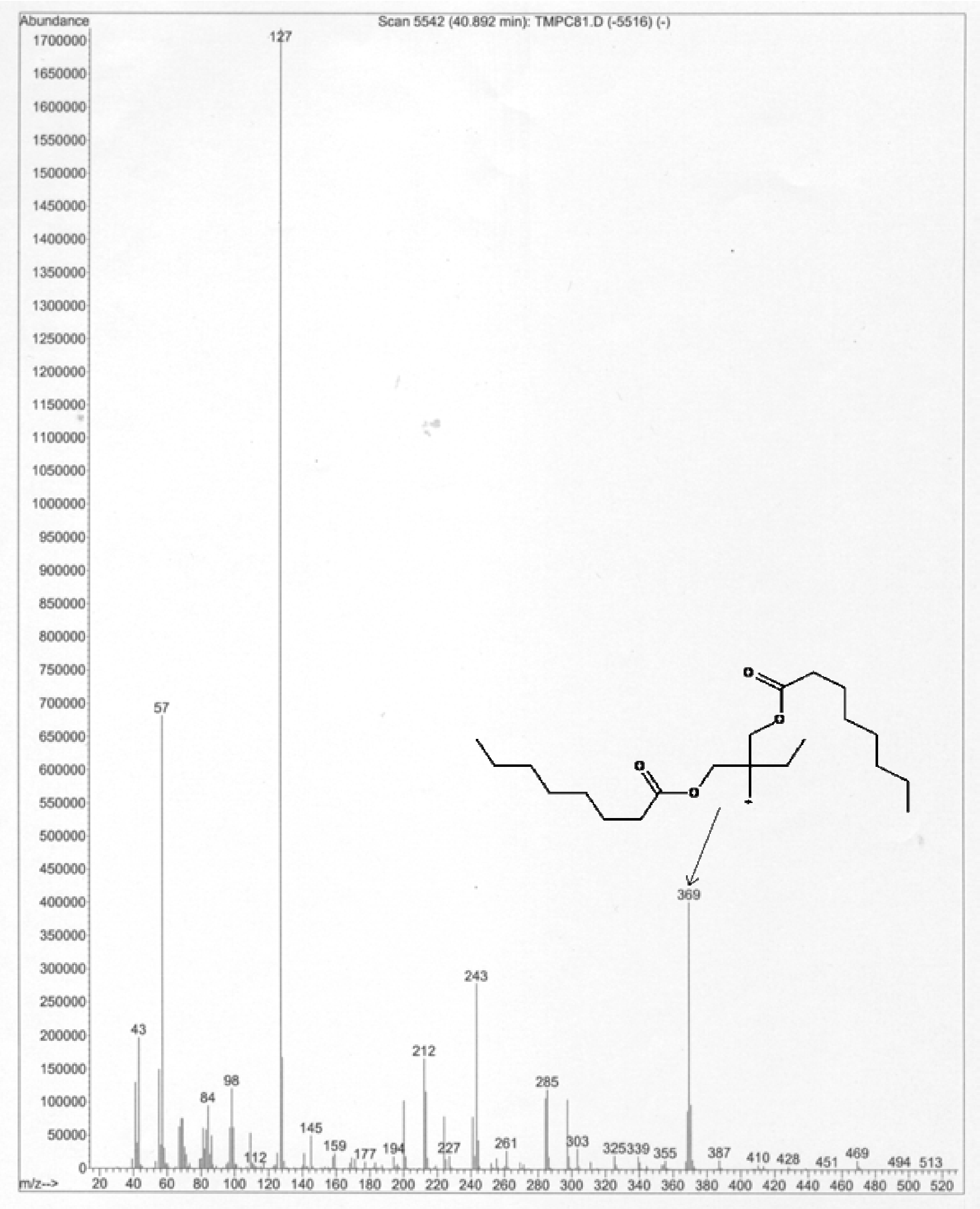


Figure A-6 Mass spectrum of TMP dioctanoic

3. Calculation of percent yield and percent selectivity for ester

Gas chromatography analyzer was used to determine products of polyol esterification. Ester products were identified using internal standard method.

The percent yield was calculated based on the results obtained from gas chromatography. Eicosane were used as internal standard.

For example:
A = exact amount of reactant (mol)
B = exact amount of internal standard was added (mol)
C = exact amount of desired product prepared (mol)
D = total volume of the reaction mixture (mL)
E = peak area of the internal standard
F = peak area of the desired product

- The calculation of the percent yield can be described as follows:

The amount of the product from the reaction mixture

$$= \left(\frac{\mathrm{B} \times \mathrm{F}}{\mathrm{E}}\right) = \mathrm{G}$$

The amount of the product in reaction mixture (D mL)

$$= \mathrm{G} \times \mathrm{D} \ = \mathrm{H}$$

The correction factor of the product can be calculated as:

$$= \mathrm{C}/\mathrm{H} \ = \mathrm{I}$$

Thus, the percentage of product can be calculated as:

$$\%\ \text{yield of product} \ = \left(\frac{\mathrm{H} \times \mathrm{I}}{\mathrm{A}}\right) \times 100$$

$$\%\ \text{selectivity of X} \ = \left(\frac{\%\ \text{yield of X}}{\%\ \text{yield of product}}\right) \times 100$$

VITAE

Mr. Piyawat Paengphua was born on June 20, 1986 in Nakhonsawan, Thailand. He obtained a Bachelor Degree of Science, major in Chemistry from Chulalongkorn University, Bangkok, Thailand in 2008. Since 2009, he has been a graduate student in Organic Chemistry at Department of Chemistry, Faculty of Science, Chulalongkorn University and completed he Master of Science Degree in 2011.

His present address is 37 Moo 7 Phaluead, Thapla, Uttradit, Thailand 53190.