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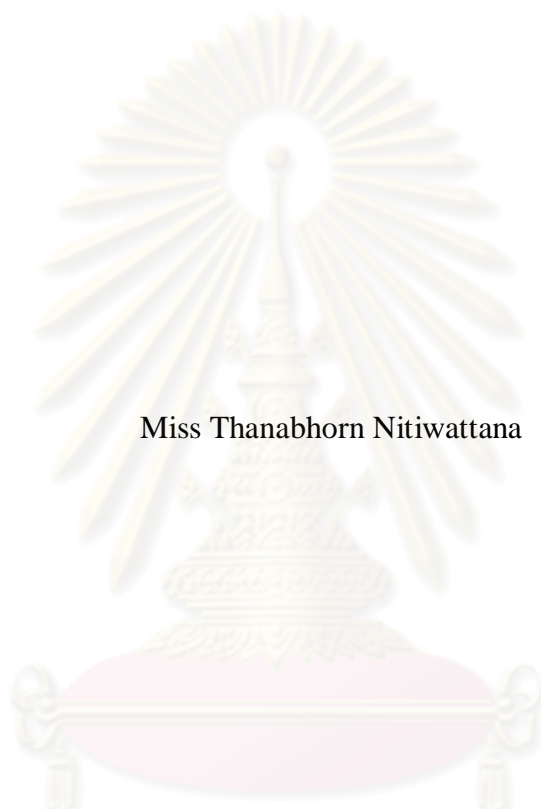
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ESTERIFICATION OF DICARBOXYLIC ACIDS OVER AMBERLYST ION-
EXCHANGE RESINS

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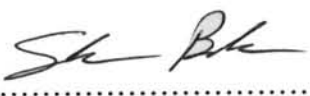
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ธนากร นิติวัดณะ : เอสเทอร์ฟิเคชันของกรดไดคาร์บอกซิลิกบนเรซินแลกเปลี่ยนไอออนแอมเบอร์ลิสต์ (ESTERIFICATION OF DICARBOXYLIC ACIDS OVER AMBERLYST ION-EXCHANGE RESINS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.ชวลิต งามจรัสศรีวิชัย, 86 หน้า

ไดเอสเทอร์สามารถถูกสังเคราะห์ผ่านเอสเทอร์ฟิเคชันของกรดไดคาร์บอกซิลิกและแอลกอฮอล์บนเรซินแลกเปลี่ยนไอออนแอมเบอร์ลิสต์ชนิดต่างๆ ได้แก่ Amberlyst 15, Amberlyst 16 และ Amberlite IR-120 เพื่อเปรียบเทียบประสิทธิภาพในการเร่งปฏิกิริยา ศึกษาผลของชนิดของเรซิน ปริมาณตัวเร่งปฏิกิริยา อัตราส่วนโดยโมลของกรดแอดิฟิกับ 2-เอทิล-1-เฮกซานอล, อุณหภูมิในการทำปฏิกิริยา เวลาในการทำปฏิกิริยา ความยาวสายโซ่ของกรดไดคาร์บอกซิลิก (กรดแอดิฟิ, กรดแอสซอลิก และกรดเซบาชิก) และโครงสร้างของแอลกอฮอล์ (*n*-ออกทานอลและ 2-เอทิล-1-เฮกซานอล) ที่มีต่อผลได้ไดเอสเทอร์และการกระจายตัวของผลิตภัณฑ์ Amberlyst 15 เป็นตัวเร่งปฏิกิริยาที่มีความว่องไวมากที่สุดในเอสเทอร์ฟิเคชันของกรดแอดิฟิกับ 2-เอทิล-1-เฮกซานอล ความว่องไวของตัวเร่งปฏิกิริยาสัมพันธ์กับขนาดรูพรุนและพื้นที่ผิวของตัวเร่งปฏิกิริยา ผลได้ไดเอสเทอร์เพิ่มขึ้นเมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยา การลดอัตราส่วนโดยโมลของกรดแอดิฟิกับ 2-เอทิล-1-เฮกซานอล ช่วยเพิ่มผลได้ไดเอสเทอร์และความเลือกจำเพาะต่อไดเอสเทอร์ การเปลี่ยนของกรดแอดิฟิและผลได้ไดเอสเทอร์เพิ่มขึ้นเมื่ออุณหภูมิและเวลาในการทำปฏิกิริยาสูงขึ้น ขนาดของกรดไดคาร์บอกซิลิกมีผลต่อผลได้ไดเอสเทอร์อย่างมีนัยสำคัญ เมื่อจำนวนคาร์บอนในสายโซ่ของกรดไดคาร์บอกซิลิกเพิ่มขึ้น ผลได้ของไดเอสเทอร์และความเลือกจำเพาะต่อไดเอสเทอร์ลดลง เนื่องจากผลของความเกะกะที่เพิ่มขึ้น Amberlyst 15 ถูกนำมาใช้ 10 ครั้งเพื่อทดสอบการนำกลับมาใช้ใหม่ ซึ่งให้เห็นว่าเป็นตัวเร่งปฏิกิริยาที่สามารถนำกลับมาใช้ใหม่โดยปราศจากการสูญเสียความสามารถในการเร่งปฏิกิริยาเมื่อใช้อะซีโตนในการล้างตัวเร่งปฏิกิริยา พลังงานกระตุ้นของปฏิกิริยานี้เท่ากับ 63.7 กิโลจูลต่อโมล ปฏิกิริยานี้เป็นไปตามกลไกของ Eley-Rideal พบว่าเกิดการดูดซับของโมเลกุล 2-เอทิล-1-เฮกซานอลและน้ำและยังพบผลของการยับยั้งของน้ำ ค่าคงที่อัตราของปฏิกิริยาเท่ากับ $2.51 \times 10^{25} \exp(-21964/T)$ ลิตร² กรัม⁻¹ โมล⁻¹ ชั่วโมง⁻¹

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต..ธนากร นิติวัดณะ.....
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THANABHORN NITIWATTANA: ESTERIFICATION OF DICARBOXYLIC ACIDS OVER AMBERLYST ION-EXCHANGE RESINS.

ADVISOR: ASST.PROF. CHAWALIT NGAMCHARUSSRIVICHAI,
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Diester can be synthesized via esterification of dicarboxylic acid with alcohol over various strong acid Amberlyst ion-exchange resins i.e., Amberlyst 15, Amberlyst 16 wet and Amberlite IR-120 to compare the catalytic efficiency. Effects of types of the resin, catalyst amount, molar ratio of adipic acid/2-ethyl-1-hexanol reaction temperature, reaction time, chain length of the diacids (adipic acid, azelaic acid and sebacic acid) and structure of alcohols (*n*-octanol and 2-ethyl-1-hexanol) on the diester yield and the product distribution have been examined. Amberlyst 15 is the most active catalyst in the esterification of adipic acid with 2-ethyl-1-hexanol. The activity was related to the pore size and specific surface area of the resin catalyst. The diester yield was increased with the increasing catalyst amount. A decrease in the adipic acid/2-ethyl-1-hexanol molar ratio resulted in an improvement of the diester yield and the diester selectivity. The adipic acid conversion and the ester yield were increased with the reaction temperature and reaction time. The size of diacid was significantly affected. When the number of carbon in the linear alkyl chain of dicarboxylic acid was increased, the diester yield and the diester selectivity were decreased due to the enhancement of steric effect. Amberlyst 15 was used for ten cycles to examine its reusability. It was indicated that the catalyst can be reused without losing catalytic activity when using acetone as solvent. The activation energy (E_a) of this reaction was found to be 63.7 kJ mol^{-1} . The reaction was found to follow Eley-Rideal mechanism that appeared adsorption of 2-ethyl-1-hexanol and water molecules and was also observed the inhibiting effect of water. The rate constant (k) can be given by $k = 2.51 \times 10^{25} \exp(-21964/T) \text{ L}^2 \text{ g}^{-1} \text{ mol}^{-1} \text{ h}^{-1}$.

Field of Study:..Petrochemistry and Polymer Science..Student's Signature..T. Nitiwattana

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ศูนย์วิทยทรัพยากร
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LIST OF ABBREVIATIONS

$^{\circ}\text{C}$: Degree Celsius
g	: Gram
mL	: Milliliter
min	: Minute
h	: Hour
THF	: Tetrahydrofuran
cm^{-1}	: Unit of wavenumber
FTIR	: Fourier Transform Infrared Spectroscopy
GC	: Gas chromatography
TGA	: Thermo Gravimetric Analysis
DA	: Dicarboxylic acid
A	: Alcohol
DE	: Diester
W	: Water
k	: Rate constant
E_a	: Activation energy

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CHAPTER I

INTRODUCTION

1.1 Statement of Problems

Lubricant is very important substance since it is used in the most of mechanical parts in machines and engines. Approximately 85 % of fluids used as lubricants are petroleum-based mineral oils [1]. Because of their low biodegradability (lower than 30 %), mineral oils are not environmentally friendly. Moreover, the world petroleum resources are limited. In order to avoid the environmental problems arising from an increase in the consumption of lubricants in various kinds of application, the utilization of biodegradable lubricants has been encouraged [2]. Diester is one of the major classes of ester-based biodegradable lube oil. Due to their dumbbell-like structure, diesters have low pour points, high flash points, shear stability, good oxidation and thermal stability, and high viscosity index [3].

Conventionally, the synthesis of diesters is performed via an esterification of corresponding dicarboxylic acids with linear or branched C₆-C₁₀ alcohols. The most widely used catalysts for the esterification are sulfuric acid and organic sulfonic acids, e.g. *p*-C₇H₇-SO₃H. These catalysts actively promote the complete conversion of the diacids, giving the high yield of diesters since they possesses high acidity and are soluble in the reaction mixture. However, at the end of the production process, a neutralisation step is necessary to stop the catalytic reaction after which a purification of the ester product can be attempted. Typically, washing with an alkali, such as sodium hydroxide solution, is applied to the neutralization, followed by another washing to remove the salt formed in the purification by which a large amount of wastewater is produced, representing a disadvantage of the conventional procedure. The washing step also changes any unreacted diacid component to salt in the discharge liquor. Moreover, some esters may be lost in the aqueous alkali phase, depending on the solubility of the esters in such a solution.

Recently, the application of heterogeneous acid catalysts to conventional esterification/transesterification for oleochemical syntheses has attracted considerable attention since the process can be simplified by using of a designed-column reactor packed with the solid catalysts. Consequently, the need of subsequent steps for the

catalyst separation and the product purification can be reduced [4-6]. A variety of materials have been used as solid acid catalysts, including clays [7], zeolites [8], heteropolyacids [9], cation-exchange resins [10], etc. More importantly, the most of heterogeneous catalysts themselves are recyclable, less toxic and non-corrosive. The migration from the strong soluble acids to strongly acidic solid for the synthesis of biolubricants via the corresponding esterification is our attempt.

In this regard, Amberlyst polymer-based catalysts, products of Rohm and Hass Company, possess unique properties, such as environmental compatibility, non-toxicity, reusability, chemical and physical stability, and can be used over a long period of reaction time [11]. Owing to the numerous advantages associated with inexpensive and no hazardous catalyst, Amberlyst resins have been explored as powerful catalysts for various acid-catalyzed organic reactions, including dehydration [12], etherification [13], esterification [14-17] and transesterification [18].

The aim of this thesis is to determine influences of the physicochemical properties, e.g. specific surface area, pore volume, pore size and crosslinking level, of various Amberlyst ion-exchange resins on the catalytic esterification of dicarboxylic acids (adipic acid, azelaic acid and sebacic acid) with alcohols (2-ethyl-1-hexanol and *n*-octanol). Effects of reaction temperature, reaction time and molar ratio of dicarboxylic acid/alcohol on the ester yield and selectivity were investigated. Furthermore, kinetic study of the esterification of adipic acid with 2-ethyl-1-hexanol over Amberlyst 15 was also examined.

1.2 Objectives

The objectives of this research are:

1. To study effects of reaction conditions on acid conversion and product selectivity in esterification of dicarboxylic acids with alcohols over Amberlyst ion-exchange resins.
2. To study kinetics of esterification of adipic acid with 2-ethyl-1-hexanol over Amberlyst 15.

1.3 Scopes of work

- 1.3.1 Review previously published research articles related to this thesis.
- 1.3.2 Design experimental procedures, and prepare equipment and reagents.
- 1.3.3 Study influences of physicochemical properties of various Amberlyst ion-exchange resins on the esterification of adipic acid with 2-ethyl-1-hexanol.
- Type of Amberlyst resin Amberlyst 15, Amberlyst 16 and Amberlite IR-120
- 1.3.4 Study effects of structure of dicarboxylic acids and alcohols on the catalytic esterification over Amberlyst ion-exchange resins.
- Type of dicarboxylic acid Adipic acid ($C_6H_{10}O_4$), azelaic acid ($C_9H_{16}O_4$) and sebacic acid ($C_{10}H_{18}O_4$)
 - Type of alcohol 2-ethyl-1-hexanol and *n*-octanol
- 1.3.5 Study effects of esterification conditions on dicarboxylic acid conversion and product selectivity.
- Amount of catalyst 0-10 wt. %
 - Molar ratio of dicarboxylic acid/alcohol mole ratio 0.25-0.50
 - Reaction time 0.5-8 h
 - Reaction temperature 90-120 °C
- 1.3.6 Characterize the reaction products by using a gas chromatography technique.
- 1.3.7 Study kinetics of catalytic esterification of adipic acid with 2-ethyl-1-hexanol over Amberlyst 15.
- 1.3.8 Study reusability and regeneration of the suitable Amberlyst ion-exchange resin.
- 1.3.9 Analyze and characterize the reaction results and write thesis.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Lubricating Oil Classification

Lubricating oils fall into the following three categories:

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

2.1.1 Animal fat/vegetable oil

The animal fat/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 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 also improve desirable properties, including viscosity index, pour point and stability. After refining, we end up with a 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 and reduce foaming [19].

2.1.3 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 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 [20]

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

2.2 Synthetic Ester Lubricants

Although the development of the synthetic esters is relatively recent, the use of esters as lubricating fluids is as old as mankind technology. Before mineral oils became worldwide available as a co-products of the petroleum-based fuel industry, lubricants were defined from animal fats and vegetable oils, which are either tri-esters of glycerine with different fatty acids, e.g., tallow and olive oil, or long chain monoesters of fatty acids with fatty alcohols, such as sperm whale oil.

The application of synthetic esters as high performance lubricating fluids was originally driven by an invention of gas turbine or jet engine for aviation. The aviation turbines are operated at higher temperatures than the formerly used piston engines and the jet aircrafts are capable of working at much higher altitudes. Consequently, the suitable lubricants for the aviation turbines are required to provide both very good stability at high temperatures and good cold flow properties. However, the mineral oils and other synthetic hydrocarbons did not deliver the combination of both properties, and diesters were adopted as the lubricant base fluids of choice for early aviation turbines. As the gas turbine technology developed, the operating temperatures increased further, and diesters have been largely substituted by polyol esters, which possess even better thermal stability. Despite an intensive research into alternative functional fluids, the polyol esters remain the best choice for the aviation turbine lubrication.

In addition to their good properties at extreme temperatures, the synthetic esters have other desirable characteristics including good lubricity, high viscosity index, low volatility, and compatibility with base fluids and standard lubricant additives. The ester base fluids with a wide range of viscosities can be designed through flexibility of fundamental chemistry and a variety of raw materials. Other key properties, such as biodegradability, are also possibly controlled by a molecular design. Consequently, the synthetic esters have found many applications outside the aviation engines. The examples include automotive crankcase and gear oils, 2-stroke engine lubricants, metal cutting and rolling fluids, air compressor lubricants, and refrigeration compressor lubricants.

2.2.1 General features and product groups [21]

Ester is defined as a class of organic compounds containing the ester functional group. They are normally manufactured by esterification of carboxylic acids with alcohols, essentially in the presence of acid catalysts and techniques of water elimination.

The physicochemical properties of the product esters can be controlled via an appropriate selection of the raw materials used by which they are mainly dependent on molecular weight, number of ester groups per molecule, and degree of branching in the hydrocarbon chain. The ester linkages exhibit a high bond energy, resulting in a good heat resistance. Moreover, they usually have good oxidation stability and excellent viscosity index and volatility characteristics [22].

There are three main classes of the synthetic esters that are currently in use as lube fluids: aromatic esters, aliphatic diesters and polyol esters.

1. Aromatic esters, as shown in Figure 2.1, are produced by the reaction of aromatic di- or poly- acids or aromatic anhydrides, such as phthalic anhydride, trimellitic anhydride, or pyromellitic anhydride, with pure monoalcohols or mixture of monoalcohols.

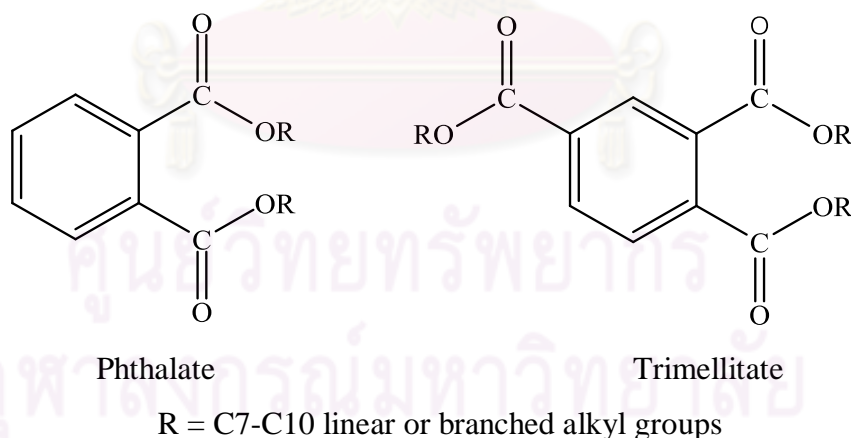
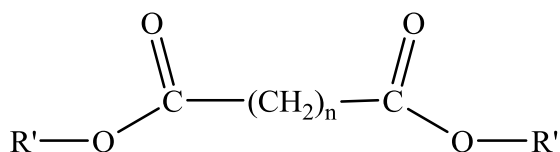


Figure 2.1 Examples of aromatic esters.

2. Diesters (Figure 2.2) can be synthesized by esterifying linear diacid with monoalcohols or mixtures of monoalcohols.



$n = 4 - 10$, $\text{R}' = \text{C7-C10}$ linear or branched alkyl groups

Figure 2.2 Chemical structure of diester.

3. As illustrated in Figure 2.3, polyol esters are esterified products of diols or polyols having a neopentyl structure, such as neopentyl glycol, trimethylol propane or pentaerythritol, and monoacids or mixtures of monoacids. Similarly, oligometric esters, generally known as complex esters, can be manufactured by the reaction of diols or polyols with di- or poly- acids/anhydrides with a monoacid or monoalcohol to act as capping reagent. The variety of the starting reagent allows the preparation of lube compounds having relatively high average molecular weights and viscosities when compared to diesters and polyol esters.

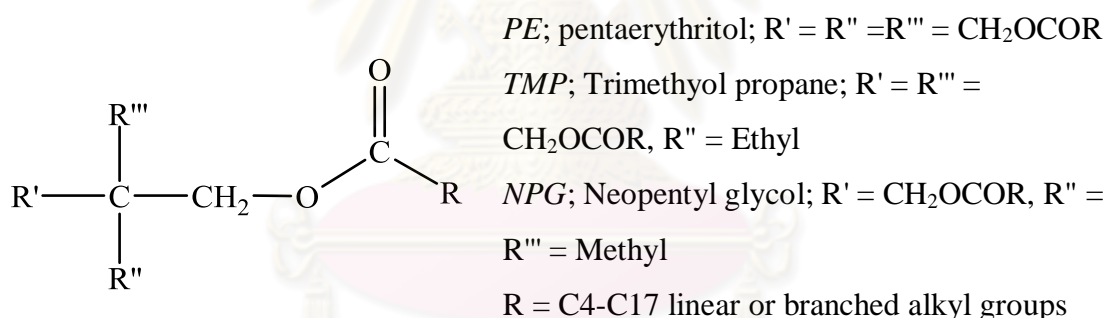


Figure 2.3 Chemical structure of polyol ester.

However, due to a distribution of molecular weights in the complex esters, their volatility characteristics are not as good as simple esters of the similar average molecular weights.

2.2.2 Manufacture of ester lubricants [23]

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

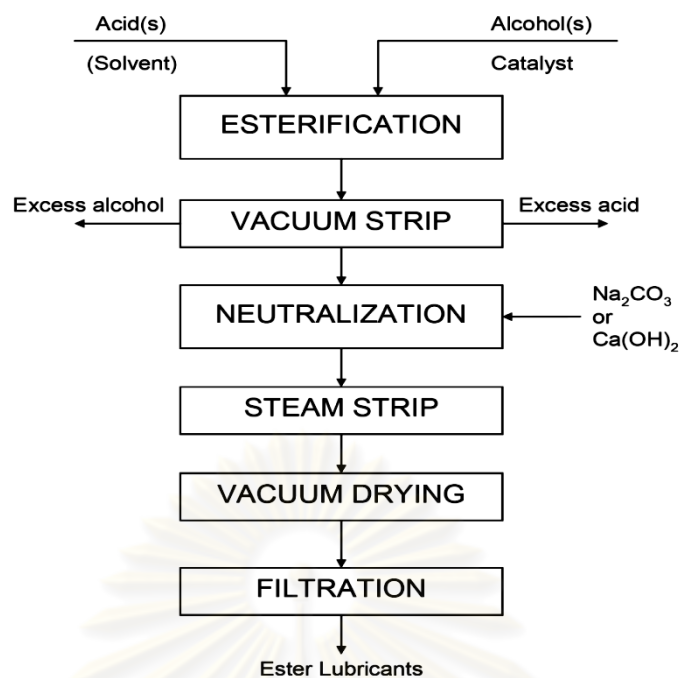


Figure 2.4 Synthesis of ester lubricants.

A schematic of the manufacturing process is given in Figure 2.4. The production of esters 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 is removed by filtration. Typical reaction conditions for titanium catalysts are 230 °C 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 can have 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

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 can have a major impact on the physical properties, hence on the performance of the 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.

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

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

2.2.3 Physicochemical properties of ester lubricants [24]

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 the following: viscosity, flow properties, lubricity, thermal stability, hydrolytic stability, solvency, and biodegradability.

Viscosity; 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.

Flow properties; 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 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, it and not 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):

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

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 2.5 (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 2.5 (b).

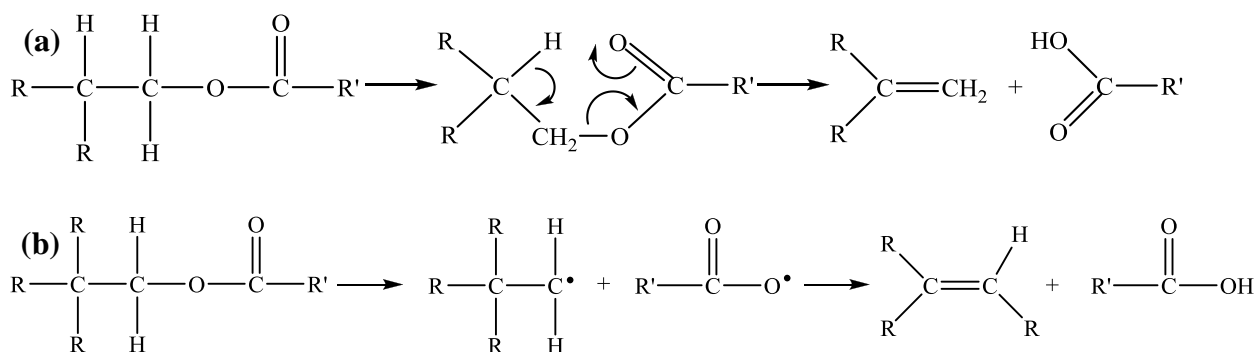
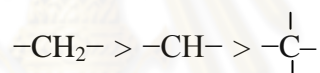


Figure 2.5 Thermal decomposition of (a) esters with β -hydrogens (e.g. dibasic acid esters) and (b) esters without β -hydrogens (e.g. polyol esters).

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,



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 follow the trend in decreasing 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 can have 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

before 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 corrosivity. 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

with esters generally having the rankings 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
- increased molecular weight of the ester.

Table 2.4 Overview of physicochemical properties of ester lubricants

	Diesters	Phthalates	Trimellitates	C35 dimer esters	Polyols	Polyoleates
Viscosity at 40 °C	6-46	29-84	47-366	90-185	14-35	8-95
Viscosity at 100 °C	2-8	4-9	7-22	13-20	3-6	10-15
Viscosity index	90-170	40-90	60-120	120-150	120-130	130-180
Pour point (°C)	-70 to -40	-50 to -30	-55 to -25	-50 to -15	-60 to -9	-40 to -5
Flash points	200/260	200/270	270/300	240/310	250/310	220/380
Thermal stability	Good	Very good	Very good	Very good	Excellent	Fair
Percentage biodegradable	75-100	46-88	0-69	18-78	90-100	80-100
Costs (PAO =1)	0.9-2.5	0.5-1.0	1.5-2.0	1.2-2.5	2.0-2.5	0.6-1.5

2.2.4 Application areas [24]

1. *Engine oils*; it is now widely accepted that synthesized fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum based oils for the formulation of modern automotive engine oils. Practical benefits which may derive from their use include improved cold starting, better fuel and oil economy, together with improved engine cleanliness, wear protection and viscosity retention during service. Fluid types used in the development of automotive crankcase oils, either commercialized or considered for commercialization, include polyalphaolefins (PAOs) – more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkylated aromatic hydrocarbons, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programs conducted over the last ten years has shown that a blend of PAO and an organic ester provides an excellent base fluid for the formulation of synthesized crankcase oils.

Low temperature viscosity is perhaps the single most important technical feature of a modern crankcase lubricant. Cold starts are a prime cause of engine wear which can be mitigated only by immediately effective lubricant circulation. Furthermore, motor vehicles are increasingly required to operate reliably in arctic conditions. Esters provide this essential low temperature fluidity and, because of their low volatility, do so without any sacrifice of lubricant efficiency at high operating or ambient temperatures. Low volatility is especially important in the context of the modern trend towards smaller sump capacities and longer oil change intervals.

2. *Two-stroke oils*; ester lubricants (such as C₃₆ dimer esters and polyoleates) offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixtures. First, the clean-burn characteristics result in less engine fouling with much reduced ring stick and lower levels of dirt built-up on ring grooves, skirts and undercrowns. Ignition performance and plug life are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil-fuel dilution ratios of 50:1 whereas esters can be used at 100:1 and even 150:1. This higher dilution factor results in reduced oil emissions which is a benefit in environmentally-sensitive applications such as marine outboard engines and chainsaw motors. Third, in some applications, such as engines used to

power snowmobile-type vehicle, low temperature performance is important. In these applications, esters with low pour point (down to $-56\text{ }^{\circ}\text{C}$) are very suitable.

Finally a 25 % decrease in the amount of PAH (polyaromatic hydrocarbons) in the exhaust emissions of a two-stroke engine has been found when a carboxylic ester has been used in place of a mineral oil. PAHs have been found to be one of the major contributors to the carcinogenic nature of exhaust emissions. Esters can also be used to reduce the level of smoke emitted by the engine.

3. *Compressor oils*; this sector of the market covers a wide range of compressor types, used for a number of different gases. Diesters and phthalates have found their major application in air compressor lubricants, but are also used in compressors handling natural gas. In reciprocating compressors, where oils of rather higher viscosity are preferred, trimellitate esters can be used. Diesters and polyol esters may also be blended with PAOs for use in the various compressor types.

Diesters have inherently good oxidation resistance and low volatilities (3-10% according to viscosity) when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, and low order of toxicity for vapour inhalation, ingestion and skin irritation, these properties make them considerably safer lubricants to use than mineral oil. Their low toxicity and high biodegradabilities can also lessen their environmental impact. Diesters generally have high viscosity indices, giving them a wide temperature range without the use of viscosity improvers. A further advantage of esters is their good thermal conductivity which allows them to conduct heat away from heat sources more effectively than mineral oils. Specific heat values of 5-10% higher than mineral oils enable esters to 'soak up' heat and allow the compressor to operate at cooler temperatures.

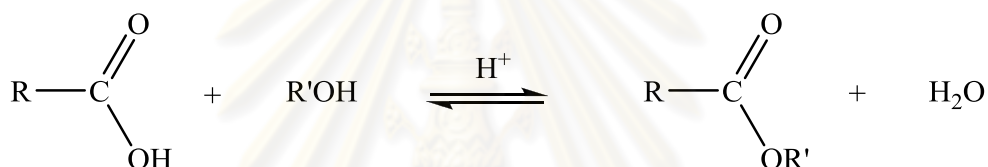
With the phasing out of chlorofluorocarbons (CFCs), owing to their potential ozone-depleting effects, the traditional naphthenic and paraffinic mineral oils currently used in refrigeration lubricants are being replaced by polyol ester oils. The main reason for this is that the traditional mineral oils are not miscible with the more polar hydrofluorocarbons (HFCs) which are replacing CFCs.

4. *Aviation oil*; the bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The requirements placed on jet engine oils, namely lubricating, oxidation and ageing stability, cannot be met by hydrocarbon oils. The first generation of oils (Type 1) were diesters but, over the last 25 years,

these have slowly lost ground to the more expensive (Type 2) polyol esters. Some diesters are still used in less-demanding applications, e.g. for small private aircraft, turbo-prop engines, etc. Type 2 aviation gas turbine lubricants are produced to a viscosity of 5 cSt (at 100 °C). For some military applications, where operability at low temperatures is vital, the corresponding viscosity is reduced to 3 cSt.

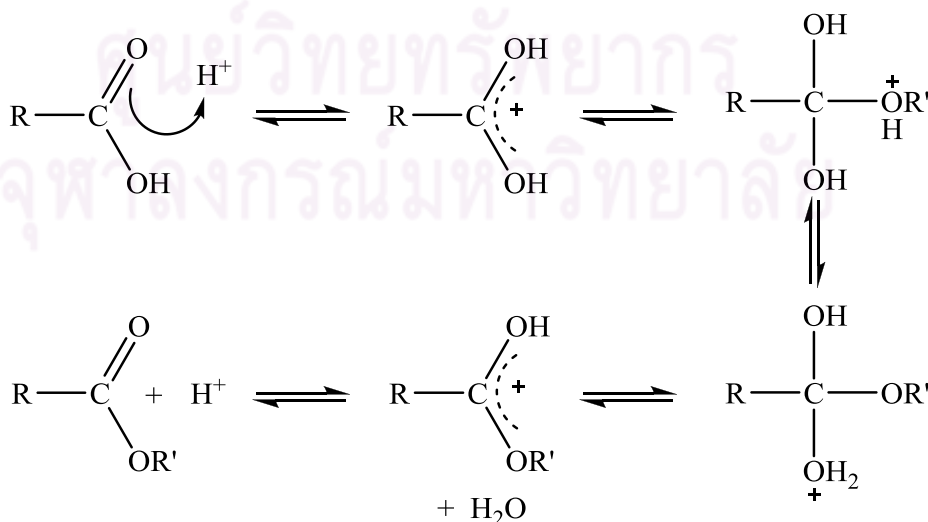
2.3 Acid Catalyst for Esterification [25]

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 [26]



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.

2.3.1 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, H₂SO₄, NaHSO₄, ClSO₃H, H₃PO₄, 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. H₂SO₄-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 CBr₄ 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 [27]. 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 -tolSO₃H, 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.

2.3.2 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	$\text{BF}_3 \cdot \text{OEt}_2$, BCl_3
Al	AlCl_3 , $\text{AlCl}_3/\text{ZnCl}_2$
Zn	ZnO , $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$
Sn	SnCl_2 , Bu_2SnO , Ph_2SnCl_2
Mn	$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$
Fe	$\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, FeCl_3
Ni	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, etc.

- $\text{BF}_3 \cdot \text{OEt}_2$ is the oldest Lewis acid to have been employed as an esterification catalyst, since the $\text{BF}_3/\text{CH}_3\text{OH}$ 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 $\text{Zn}(\text{OTf})_2$. An equimolar mixture

of carboxylic acid and alcohol is esterified, but yields are less than 90 %. Smooth esterification is catalyzed by $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{TiO}(\text{acac})_2$. The catalyst is water-tolerant and neutral to leave various functional groups intact. Alcohols are acetylated by heating at reflux with $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in acetic acid. Fe (III) salts are also effective. $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ 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 $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ and FeCl_3 . Addition of a small amount of H_2SO_4 greatly increases the catalytic activity of $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$. Moreover, anhydrous $\text{Fe}_2(\text{SO}_4)_3$ is highly active for catalyzing acetylation of alcohols in acetic acid. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ catalyst.

- Cupric salts are another class of species that work as catalysts. $\text{CuCl}_2 \cdot n\text{H}_2\text{O}$ catalyzes conversion of carboxylic acids in methanol solvent at 130 °C, while $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ effects acetylation of alcohols in refluxing acetic acid. $\text{Cu}(\text{OTf})_2$ is used for acetylation of alcohols but to a somewhat limited extent. Cupric methanesulfonate ($\text{Cu}(\text{OMs})_2$) 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. $\text{MoO}(\text{acac})_2$ also catalyzes transformation of propanoic acid into esters in refluxing alcohols.

- $\text{Sc}(\text{OTf})_3$ 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.

- $\text{HfCl}_4 \cdot 2\text{THF}$ 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 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$. Combination of $\text{Zr}(\text{O}^i\text{Pr})_4$ with $\text{Fe}(\text{O}^i\text{Pr})_3$ 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 [28]. 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.

2.3.3 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 °C, 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.

- Wofatit KSP 200; esterification of chiral α -hydroxy carboxylic acids without racemization is feasible by heating in EtOH or MeOH/CHCl₃ in the presence of the ion-exchange resin Wofatit 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 °C 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 ClSO₃H 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.

- Nb₂O₅·nH₂O; this catalyst is claimed to be more active than cation-exchange resin, SiO₂·AlO₃, 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.

- $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ 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 [29]. 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 $\text{SnO}_2 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40})$ followed by calcination. Solid superacid of sulfated tin oxide, $\text{SO}_4^{2-}/\text{SnO}_2$, is a highly active catalyst for condensation between acids and alcohols.

Similarly, titanium superacid, $\text{SO}_4^{2-}/\text{SnO}_2$, 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, $\text{H}_3\text{PO}_4\text{W}_{12}\cdot\text{H}_2\text{O}$. 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. $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ can be employed for esterification of salicylic acid with aliphatic and benzylic alcohols. Cobalt-containing polyoxometalate, $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$, 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. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can be immobilized onto hydrous zirconia, which catalyzes reactions between glacial acetic acid and cyclohexanol and between acetic acid and isoamyl alcohol. $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ 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 ; $\text{H}_3\text{PMo}_{12}\text{O}_{40}$; $\text{H}_3\text{PW}_{12}\text{O}_{40}$. All of these supported catalysts are effective for esterification. Grinding $\text{Fe}(\text{ClO}_4)_3(\text{ROH})_6/\text{SiO}_2$ 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. $\text{Hf}[\text{N}(\text{SO}_2\text{C}_8\text{F}_{17})_4]$ supported on fluorosulfonated silica gel efficiently catalyzes esterification of methacrylic acid with methanol. Supporting $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ 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. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 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 $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ 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.

2.4 Step in a Heterogeneous Catalytic Reaction [30]

In heterogeneous catalysis, the catalytic action involves the adsorption of reactant molecules on active sites on the surface of the solid catalysts; therefore, the transport of those molecules from the fluid phase to the surface, where the catalytic reaction effectively occurs, must be considered in the general mechanism. Similarly, the molecules of the reaction products are eventually desorbed and transferred in the opposite direction from inside the solid pores to the fluid phase.

Hougen and Watson and others have broken down the steps that occur on a molecular scale in the following manner.

1. Mass transfer of reactants from the main body of the fluid to the gross exterior surface of the catalyst particle.
2. Molecular diffusion and/or Knudsen flow of reactants from the exterior surface of the catalyst particle into the interior pore structure.
3. Chemisorptions of at least one of the reactants on the catalyst surface.
4. Reaction on the surface.
5. Desorption of (chemically) adsorbed species from the surface of the catalyst.
6. Transfer of products from the interior catalyst pores to the gross external surface of the catalyst by ordinary molecular diffusion and/or Knudsen diffusion.

7. Mass transfer of products from the exterior surface of the particle into the bulk of the fluid.

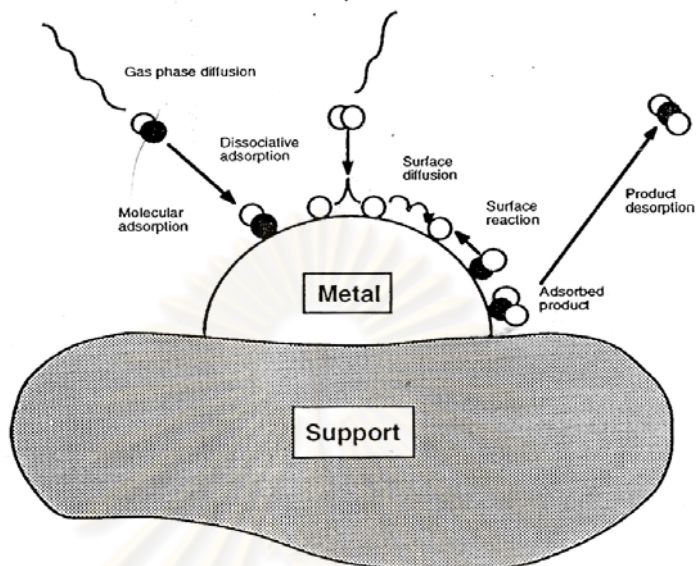


Figure 2.6 Steps in heterogenous catalysis [31]

Several of these steps are shown in Figure 2.6. Of course, if the catalyst is nonporous, steps 2 and 6 are absent. Steps 1, 2, 6, and 7 are obviously physical processes, while steps 3 to 5 are basically chemical in character. The rates of the various steps depend on a number of factors in addition to the concentration profiles of the reactant and product species.

Steps 1 and 7 are highly dependent on the fluid flow characteristics of the system. The mass velocity of the fluid stream, the particle size, and the diffusional characteristics of the various molecular species are the pertinent parameters on which the rates of these steps depend. These steps limit the observed rate only when the catalytic reaction is very rapid and the mass transfer is slow. Anything that tends to increase mass transfer coefficients will enhance the rates of these processes. Since the rate of these steps are only slightly influenced by temperature, the influence of these processes on the overall conversion rate will vary as the temperature changes. Their influence is often negligible at low temperatures, but may be quite significant at higher temperatures.

2.5 Classification of reaction mechanisms [32]

Mass transport to, from and on the surface plays an essential role in surface reactions. When molecules are transferred between phases it takes a finite time for them to equilibrate. Furthermore, we know that not every collision between a molecule and a surface leads to sticking. These characteristics affect the course of reactions at surfaces.

2.5.1 Langmuir–Hinshelwood mechanism

The most common surface reaction mechanism is one in which both reactants are adsorbed on the surface, where they collide and form products. This is known as the Langmuir–Hinshelwood (L–H) mechanism. Adsorption, desorption and surface diffusion play essential roles in the L–H mechanism. Although it might be expected that the reaction rate should depend on the surface coverage of both species, the rate law may be complex and depend on the reaction conditions. Ultimately, the rate law can be properly interpreted only when the complete reaction mechanism is understood.

The dynamics of an L–H reaction involves a convolution of the dynamics of adsorption, desorption and diffusion. In a multistep reaction mechanism, generally one reaction is the slowest and therefore determines the overall rate. This is known as the rate-determining step (RDS). The dynamics of the RDS is, therefore, the most important dynamics for any given L–H reaction system. The RDS can be any one of a number of different types of surface reactions for example, adsorption, adsorbate decomposition, diffusion of an adsorbate to a reactive site or desorption of a product.

2.5.2 Eley–Rideal mechanism

A surface reaction need not involve two surface species. If a gas-phase molecule strikes an adsorbed molecule there is a possibility that the collision leads to reaction and that the product escapes directly into the gas phase. This mechanism is known as the Eley–Rideal (E–R) mechanism. The reaction rate is expected to depend on the coverage of the adsorbed species and the pressure of the other reactant. The products of such a reaction, in contrast to L–H products, should be highly energetic and have a memory of the initial conditions of the gas-phase reactant. This is because

the incident reactant is not accommodated with the surface and does not give up part of the exothermicity of the reaction to the surface in the form of its heat of adsorption. Great efforts have been made to prove that this mechanism occurs. It is rather unlikely for molecules to undergo an E–R reaction. However, radicals are much likely to react by this mechanism.

2.5.3 Hot atom mechanism

The previous two mechanisms represent the extremes in equilibration or lack thereof of the reactants. If one of the reactants were adsorbed while the other was not yet fully accommodated to the surface. This is the hot precursor or hot-atom (HA) mechanism. Such a mechanism would be quite interesting dynamically and would certainly lead to complex kinetics.

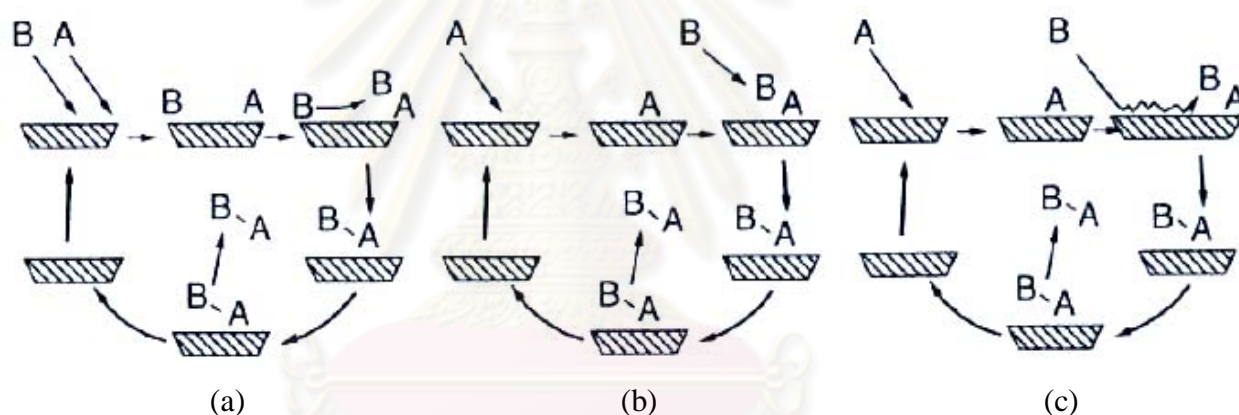


Figure 2.7 Schematic of (a) Langmuir–Hinshelwood, (b) Eley–Rideal and (c) hot–atom mechanisms for the reaction $A + B \longrightarrow AB$ and $AB \longrightarrow A + B$ [33].

Figure 2.7 shows a schematic of these three mechanisms for a hypothetical reaction $A + B \longrightarrow AB$. In the Langmuir–Hinshelwood mechanism, A and B first adsorb onto the surface of the catalyst. Next, the adsorbed A and B react to form an adsorbed A–B complex. Finally, the A–B complex then desorbs. In the Eley–Rideal mechanism, the reactant A chemisorbs. The A then reacts with an incoming B molecule to form an A–B complex. The A–B complex then desorbs. In hot precursor or hot-atom mechanism, A adsorbs. Next, B collides with the surface, and enters a mobile precursor state. The precursor rebounds along the surface until it encounters

an adsorbed A molecule. The precursor then reacts with the A to form an A–B complex which desorbs.

2.6 Ion exchange [34]

Ion exchangers are solid materials that are able to take up charged ions from a solution and release an equivalent amount of other ions into the solution. The ability to exchange ions is due to the properties of the structure of the materials. The exchanger consists of a so-called matrix, with positive or negative excess charge. This excess charge is localized in specific locations in the solid structure or in functional groups. The charge of the matrix is compensated by the so-called counterions, which can move within the free space of the matrix and can be replaced by other ions of equal charge sign.

The pores sometimes contain not only counterions but also solvent. When the exchanger is in contact with the liquid phase, the solvent can move through the exchanger and cause “swelling” to an extent that depends on the kind of counterions. Some electrolytes can also penetrate into the exchanger along with the solvent. As a result, there are additional counterions, the so-called coions, which have the same charge sign as the fixed ions.

Normally, an exchanger has many open areas of variable size and shape that are altogether called “pores”. Only a few inorganic exchangers contain pores of uniform cross section. So, the exchangers exhibit a three-dimensional network of channels with irregular size.

Although ion exchange is similar to sorption since a substance is captured by a solid in both processes, there is a characteristic difference between them: ion exchange is a stoichiometric process in contrast to sorption. It means that in the ion-exchange process, for every ion that is removed, another ion of the solute takes place.

Ion exchange can be seen as a reversible reaction involving chemically equivalent quantities. The water-softening reaction $\text{Ca}^{2+}(\text{aq}) + 2\text{Na}^+(\text{s}) \rightarrow \text{Ca}^{2+}(\text{s}) + 2\text{Na}^+(\text{aq})$ constitutes a characteristic example of cation exchange. However, the characterization of an ion exchange as a “chemical process” is rather misleading. Ion exchange is in principle a redistribution of ions between two phases by diffusion, and chemical factors are less significant or even absent. The absence of any actual chemical reaction explains why the heat evolved in the course of an ion

exchange is usually very small to negligible, often less than 2 kcal/mol. Only when an ion exchange is accompanied or followed by a reaction such as neutralization can the whole phenomenon be characterized as “chemical”. A characteristic example is in chelating resins where the ion exchange is followed by a chemical reaction and bond formation between the incoming ion and the solid matrix.

Ion removal by solid could involve more phenomena, as for example in inorganic natural materials where ion uptake is attributed to ion exchange and adsorption processes or even to internal precipitation mechanisms.

2.6.1 Chemical specification [35]

2.6.1.1 Matrix

The common choice is between ‘styrene-divinylbenzene’ or ‘acrylic-divinyl benzene’ copolymer. In the case of cation exchange resins selection is easily made since the acrylic products are weakly acidic while the styrenic resins are strongly acidic. Therefore for cation exchange the choice of copolymer is primarily decided by the process application and operating pH. The situation is very different with anion exchange resins since the two types of matrix pertain to products of both weak and strong functionality. Where anion exchange resins are concerned the choice between an acrylic resin and its styrenic equivalent is often made on considerations of operating exchange capacity, physical strength, and fouling resistance to complex high molecular weight organic anions.

Disregarding structural features (gel or macroporous) for the time being, the acrylic matrix is particularly tough being more elastic than the more rigid styrene-based copolymer. However the elastic resilience of the acrylic matrix could be of concern where columns of resin operate under a high net compression force (hydraulic pressure drop) since this gives rise to resin bead compression and bed compaction resulting in impeded flows and poor liquid phase distribution (channelling). It must be stressed that in relation to mechanical strength there are no infallible rules as such, but rather guidelines for resin selection which very much depend upon the nature of the application and the associated equipment engineering design. The type of copolymer matrix is not usually the single most important selection criterion with regard to physical strength since both resin structure and

degree of crosslinking contribute greatly in this respect. Figure 2.8 shows the diagrammatic representation of the resin gel-electrolyte phase.

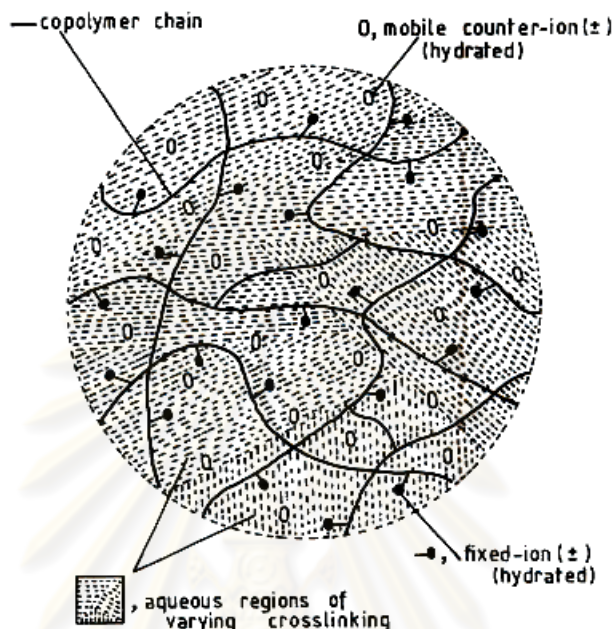


Figure 2.8 Diagrammatic representation of the resin gel-electrolyte phase.

2.6.1.2 Structure

Here, the choice is between gel and macroporous materials, all other considerations assumed equal. The polymer structure of the resin influences the mechanical strength, swelling characteristics, ion exchange equilibria, and exchange kinetics properties of all resins. Macroporous copolymers, being highly crosslinked, are generally tougher than their gel equivalents and are more resistant to physical breakdown through mechanical forces, osmotic volume changes, and chemical degradation of crosslinking through the action of oxidizing agents.

Macroporous resins, being highly crosslinked, possess quite a heterogeneous distribution of structurally dense and tortuous regions of high charge density, and it is for this reason that the affinity of a macroporous resin for a given inorganic ion is usually greater than that for a gel resin, and sometimes the rate of exchange can be discernibly slower for macroporous resins when compared with gel equivalents. But where exchange of large, high molecular weight species are concerned the macroporous property becomes important in providing an easier

diffusion path for the uptake and subsequent release of such species. Finally, because macroporous resins possess real pores, the number of functional groups per unit dry weight of matrix is usually less than that for an equivalent gel product as reflected by their slightly lower dry weight capacities.

2.6.2 Characterization of ion-exchange resins

The ion exchange characteristics of resins available commonly are shown in Table 2.5. These characteristics are divided into two mainly kinds (physical and chemical). Typically, an ion exchange resin is described as being weak or strong, acidic or basic, cationic or anionic. The charge on the counter-ion is important in ion exchange process. While ion exchange resins are in the aqueous solution, they will be hydrated and dissociate to yield equivalent amounts of oppositely charged ions. In conventional aqueous acid or base solutions, resins may be neutralized to give the appropriate salt form. The degree of dissociation is dependent on an apparent equilibrium constant (or pK value) which defines the electrolyte strength of the exchanger and is usually derived from a theoretical treatment of pH titration curves.

Table 2.5 Classification of terms employed to describe ion exchange resins [35]

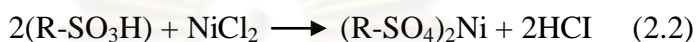
General Classification	
Chemical	Physical
Matrix (polymer structure)	Appearance (physical form)
Crosslinking (% DVB)	Particle size
Functional group	Density
Ionic form (as supplied)	
Water content	
Ion exchange capacity	
pH range	

2.6.3 Resin types [36]

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose

exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

1. *Strong Acid Cation Resins*; strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO₃H) and salt (R-SO₃Na) form. They can convert a metal salt to the corresponding acid by the reaction:



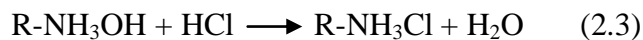
The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na⁺ and H⁺ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionization; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be converted to the sodium form with a sodium chloride solution. For Equation 2.2 hydrochloric acid (HCl) regeneration would result in a concentrated nickel chloride (NiCl₂) solution.

2. *Weak Acid Cation Resins*; in a weak acid resin, the ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group (SO₃H⁺) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated.

Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH.

3. *Strong Base Anion Resins*; strong base resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH⁻)

form for water deionization. They will react with anions in solution and can convert an acid solution to pure water:



Regeneration with concentrated sodium hydroxide (NaOH) converts the exhausted resin to the hydroxide form.

4. *Weak Base Anion Resins*; weak base resins are like weak acid resins. In that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0.

The weak base resin does not have a hydroxide ion form as does the strong base resin. Consequently, regeneration needs only to neutralize the absorbed acid, it need not provide hydroxide ions. Less expensive weakly basic reagents such as ammonia (NH₃) or sodium carbonate can be employed.

Heavy-Metal-Selective Chelating Resins; chelating resins behave similarly to weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins are analogous to chelating compounds found in metal finishing wastewater; that is, they tend to form stable complexes with the heavy metals. In fact, the functional group used in these resins is an EDTA compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

The high degree of selectivity for heavy metals permits separation of these ionic compounds from solutions containing high background levels of calcium, magnesium, and sodium ions. A chelating resin exhibits greater selectivity for heavy metals in its sodium form than in its hydrogen form. Regeneration properties are similar to those of a weak acid resin; the chelating resin can be converted to the hydrogen form with slightly greater than stoichiometric doses of acid because of the fortunate tendency of the heavy metal complex to become less stable under low pH conditions. Potential applications of the chelating resin include polishing to lower the heavy metal concentration in the effluent from a hydroxide treatment process or directly removing toxic heavy metal cations from wastewaters containing a high concentration of nontoxic, multivalent cations.

2.7 AMBERLYST™ Ion Exchange Resins [37]

AMBERLYST™ is a trademark of Rohm and Haas Company, Philadelphia, USA. AMBERLYST™ polymer based catalysts and ion exchange resins involve mostly the use of functionalized styrene divinylbenzene copolymers with different surface properties and porosities. The functional group is generally of the sulphuric acid type. These resins are supplied as gellular or macroreticular spherical beads. AMBERLYST™ polymeric resins have been used for 40 years in a wide variety of reactions and purification processes.

Amberlyst™ resins have been optimized for their particular application over the past 40 years and represent in many applications the benchmark of the industry. They have been developed in respect to conversion and selectivity, prolonged lifetime, chemical and physical stability, and capacity.

AMBERLYST™ catalysts are available in a wide range of particle sizes (from 0.3 mm to 1.2 mm) which have been optimized for their end use to allow good selectivity, low pressure drop and lowest cost operations.

Table 2.6 List of Reactions and Recommended Polymeric General Catalysts

Reaction	Reaction Product	Amberlyst™ Catalysts
Aldolization	Diacetone alcohol and other Aldols	A26 OH
Alkylation	Alkylphenols	15Dry, 35Dry, 36Dry
Condensation	Bisphenol A Phenol (Condensation of Carbonyland furan impurities)	31Wet, 33, 121Wet, 131Wet, 232Wet 16Wet, 36Wet
Dimerization	Iso-octene and Iso-octane	35Wet, 36Wet
Esterification	Acrylates Acetates Fatty Acid esters	16Wet, 131Wet, 39Wet, 46 15Wet, 16Wet, 36Wet, 131Wet BD20, 15Wet, 36Wet, 70
Etherification	Fuel ethers	15Wet, 35Wet, CH10
Hydrogenation	MIBK TAME	CH28, CH10
Hydration	Alcohols from light olefins	15Wet, 70

Besides their catalytic performance, Amberlyst™ polymer catalysts are easy to handle and show a low degree of corrosivity. They are the catalysts of choice for some large markets such as fuel ethers, and bisphenol A. Alternatively these catalysts can be doped with various metals to enhance their catalytic properties. Today more and more neutral adsorbents with extended surface properties are used as carriers for biocatalysts and metal complexes. The products of AMBERLYST™ resins are summarized in Table 2.7.

Table 2.7 The available products of AMBERLYST™ polymer based catalysts and ion exchange resins

Product name	Type	Matrix	Surface area ^[1] (m ² /g)	Average pore diameter (Å)	Min. capacity		Moisture content	Max. temp. (°C)
					(eq/kg) ^[2]	(eq/L)		
Amberlyst 15Dry	Strong acid	MR ^[3]	53	300	4.7	-	≤ 1.6	120
Amberlyst 15Wet	Strong acid	MR	53	300	4.7	1.7	52 – 57	120
Amberlyst 16Wet	Strong acid	MR	30	250	4.8	1.7	52 – 58	130
Amberlyst 31Wet	Strong acid	Gel	-	-	4.8	1.35	63 – 67	130
Amberlyst 35Dry	Strong acid	MR	50	300	5.0	-	≤ 3.0	150
Amberlyst 35Wet	Strong acid	MR	50	300	5.2	1.9	51 – 57	150
Amberlyst 36Dry	Strong acid	MR	33	240	5.4	-	≤ 1.65	150
Amberlyst 36Wet	Strong acid	MR	33	240	5.4	1.9	53 – 59	150
Amberlyst 39Wet	Strong acid	MR	32	230	5.0	1.15	60 – 66	130
Amberlyst 70	Strong acid	MR	36	220	2.65	0.95	53 – 59	190
Amberlyst 121Wet	Strong acid	Gel	-	-	4.8	0.73	74 – 84	130
Amberlyst 131Wet	Strong acid	Gel	-	-	4.8	1.35	62 – 68	130
Amberlyst CH10	Strong acid	MR	33	240	4.8	1.6	52 – 58	130
Amberlyst CH28	Strong acid	MR	36	260	4.8	1.6	52 – 58	130
Amberlyst A21	Weak base	MR	35	110	4.6	1.3	54 – 60	100
Amberlyst A26OH	Strong base	MR	30	290	4.2	0.8	66 – 75	60

Notes:

^[1]Nitrogen BET

^[2]Dry weight

^[3]Macroreticular

2.8 Literature Reviews

Rahman *et al.* [38] studied the enzymatic synthesis of methyl adipate via green esterification of adipic acid and methanol in hexane. Lipase from *Candida rugosa* immobilised onto various layered double hydroxides (LDHs) by a reproducible and simple method of physical adsorption was used as biocatalyst with promising result. Mg/Al-NO₃⁻, Zn/Al-NO₃⁻ and Ni/Al-NO₃⁻ of LDHs with molar ratio of M²⁺/M³⁺ = 4:1 were synthesized by co-precipitation method with continuous agitation. The percentages of protein loading on Mg/Al-NO₃⁻, Zn/Al-NO₃⁻ and Ni/Al-NO₃⁻ were 71%, 67% and 58%, respectively, due to the larger surface area, porosity and basal spacing of the supports. Parameter studies of reaction time, reaction temperature, water activity, thermostability, storage, leaching and reusability were investigated and optimised. Optimum conditions to produce adipate ester upto 80 % were reaction time; 2.5 h, temperature; 50 °C, and water activity; 0.53, respectively. Increased in optimization conditions and enhanced stability properties were found after immobilisation compared to the native lipase.

Liu *et al.* [39] studied the impact of carboxylic acid chain length on the kinetics of liquid-phase acid-catalyzed esterification. Using sulfuric acid and a commercial Nafion/silica composite solid acid catalyst (SAC-13), initial kinetics were measured for the reactions of a series of linear chain carboxylic acids (acetic, propionic, butyric, hexanoic, and caprylic acid) with methanol at 60 °C. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain increased for both H₂SO₄ and SAC-13. This trend is discussed in terms of the polar and steric effects of the alpha-substituent to the carboxylic group and evaluated by a Taft-type correlation. Using a mechanistically based kinetic model, the reaction kinetic parameters of SAC-13 catalysis were determined and compared for different carboxylic acids. Moreover, important parameters, such as water deactivation, catalyst reusability, and regeneration, were also affected by the size of the carboxylic acid used. Using THF washing, the Nafion/SiO₂ nanocomposite catalyst showed good reusability in the esterification of low-molecular-weight acids. However, the catalyst experienced continuous activity loss in consecutive reaction cycles using the larger caprylic acid. Catalyst deactivation was probably due to accumulation of the carboxylic acid molecules/intermediates on or in the nanodomains of the Nafion resin.

Such an accumulation may have been caused by the irreversible adsorption of carboxylic acids on Brønsted sites and/or their entanglement with the polymeric chains of the Nafion nanoparticles. Effective regeneration is needed to improve the applicability of SAC-13 in the esterification of large FFAs.

Mansoori and Sejidov [40] studied the production of mixed-synthetic diester base oils from the waste of electrochemical production of sebacic acid (mixtures of methyl esters of dicarboxylic acids, $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, $n = 4, 6, 8$). The mixtures of methyl esters of dicarboxylic acids are transesterified by pure alcohols and also different mixtures of aliphatic monohydric alcohols, C6-C10 of iso- and normal structure, in the presence of a new catalyst system (tetra-*n*-butyl orthotitanate, $\text{Ti}(\text{O}-n\text{-Bu})_4$). The obtained mixed diester oils showed similar thermal properties and low pour point (minimum $-70\text{ }^\circ\text{C}$), and improved viscosity temperature properties compared with commercially available dioctyl sebacate (DOS) and dioctyl adipate (DOA) diester oils.

Gryglewicz and Oko [41] studied the synthesis of new oligomeric esters of dicarboxylic acids, which can be excellent additives for improving properties of synthetic oils. Further studies will be focused on the use of esters as components of engine oils. Oligomeric esters of adipic acid and sebacic acid were synthesized using neopentyl glycol, appropriate dimethyl adipate or dimethyl sebacate and 2-ethylhexanol as the starting material. The obtained results show that straight adipates and sebacates of 2-ethylhexanol and 3, 5, 5-trimethylhexanol as well as oligomeric esters in which molecules are terminated with 2-ethylhexyl group can be used as component of lubricating oils. The addition of these esters reduced the pour point by a few degrees in comparison with the tested base oil. The temperature fell below $40\text{ }^\circ\text{C}$. The presence of esters significantly improved the viscosity index. A positive influence of esters on the lubricating properties of the formulated oil was also observed. On the contrary, dialkyl carbonates show too low boiling point, which is indicated by the high amount of volatile components, 19-22 %, in final product. Adipic and sebacic oligomers containing methoxyl groups in their structures proved to be immiscible with polyalphaolefins.

Altioikka and Odes [42] studied the kinetics of esterification of acrylic acid with propylene glycol in the presence of Amberlyst-15 as a heterogeneous catalyst. The reaction was realized in a batch reactor at different temperatures and initial

reactant mol ratios. The simultaneous dimerization/polymerization of acrylic acid and products, in addition to the reversible esterification reaction, was proposed as the reaction mechanism. It was also concluded that the selectivity of hydroxypropyl acrylate is significantly low at high conversion levels of acrylic acid. Therefore, to work at low conversion with a proper recycle of unreacted stream, after product separation, is recommended in industrial usage. Kinetic equations corresponding to the reaction mechanism have also been developed. Temperature dependence of the reaction rates and activation energies was determined.

Reddy *et al.* [43] studied the esterification of dicarboxylic acids with various alcohols and phenols in presence of metal exchanged montmorillonite clay catalyst (M^{n+} -mont; $Mn = Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+},$ and Ni^{2+}). Among the catalysts used, Al^{3+} -mont was found to be the most effective, as it gave good to excellent yields of esters under mild reaction conditions. The heterogeneous catalyst presented here can be regenerated and reused.

Özbay *et al.* [44] studied the activities of resins (Amberlyst-15 (A-15), Amberlyst-35 (A-35), Amberlyst-16 (A-16) and Dowex HCR-W2) in direct free fatty acids (FFA) esterification were examined in the temperature range of 50–60 °C and the effect of catalyst amount (1-2 wt.%) on FFA conversion was also analyzed. FFA conversion increased with increasing reaction temperature and catalyst amount. Order of catalytic activities was found as $A-15 > A-35 > A-16 > Dowex\ HCR-W2$. This was related to the size of average pore diameters and magnitude of BET surface area. Highest FFA conversion (45.7 %) was obtained over strong acidic macroreticular ion-exchange resin A-15 at 60 °C with 2 wt.% catalyst amount.

CHAPTER III

EXPERIMENTALS

3.1 Chemicals

3.1.1 Commercial catalysts

1. Sulfuric acid (H_2SO_4 , 98 %) (JT. Baker)
2. Amberlyst 15 dry (Sigma Aldrich)
3. Amberlyst 16 wet (Sigma Aldrich)
4. Amberlite IR-120 (Sigma Aldrich)

3.1.2 Chemicals for esterification

1. Adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$) (AR grade, Fluka)
2. Azelaic acid ($\text{C}_9\text{H}_{16}\text{O}_4$) (AR grade, Fluka)
3. Sebacic acid ($\text{C}_{10}\text{H}_{18}\text{O}_4$) (AR grade, Sigma Aldrich)
4. 2-ethyl-1-hexanol ($\text{C}_8\text{H}_{18}\text{O}$) (AR grade, Fluka)
5. *n*-Octanol ($\text{C}_8\text{H}_{18}\text{O}$) (AR grade, Panreac sintesis)
6. Pyridine ($\text{C}_5\text{H}_5\text{N}$) (AR grade, Qrec)
7. Nitrogen gas (99.99 %, TIG)

3.1.3 Chemicals for reaction product analysis

1. N-methyl-N-(trimethylsilyl)trifluoroacetamide ($\text{C}_6\text{H}_{12}\text{F}_3\text{NOSi}$, Derivatization grade, Sigma Aldrich)
2. Methyl heptadecanoate ($\text{C}_{18}\text{H}_{36}\text{O}_2$) (GC grade, Fluka)
3. Eicosane ($\text{C}_{20}\text{H}_{42}$) (GC grade, Fluka)
4. Heptane (C_7H_{16}) (AR grade, MERCK)

3.2 Instruments and Equipments

1. Three-neck round bottom flask 50 mL
2. Beaker, 250, 600 and 1000 mL
3. Magnetic bar
4. Hot plate stirrer

5. Dropper
6. Parafin bath
7. Condensor
8. Thermometer
9. Oven
10. Desiccator
11. Stopper
12. Filter paper, No. 1
13. Rotary evaporator

3.3 Reaction Product Analysis

The ester content, equivalent to monoester and diester yield, was determined by a Agilent Technologies 7890A gas chromatograph equipped with a 15-m DB-5HT capillary column and a flame ionization detector (FID). The chromatograms of standard solution are shown in APPENDIX A.

Table 3.1 GC conditions for determination of ester content

Condition	Value
Carrier gas (He) flow rate	3.0 mL/min
Make up gas (N ₂) pressure	40 mL/min
Hydrogen pressure (for FID)	30 mL/min
Air pressure (for FID)	400 mL/min
Detector temperature	310 °C
Split ratio	off
Injection port temperature	310 °C
Inject volume	0.1 µL
Initial column temperature	50 °C
Ramp rate	15 °C/min
Final column temperature	310 °C

The ester products were quantified according to an internal standard method. *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) was used to convert the remaining fatty acid and the products in the form of monoester to more volatile derivatives. The calculation of the percent yield can be seen in APPENDIX B.

3.4 Experimental Procedure

3.4.1 Esterification of dicarboxylic acids over acid ion-exchange resins

Esterification of dicarboxylic acid (adipic acid, azelaic acid and sabacic acid) with alcohol (2-ethyl-1-hexanol and *n*-octanol) was carried out in a three-neck round bottom flask equipped with N₂ line (flow rate of 50 mL min⁻¹). A water-cooled condenser was connected to the gas outlet in order to remove the water generated as by-product. In a typical reaction, a dicarboxylic acid was completely dissolved in 2-ethylhexanol in the flask at maintain constant temperature. The reaction temperature was controlled by a liquid paraffin bath. Subsequently, a catalyst was added into the reaction mixture under stirring. Several reaction parameters were adjusted to optimize the reaction conditions. A certain quantity of the reaction mixture was withdrawn from the reactor at 0.5, 1, 3, 5 and 8 h after which it was immediately diluted with pyridine for a GC analysis. After the course of reaction (8 h), the catalyst was recovered by a filtration, and washed with various solvents to remove the organic phase covering the resin particles.

3.4.2 Study on the effect of type of resin catalyst

Esterification of adipic acid with 2-ethyl-1-hexanol was carried out using Amberlyst 15, Amberlyst 16 wet and Amberlite IR-120. The reaction was performed in the same way to general procedure in Section 3.4.1.

3.4.3 Study on the effect of catalyst amount

The effect of catalyst amount was studied in the same way to general procedure in Section 3.4.1, but the amount of catalyst was changed to 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, 5 wt.% and 10 wt.% based on adipic acid.

3.4.4 Study on the effect of molar ratio of adipic acid to 2-ethyl-1-hexanol

The effect of molar ratio of adipic acid to 2-ethyl-1-hexanol was studied in the same way to general procedure in Section 3.4.1, but the molar ratio of adipic acid to 2-ethylhexanol was varied to 0.25, 0.33 and 0.5.

3.4.5 Study on the effect of reaction temperature

The effect of reaction temperature was studied in the same way to general procedure but the reaction temperature was varied to 90, 100, 110 and 120 °C.

3.4.6 Study on the effect of reaction time

The effect of reaction time was studied in the same way to general procedure but the reaction time was varied in the range 0.5-10 h.

3.4.7 Study on the effect of chain length of dicarboxylic acid

Esterification of various dicarboxylic acids with 2-ethyl-1-hexanol was carried out using adipic acid, azelaic acid and sebacic acid as reactants. The reaction was performed in the same way to general procedure in Section 3.4.1.

3.4.8 Study on the effect of structure of alcohol

Esterification of adipic acid with various alcohols was carried out using *n*-octanol and 2-ethyl-1-hexanol as reactants. The reaction was performed in the same way to general procedure in Section 3.4.1.

3.5 Catalyst Reusability

After the course of reaction in Section 3.4.1, the catalyst was recovered by a filtration, and washed with various solvents (hexane, tetrahydrofuran, acetone and methanol) to remove the organic phase covering the resin particles from each reaction cycle and dried at 100 °C overnight before a new cycle was started with fresh reactants.

3.6 Kinetics Study

The experiments were conducted in a three-neck round bottom flask equipped with N₂ line (flow rate of 50 mL min⁻¹). A water-cooled condenser was connected to the gas outlet in order to remove the water generated as by-product. In a typical reaction, 2-ethyl-1-hexanol and catalyst was mixed into reactor and heated to desired temperature. Adipic acid, at the same temperature, was added finally and this time was taken as zero time for a run. Reaction temperature was controlled in the range of 90-110 °C. A certain quantity of the reaction mixture was withdrawn from the reactor at 0.5 h after which it was immediately diluted with pyridine for a GC analysis.

3.7 Characterization of Catalyst

3.7.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was recorded on a Perkin Elmer 2000 in the range of 400–4000 cm⁻¹. During sample preparation, the acid ion-exchange resin was briefly exposed to ambient atmosphere and diluted in KBr powder at 5 wt%. Pure KBr powder was used as the background.

3.7.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris Diamond TG/DTA. Approximately 10 mg of acid ion-exchange resin was used and the temperature was ramped from room temperature to 1000 °C under nitrogen at a heating rate of 10 °C/min. Degradation temperatures of the samples was calculated from TGA plot.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Esterification of dicarboxylic acids over acid ion-exchange resins

4.1.1 Effects of type of resin catalyst

The effect of type of resin catalyst on esterification of adipic acid with 2-ethyl-1-hexanol is shown in Table 4.1. It can be seen that Amberlyst 15 gave the bis (2-ethylhexyl) adipate yield of 61 % and the bis (2-ethylhexyl) adipate selectivity of 72.8 %.

Table 4.1 Effects of type of resin catalyst on the ester yield and the product distribution

Catalyst	Ester yield (wt.%)		Ester selectivity (%)	
	mono-	di-	mono-	di-
Amberlyst 15	22.7	61.0	27.2	72.8
Amberlyst 16 ^a	29.7	53.0	35.9	64.1
Amberlite IR-120 ^a	32.3	49.9	39.3	60.7

Esterification conditions: adipic acid/2-ethyl-1-hexanol molar ratio, 0.5; catalyst mass, 3 wt.%; reaction temperature, 110 °C; reaction time, 5 h.

^a Prior to use, the catalysts were dried at 100 °C for 2 h.

As discussed for the physicochemical properties of acid ion-exchange resins are shown in Table 4.2. Amberlyst 15 has the highest values of surface area, pore volume and pore size. All catalysts (Amberlyst 15, Amberlyst 16 wet and Amberlite IR-120) have a similar concentration of acid sites. Amberlyst 16 and Amberlite IR-120 has low crosslinking level. Consequently, it can easily swell in the reaction media, probably allowing the active sites more accessible for the reactants. Comparative study on the esterification performance of the ion-exchange resins indicated that Amberlyst 15 gave the highest percentage of the diester yield and the diester selectivity. It should be due to a relatively large pore volume and a high surface area of Amberlyst 15. In case of Amberlyst 16 wet, the presence of residual

water, after the drying, is likely to retard the reaction. Water molecule has a high affinity to the proton of the acid site, hampering the protonation of the diacid reactant.

Table 4.2 Physicochemical properties of acid ion-exchange resins used in this study

Catalyst	Surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (Å)	Concentration of acid sites (mmol g ⁻¹)	Crosslinking level[44]
Amberlyst 15[45]	53	0.4	300	≥ 4.7	High
Amberlyst 16 wet[46]	30	0.2	250	≥ 4.8	Low
Amberlite IR-120[47]	1.53	0.01	288	4.4	Low

4.1.2 Effects of catalyst amount

The effect of catalyst loading on the esterification reactions has also been studied using different amount of Amberlyst 15 (1, 2, 3, 4, 5 and 10 wt.% based on adipic acid). Catalyst loading is an important parameter that needs to be optimized to increase the ester yield.

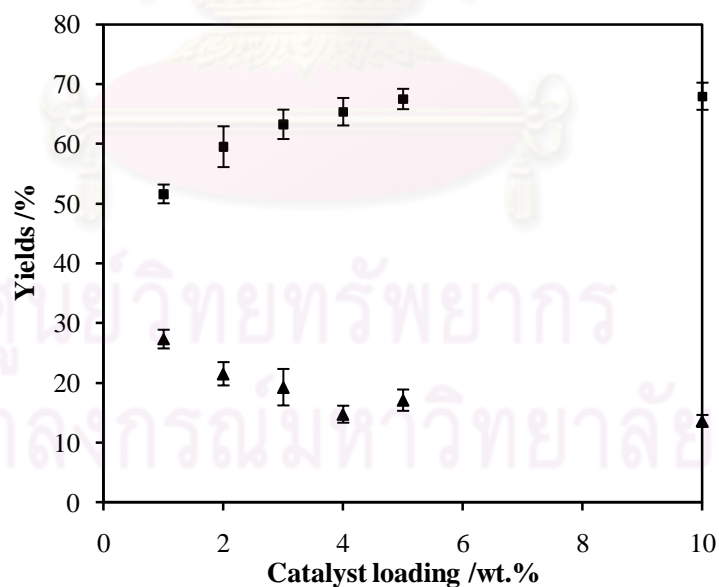


Figure 4.1 Influence of catalyst amount on the esters yield over Amberlyst 15.

Reaction conditions: adipic acid/2-ethyl-1-hexanol molar ratio, 0.5; temperature, 110 °C; reaction time, 5 h. (Symbols: (▲) monoester and (■) diester)

From the figure, it can be indicated that the maximum yield of bis (2-ethylhexyl) adipate ($\sim 65\%$) has been achieved in presence of 10 wt.% Amberlyst 15, which was similar to the presence of 4 wt.% catalyst ($\sim 63\%$) as seen in Figure 4.1. The increase in the yield of bis (2-ethylhexyl) adipate with the increasing catalyst amount is expected because total surface area of the catalyst is increased and also more catalytic active sites are available [48]. However, increasing the amount of Amberlyst 15 from 4 to 10 wt.% did not distinctly benefit due to problem of mixing.

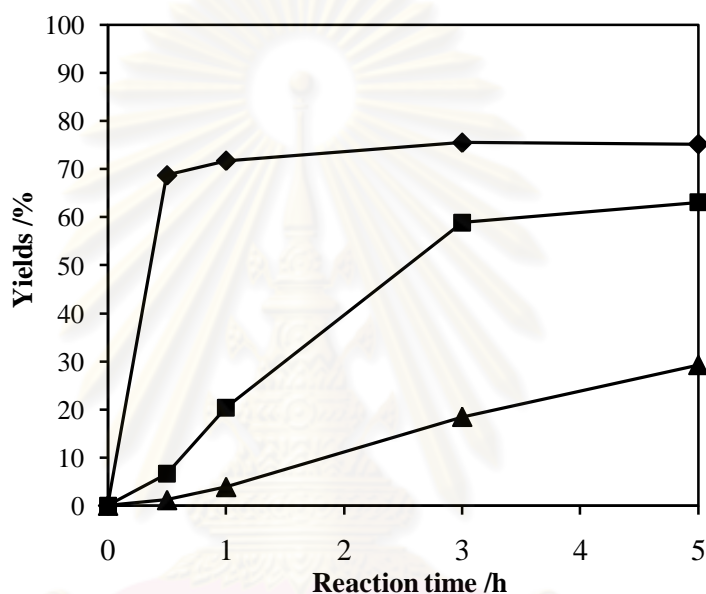


Figure 4.2 Esterification of adipic acid in presence of 1 wt.% conc. H₂SO₄, 4 wt.% Amberlyst 15 and in absence of catalyst on the diester yield. Reaction conditions: adipic acid/2-ethyl-1-hexanol molar ratio, 0.5; temperature, 110 °C; reaction time, 5 h. (Symbols: (▲) without catalyst, (■) Amberlyst 15 and (◆) H₂SO₄)

The same experiment has been repeated without catalyst using a well-known catalyst H₂SO₄ to compare the catalytic efficiency of Amberlyst 15. In this study, we have found that the esterification of adipic acid with 2-ethyl-1-hexanol spontaneously occurred without the addition of catalyst, giving a low yield of bis (2-ethylhexyl) adipate ($\sim 29.2\%$). When catalysts were applied to the reaction, the diester yield was improved, regardless the types of catalyst. The efficiency of H₂SO₄ showed that the formation of diesters in esterification significantly increased within the initial 1 h and after that the diester yield reached saturation. While the

heterogeneous catalyst (Amberlyst 15) slightly increased due to the effect of diffusion limitation within pores.

4.1.3 Effects of molar ratio of adipic acid to 2-ethyl-1-hexanol

Effect of molar ratio of adipic acid to 2-ethyl-1-hexanol on the esterification over Amberlyst 15 was also studied, as shown in Table 4.3.

Table 4.3 Effects of adipic acid/2-ethyl-1-hexanol molar ratio on the ester yield and the product distribution

adipic acid: 2-ethyl-1-hexanol molar ratio	Ester yield (wt.%)		Ester selectivity (%)	
	mono-	di-	mono-	di-
0.25	6.3	77.1	7.8	92.2
0.33	3.9	83.7	4.5	95.5
0.5	15.8	66.3	19.3	80.7

Esterification conditions: catalyst mass, 4 wt.%; reaction temperature, 110 °C; reaction time, 5 h.

The results in this table indicated an increase in the ester yield and the diester selectivity with a decrease in the molar ratio of adipic acid/2-ethyl-1-hexanol. When the amount of 2-ethyl-1-hexanol was increased, the transformation of the monoester to diester was successfully facilitated by the excess alcohol molecules. With further enhancing the ratio beyond 0.25, the yield decreased slightly due to the dilution of adipic acid by the excess 2-ethyl-1-hexanol.

4.1.4 Effects of reaction temperature

Esterification of adipic acid with 2-ethyl-1-hexanol in the presence of a catalytic amount (4 wt.%) of Amberlyst 15 at 90-120 °C temperature was examined.

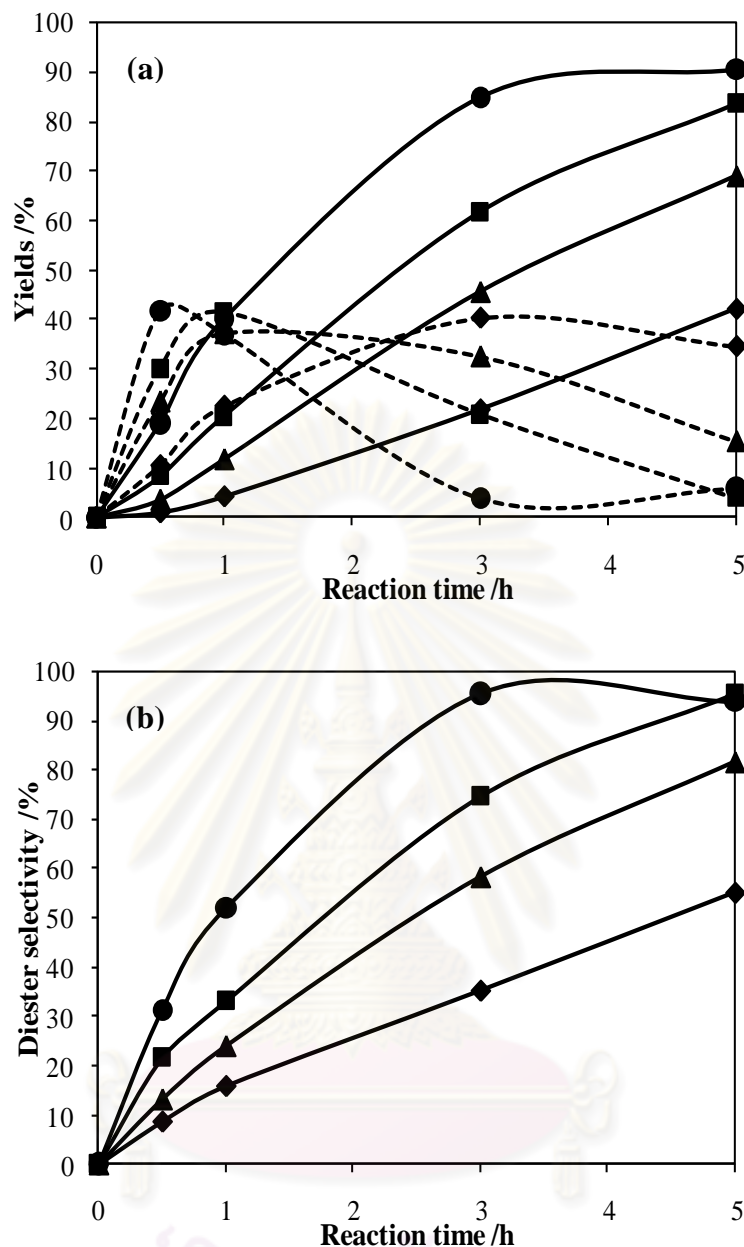


Figure 4.3 Influence of reaction temperature on (a) the esters yield and (b) the diester selectivity over Amberlyst 15. Reaction conditions: adipic acid/2-ethyl-1-hexanol molar ratio, 0.33; catalyst mass, 4 wt.%; reaction time, 5 h. (Symbols: (♦) 90, (▲) 100, (■) 110, (●) 120 °C, (······) monoester and (—) diester)

Figure 4.3 shows the influences of reaction temperature on the ester yield and the diester selectivity. The formation of ester products was promoted concomitantly with an increase in the selectivity to diester when the temperature was raised from 90 to 110 °C. As the reaction temperature is increased, all reactant molecules will gain more kinetic energy that will eventually accelerate the mass transfer rate between the

reactants-catalyst phases that resulted in the formation of diesters in a shorter time [49]. However, the conversion of adipic acid was decreased inversely with the monoester selectivity at 120 °C. It should be due to a hydrolysis of the ester products with water generated as the esterification by-product.

4.1.5 Effects of reaction time

The ester yield and remaining carboxylic acid with various reaction times was shown in Figure 4.4. The esterification of adipic acid with 2-ethyl-1-hexanol was varied in the range 0.5-10 hours over Amberlyst 15, as can be seen from Figure 4.4.

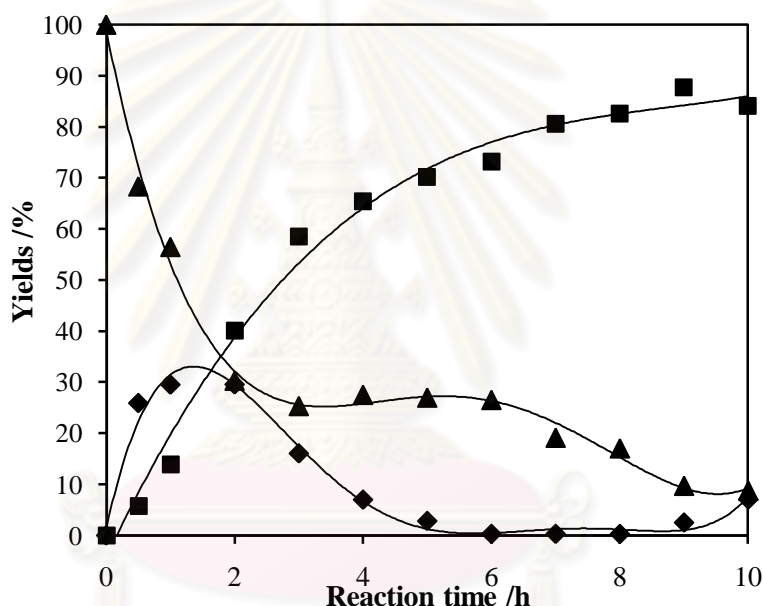


Figure 4.4 Influence of reaction time on the ester yield over Amberlyst 15. Reaction conditions: adipic acid/2-ethyl-1-hexanol molar ratio, 0.33; catalyst mass, 4 wt.%; reaction temperature, 110 °C. (Symbols: (▲) adipic acid, (◆) monoester and (■) diester)

Figure 4.4 shows the reaction time profile that showed the high conversion processed rapidly within 1 h to converse to monoester and diester which giving higher monoester and lower diester yield (~ 29.6 and 13.9 %, respectively) due to the formation of diester will be produced via monoester. Consequently, the monoester yield slightly decreased and the diester yield dramatically increased. After reaction for over 8 h, the remaining diacid and diester yield kept constant as it reached

equilibrium, beyond the diester yield around 82.6 %. In addition, the increase in monoester yield was observed, suggesting that the reverse reaction occurred after a long reaction time up to 8 h.

4.1.6 Effects of chain length of dicarboxylic acid

The effects of carbon chain length of dicarboxylic acids, including adipic acid, azelaic acid and sebacic acid with the number of carbon atom of 6, 9 and 10, respectively, in the esterification with 2-ethyl-1-hexanol over Amberlyst 15 are shown in Table 4.4.

Table 4.4 Effects of chain length of dicarboxylic acid on the ester yield and the product distribution

Dicarboxylic acids	Ester yield (wt.%)		Ester selectivity (%)	
	mono-	di-	mono-	di-
Adipic acid (C ₆ H ₁₀ O ₄)	0.3	82.6	0.4	99.6
Azelaic acid (C ₉ H ₁₆ O ₄)	6.5	71.8	8.3	91.7
Sebacic acid (C ₁₀ H ₁₈ O ₄)	10.6	65.1	14.0	86.0

Esterification conditions: Dicarboxylic acid/2-ethyl-1-hexanol molar ratio, 0.33; catalyst mass, 4 wt.%; reaction temperature, 110 °C; reaction time, 8 h.

The reaction results in Table 4.4 indicated the maximum yield of diester that obtained from adipic acid, giving the diester yield of 82.6 % and the diester selectivity of 99.6 %. The reactivity loss per additional –CH₂– moiety was greatest for the small diacids from adipic acid to sebacic acid. The size of diacid significantly affected the diester yield and the selectivity to diester as well. The two reasons contribute to the decreased diacid reactivity with chain length: an inductive effect and a steric effect [50]. The inductive effect results from the increase in electron-releasing ability of the acid with lengthening alkyl chain. Although the inductive effect facilitates the protonation of the carbonyl oxygen, it also lowers the electrophilicity of the carbonyl carbon, resulting in a more energy-hindered rate-limiting nucleophilic attack by the alcohol. The steric component affecting dicarboxylic acid reactivity is also the

decisive factor for acid-catalyzed esterification [51, 52]. As a consequence of a steric effect, the ester yield of sebacic acid to the corresponding esters occurred at lesser extent. Since the diester possesses the largest molecular size in the reaction system, its formation is relatively limited within the confined space of the catalyst pores.

4.1.7 Effects of structure of alcohol

The reactivity differences with two kinds of alcohols of different structure (*n*-octanol and 2-ethyl-1-hexanol) for esterification with adipic acid at 110 °C catalyzed by Amberlyst 15, as seen in Figure 4.5.

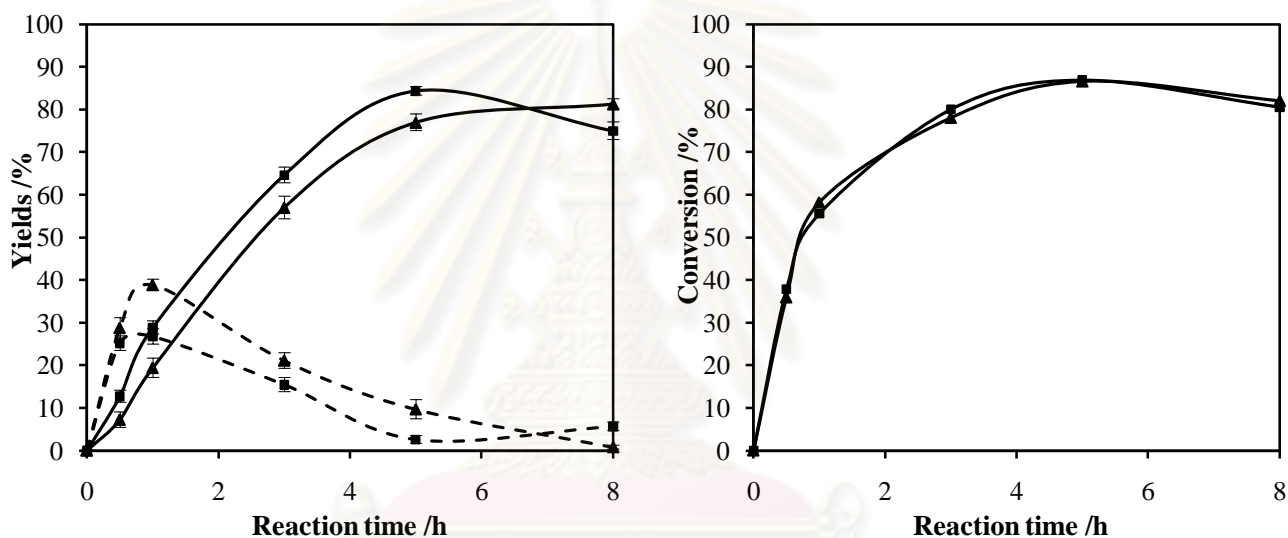


Figure 4.5 Effects of structure of alcohol on (a) the ester yield and (b) adipic conversion over Amberlyst 15. Reaction conditions: adipic acid/alcohol molar ratio, 0.33; catalyst mass, 4 wt.%; reaction temperature, 110 °C. (Symbols: (▲) 2-ethyl-1-hexanol, (■) *n*-octanol, (.....) monoester and (—) diester)

It can be seen in Figure 4.5 that the adipic acid conversion with linear alcohol is similar to branch alcohol. Therefore the molar mass of alcohol influences the diffusion rate [53]. Moreover, the diester yield of branch alcohol was higher than the diester of linear alcohol since 2-ethyl-1-hexanol is more steric. The decrease in diester yield of linear alcohol was observed that the reverse reaction occurred after a long reaction time (8 h).

4.2 Catalyst reusability

To study catalyst reusability Amberlyst 15 was used several times for esterification of adipic acid with 2-ethyl-1-hexanol using 2 wt.% of catalyst (based on adipic acid). After completion reaction the catalyst was filtered, washed with several solvent (hexane, tetrahydrofuran, acetone and methanol) to remove substances, products and by-products adhering to the surface and active site of the catalysts, dried at 100 °C overnight and reused, as seen in Figure 4.6.

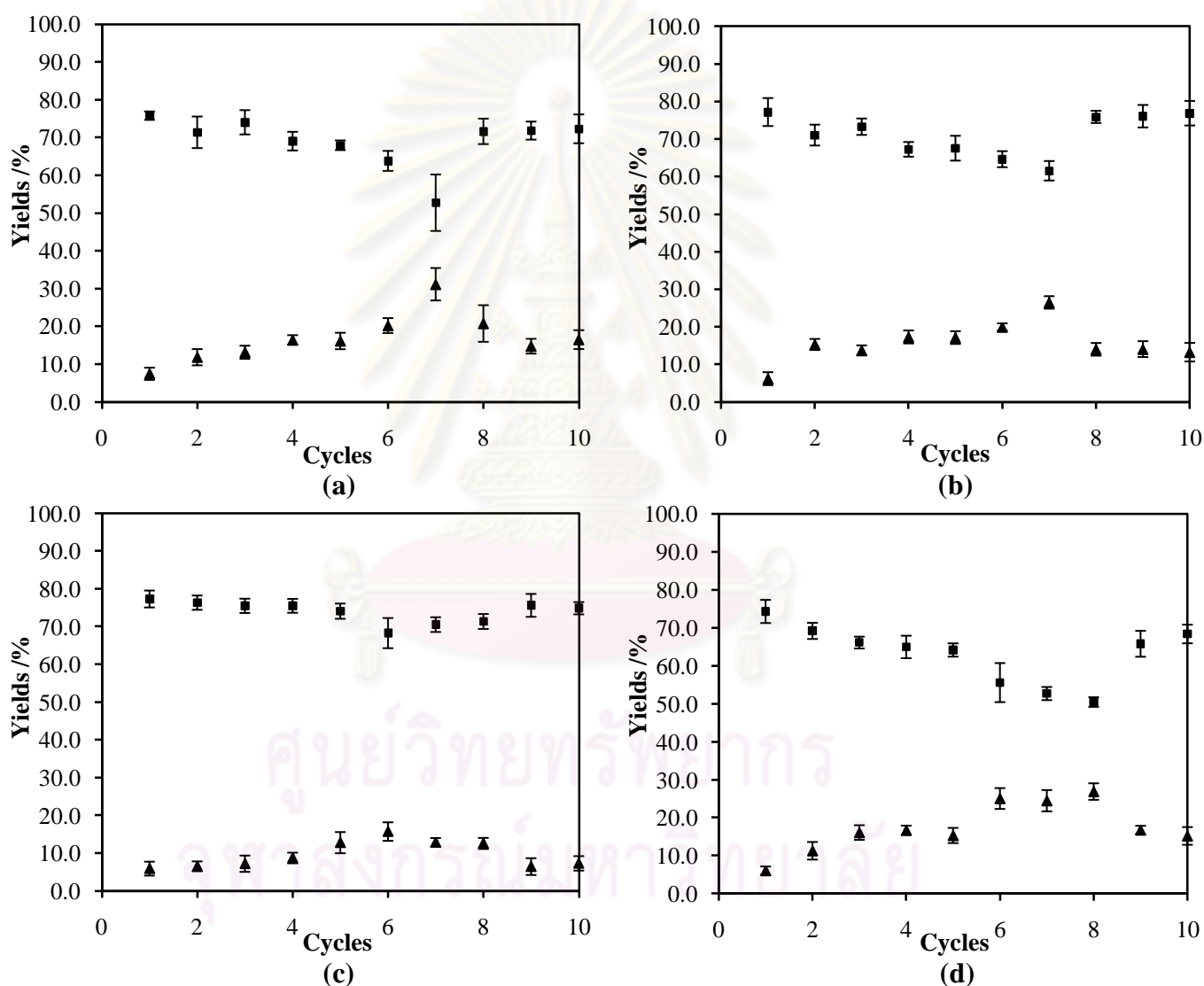


Figure 4.6 Amberlyst 15 deactivation following multiple reaction cycles of esterification of adipic acid with 2-ethyl-1-hexanol at 110 °C with solvent washing (a) hexane, (b) tetrahydrofuran (THF), (c) acetone and (d) methanol and drying between cycles. (Symbols: (▲) monoester and (■) diester)

Reaction conditions: stirring rate, 150 rpm; adipic acid/2-ethyl-1-hexanol molar ratio, 1:3; catalyst mass, 2 wt%; reaction temperature, 110 °C.

According to the obtained results (Figures 4.6 (a)-(d)), it can be observed that the monoester yield acquired from the regenerated catalyst by hexane (non-polar solvent) in the further cycle of catalysis was greater than that of the regenerated catalyst by polar ones. This results might be due to the reactants and the others by products were not eroded from the acid sites of Amberlyst 15 by hexane resulted in the decrease in acid site amount of the catalyst. On the contrary, the monoester yield, which was regenerated by methanol, was slightly increased and associated with the decrease in the diester yield. It can be postulated that the brunt hydrogen bonds occurred between the polar solvent and the acid site of the Amberlyst 15, resulting in the depletion of acid site and the decrease in the diester yield as can be seen in Figure 4.6 (d). However, the ester products (mono- and di- ester) can also be eroded in the regeneration by THF and acetone. These two kinds of solvent were a moderate polar solvent compared to methanol. Nevertheless, the diester yield obtained from the regenerated Amberlyst 15 by THF (Figure 4.6 (b)) decreased lower than that its value should be, while the diester yield that gained by the regenerated Amberlyst 15 by acetone did not change compared to the yield in the first reaction. According to the results, it can be concluded that acetone is the effective solvent to regenerate Amberlyst 15.

After a catalytic reaction for ten times, the spent catalyst has been analyzed by FT-IR spectroscopy in Figures 4.7 (b-d). Figure 4.7 (a) shows the FT-IR spectra of Amberlyst 15 that represented the broad band at 3426 cm^{-1} was attributed to the uncoordinated water (O–H stretching). The band due to the asymmetric axial deformation of the $-\text{SO}_3\text{H}$ groups at 1360 cm^{-1} was present.

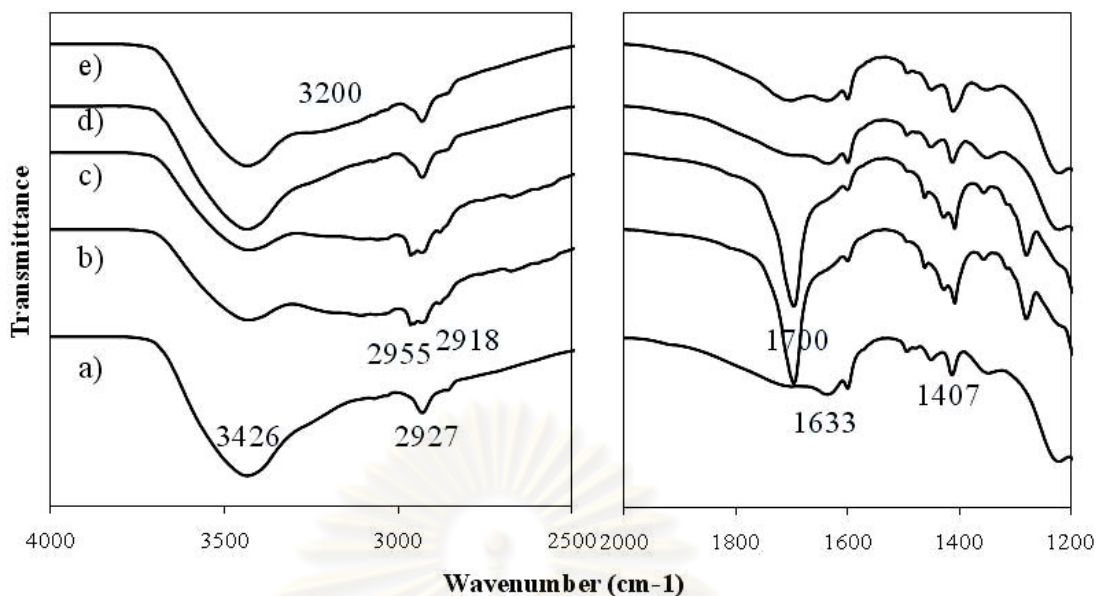


Figure 4.7 FT-IR spectra of (a) fresh Amberlyst 15 (b-e) spent Amberlyst 15 washed with various solvent (b) hexane, (c) tetrahydrofuran, (d) acetone and (e) methanol.

Figures 4.7 (b) and (c) the appearance of an additional band at 1700 cm^{-1} that should correspond to the C=O group and several bands detected in the region of $2900\text{-}3000\text{ cm}^{-1}$ for the C–H stretching. These bands occurred due to the adsorbed substances or the products. Moreover, the intensity of band at 3426 cm^{-1} decreased due to the adsorption of substances or products instead of water. On the other hand, Figures 4.7 (d) and (e) were corresponded with the spectrum of the fresh Amberlyst 15. This result was confirmed by Thermogravimetric analysis (TGA), as shown in Figure 4.8. The TGA curves showed that the fresh and spent Amberlyst 15 were washed by various solvents i.e., hexane, tetrahydrofuran, acetone and methanol. The TGA curve of the fresh Amberlyst 15 (Figure 4.8 (a)) illustrated that the degradation occurred in four steps. The first weight loss between $50\text{-}200\text{ }^{\circ}\text{C}$ was mainly due to water, corresponding to 15 %. The second step was indicated to the desulfonation of the resin occurred between $200\text{-}350\text{ }^{\circ}\text{C}$. The third step started around $360\text{ }^{\circ}\text{C}$ and was complete at $470\text{ }^{\circ}\text{C}$ due to the cross-link cleavage. The finally weight loss step took place between $500\text{-}650\text{ }^{\circ}\text{C}$ since the degradation of various aromatic compounds i.e., styrene and benzene [54]. The TGA profile of the fresh Amberlyst 15 is similar to the Figures 4.8 (d) and (e).

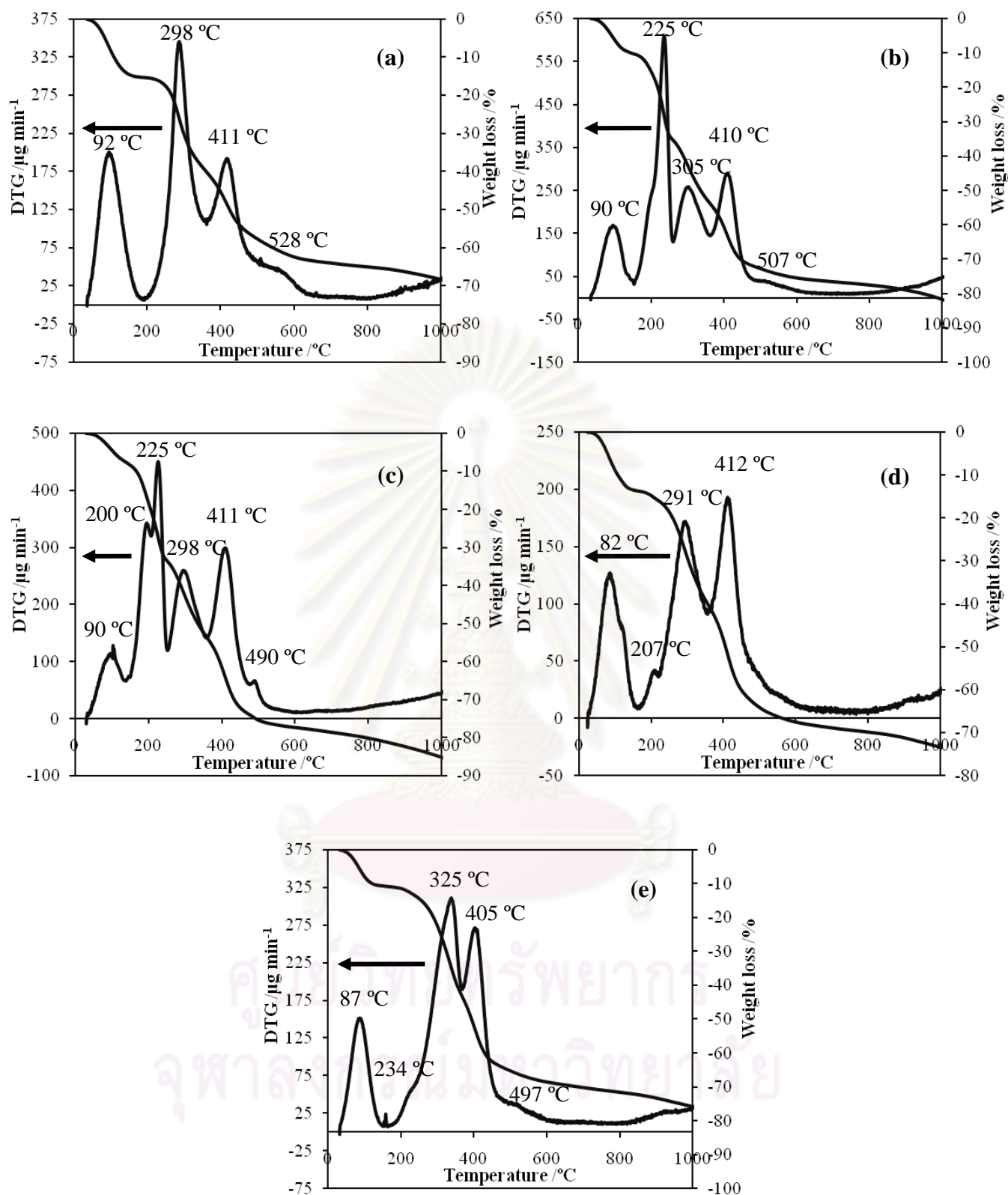


Figure 4.8 The weight loss and DTG curves of (a) fresh Amberlyst 15 (b-e) spent Amberlyst 15 washed with various solvent (b) hexane, (c) tetrahydrofuran, (d) acetone and (e) methanol.

In Figures 4.8 (b) and (c) gave the percentage weight loss of the first step of 9 and 11, respectively, which less than that of the fresh Amberlyst 15 (Figure 4.8 (a)). Additionally, it was clearly seen that the thermograms appeared the other weight loss step took place between 150-250 °C due to the decomposition of the adsorbed reactants or products on the active sites, corresponding to 25 % and 23 %, as shown in Figures 4.8 (b) and (c). Owing to the reactants or products can replace adsorbed water. The degradation temperature and percentage of weight loss are summarized in APPENDIX C.

4.3 Kinetic study

The kinetic data for the formation of bis (2-ethylhexyl) adipate was obtained from esterification of adipic acid with 2-ethyl-1-hexanol in the presence of Amberlyst 15. The activation energy (E_a) was calculated from the plot of $\ln k$ versus $1/T$, as seen in Figure 4.9.

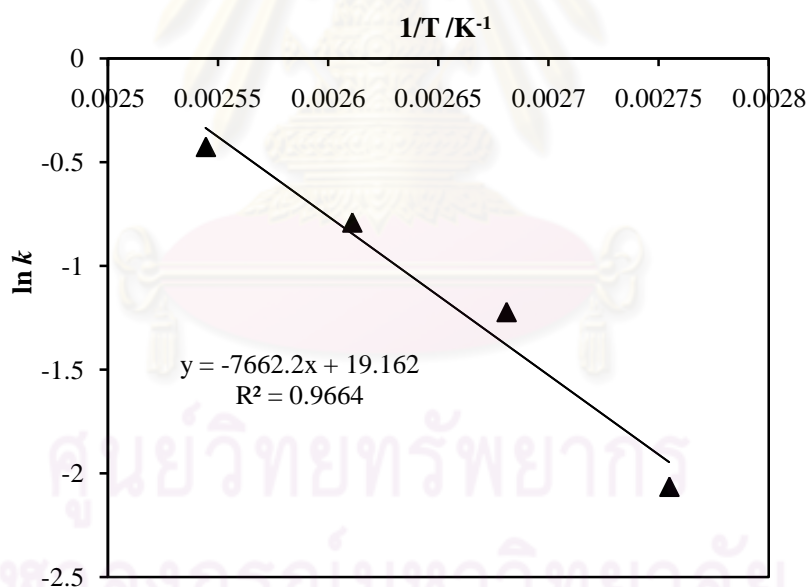


Figure 4.9 Plot of $\ln k$ vs. $1/T$ for the esterification of adipic acid with 2-ethyl-1-hexanol using Amberlyst 15 (from initial reaction rate data). Reaction conditions: adipic acid/2-ethyl-1-hexanol molar ratio, 1:3; catalyst mass, 4 wt.%.

The plot of $\ln k$ versus $1/T$ (Figure 4.9), constructed from the data obtained at different temperature of the reaction followed by the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

or

$$\ln k = \ln A - \frac{E_a}{RT}$$

where k is the rate constant, E_a is the activation energy, R is gas constant and T is the reaction temperature in Kelvin. The value of activation energy has been found to be 63.7 kJ mol^{-1} .

The initial reaction rate was determined from experimental data by varying the concentration of the substance when kept the other substances constant. The results are shown in Figures 4.10-4.13.

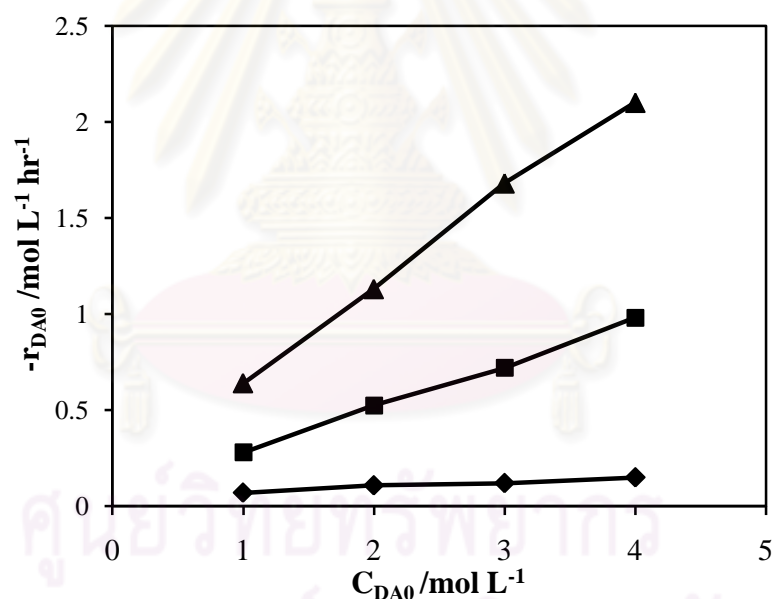


Figure 4.10 Effect of dicarboxylic acid concentration on initial rate. (Symbols: (◆) 90 °C, (■) 100 °C and (▲) 110 °C)

As seen in Figure 4.10, the initial rate increased linearly with increasing the concentrations of adipic acid.

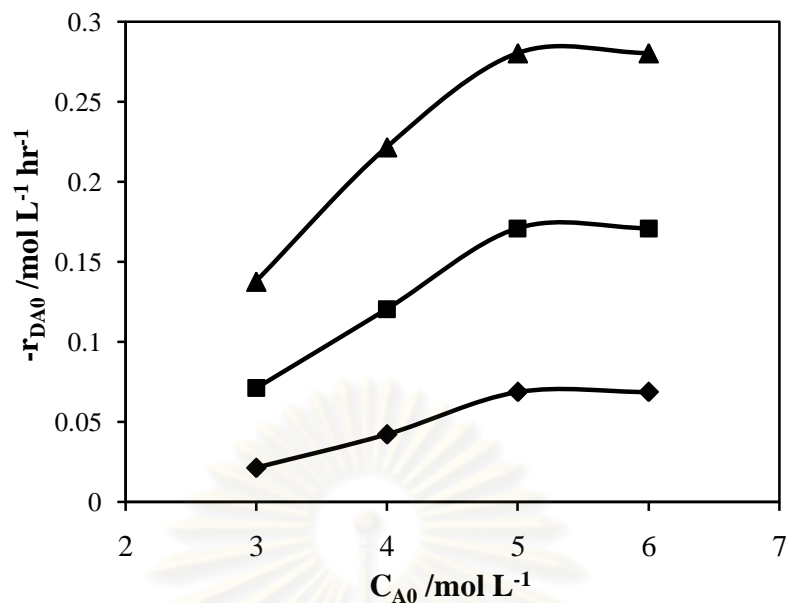


Figure 4.11 Effect of alcohol concentration on initial rate. (Symbols: (♦) 90 °C, (■) 100 °C and (▲) 110 °C)

Figure 4.11 shows increasing of the initial concentrations of 2-ethyl-1-hexanol after 5 mol L⁻¹, initial rate kept constant as it reached equilibrium that is similar to Langmuir isotherm.

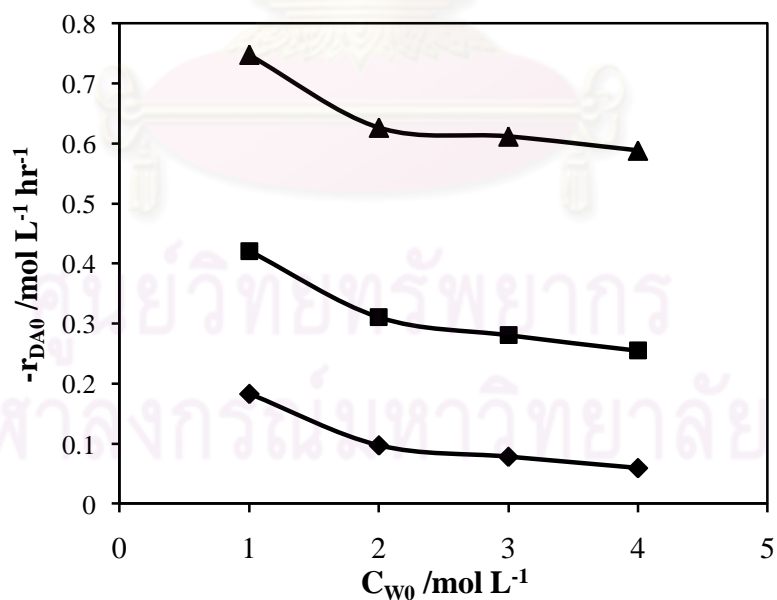


Figure 4.12 Effect of water concentration on initial rate. (Symbols: (♦) 90 °C, (■) 100 °C and (▲) 110 °C)

Figure 4.12 shows the inhibiting effect of water on the initial rate, it was found that initial rate slightly decreased with the presence of water. Figure 4.13 shows the independence of bis (2-ethylhexyl) adipate concentration to the initial rate.

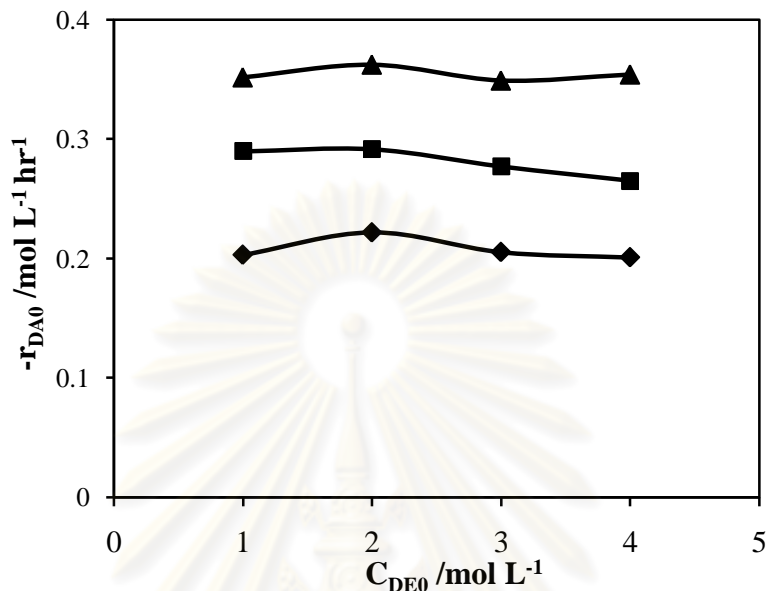
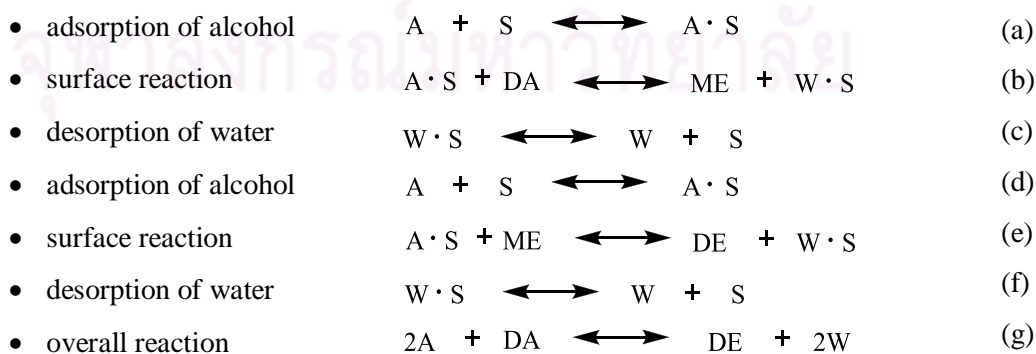


Figure 4.13 Effect of diester concentration on initial rate. (Symbols: (◆) 90 °C, (■) 100 °C and (▲) 110 °C)

From Figures 4.10-4.13 can conclude that the reaction mechanism follows by Eley–Rideal model, which is the reaction takes place between adsorbed molecules of alcohol and molecules of water in the bulk of the catalyst surface. Figures 4.10-4.13 also indicate that the reaction is sensitive to temperature. Since this reaction is controlled by the surface reaction step. The mechanism of esterification of adipic acid with 2-ethyl-1-hexanol can be given as follows:



where S denotes to vacant sites of the catalyst surface. For these assumptions the reaction rate expression can be given by and subscripts DA, A, ME, DE and W refer to dicarboxylic acid, alcohol, monoester, diester and water.

$$-r_{DA} = \frac{k \frac{m}{V} \left(C_{DA} C_A^2 - \frac{C_{DE} C_W^2}{K_e} \right)}{1 + K_A C_A^2 + K_W C_W^2} \quad (1)$$

where k is the reaction rate constant, K_e is the equilibrium constant of the reaction, K_A and K_W are the adsorption equilibrium constants, m is the amount of catalyst, V is the volume of the reaction mixture.

For the initial rate with the absence of product can be reduced to:

$$-r_{DA0} = \frac{km C_{A0}^2}{V(1 + K_A C_{A0}^2)} C_{DA0} \quad (2)$$

A plot of $-r_{DA0}$ versus C_{DA0} gives a straight line with slope of $kmC_{A0}^2/V(1 + K_A C_{A0}^2)$ at different temperatures, as shown in Figure 4.10. If equation (2) is rearranged for variable C_A values:

$$-\frac{1}{r_{DA0}} = \frac{VK_A}{kmC_{DA0}} + \frac{V}{kmC_{DA0}} \frac{1}{C_{A0}^2} \quad (3)$$

A plot of $-1/r_{DA0}$ versus $1/C_{A0}^2$ gives a straight line with slope of V/kmC_{DA0} and intercept of VK_A/kmC_{DA0} at different temperatures, as shown in Figure 4.14.

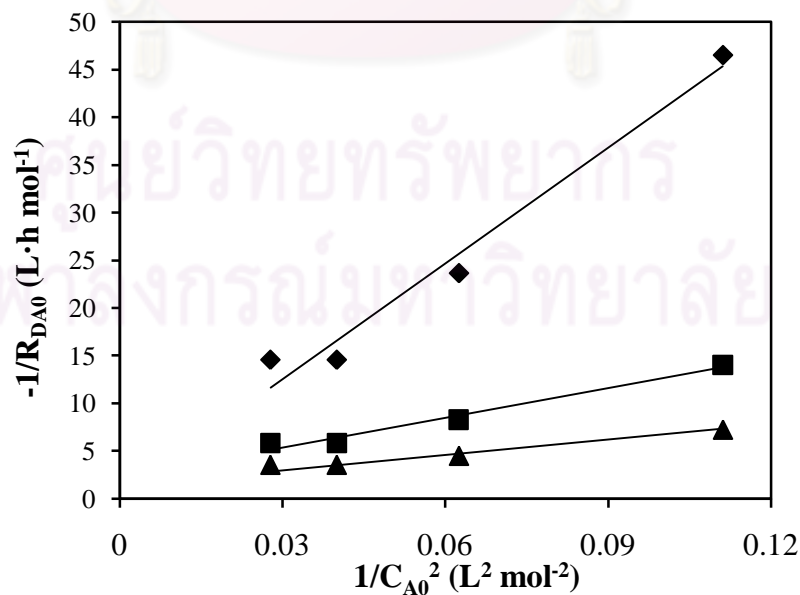


Figure 4.14 Plot of $-1/r_{DA0}$ versus $1/C_{A0}^2$ at different temperatures. (Symbols: (◆) 90 °C, (■) 100 °C and (▲) 110 °C)

The inhibiting effect of water concentration with no diester present initially was determined:

$$-r_{DA} = \frac{k \frac{m}{V} (C_{DA} C_A^2)}{1 + K_A C_A^2 + K_W C_W^2} \quad (4)$$

from which the following equation can be given:

$$-\frac{1}{r_{DA0}} = \frac{V(1 + K_A C_{A0}^2)}{kmC_{DA0}C_{A0}^2} + \frac{VK_W}{kmC_{DA0}C_{A0}^2} C_{W0}^2 \quad (5)$$

A plot of $-1/r_{DA0}$ versus C_{W0}^2 gives a straight line with slope of $VK_W/kmC_{DA0}C_{A0}^2$ and intercept of $V(1 + K_A C_{A0}^2)/kmC_{DA0}C_{A0}^2$ at different temperatures, as shown in Figure 4.15.

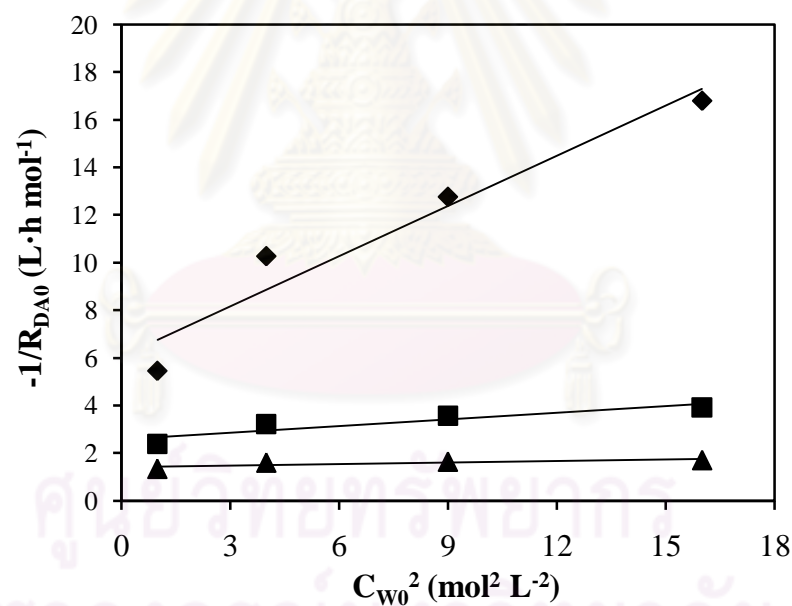


Figure 4.15 Plot of $-1/r_{DA0}$ versus C_{W0}^2 at different temperatures. (Symbols: (◆) 90 °C, (■) 100 °C and (▲) 110 °C)

The values of the slope and intercept of the lines, as shown in Figures 4.10, 4.14 and 4.15 were summarized in Table 4.5.

Table 4.5 The values of slope and intercept of the lines in Figures 4.7, 4.11 and 4.12

T (K)	Equation (2)	Equation (3)		Equation (5)	
	$kmC_{A0}^2/V(1 + K_A C_{A0}^2)$	$V/(kmC_{DA0})$	VK_A/kmC_{DA0}	$VK_W/kmC_{DA0}C_{A0}^2$	$V(1 + K_A C_{A0}^2)/kmC_{DA0}C_{A0}^2$
363	0.0415	404.73	0.3917	0.702	6.0633
373	0.247	103.67	2.2434	0.0929	2.5727
383	0.5447	53.201	1.4017	0.0203	1.4143

k , K_A and K_W were obtained at different temperatures. The resulting values are presented in Table 4.6.

Table 4.6 The resulting values of k , K_A and K_W

T (K)	k (L ² g ⁻¹ mol ⁻¹ h ⁻¹)	K_A (L mol ⁻¹)	K_W (L mol ⁻¹)
363	0.1065	0.0009	0.1238
373	1.0496	0.0216	0.2821
383	2.4795	0.0263	1.6111

The resulting values in Table 4.7 were applied to the Arrhenius equation, the dependence of temperature of the constants was found to be:

$$k = 2.51 \times 10^{25} \exp\left(\frac{-21964}{T}\right)$$

$$K_A = 2.76 \times 10^{25} \exp\left(\frac{-23640}{T}\right)$$

$$K_W = 1.95 \times 10^{20} \exp\left(\frac{-17776}{T}\right)$$

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this thesis, the diesters were synthesized via esterification of dicarboxylic acid (adipic acid, azelaic acid and sebacic acid) with alcohol (*n*-octanol and 2-ethyl-1-hexanol) over various strong acid Amberlyst ion-exchange resins (Amberlyst 15, Amberlyst 16 wet and Amberlite IR-120) to compare the catalytic efficiency under nitrogen atmosphere. The effect of catalyst amount (1-10 %), molar ratio of adipic acid/2-ethyl-1-hexanol (0.25-0.5), reaction temperature (90-120 °C), reaction time (0.5-10 h), chain length of the dicarboxylic acids and structure of alcohols were examined. The reusability of Amberlyst 15 has been also investigated. Thermogravimetric/differential thermal analysis (TG/DTA) and Fourier transform infrared spectroscopy (FT-IR) were applied to reveal the presence of catalyst deactivation. The kinetics of esterification of adipic acid with 2-ethyl-1-hexanol has been studied. The following conclusions can be attained:

- Amberlyst 15 is the most active catalyst in the esterification of adipic acid with 2-ethyl-1-hexanol. The catalyst activity was related to the pore size and specific surface area of the resin.
- The diester yield was increased with the increasing catalyst amount because the active sites of catalyst are increased. A decrease in the adipic acid/2-ethyl-1-hexanol ratio resulted in an improvement of the diester yield and the diester selectivity.
- The diacid conversion and the ester yield were increased with the reaction temperature and reaction time but after reaction for over 8 h, the remaining diacid and diester yield kept constant.

- The size of diacid significantly affected the diester yield and the selectivity to diester as well. When the number of carbon in the linear alkyl chain was increased, the diacid conversion and the diester yield were decreased due to the enhanced of steric effect.
- The conversion of adipic acid with linear alcohol is similar to branch alcohol. Since the molar mass of alcohol influences the diffusion rate.
- The regenerated Amberlyst 15 is very efficient when using acetone as solvent. The adsorption of substances i.e., adipic acid, 2-ethyl-1-hexanol, monoester and water resulted in the catalyst deactivation.
- The activation energy (E_a) of this reaction was found to be 63.7 kJ mol^{-1} . The reaction was found to follow Eley–Rideal mechanism that appeared adsorption of 2-ethyl-1-hexanol and water molecules and was also observed the inhibiting effect of water. The rate constant (k) can be given by $k = 2.51 \times 10^{25} \exp(-21964/T) \text{ L}^2 \text{ g}^{-1} \text{ mol}^{-1} \text{ h}^{-1}$. The adsorption equilibrium constant of 2-ethyl-1-hexanol and water were calculated to be $K_A = 2.76 \times 10^{25} \exp(-23640/T)$ and $K_w = 1.95 \times 10^{20} \exp(-17776/T) \text{ L mol}^{-1}$, respectively.

5.2 Recommendations

- Study in detail on physicochemical properties of diester.
- Explore to the use of Amberlyst 15 to the other reactor type e.g. fixed bed reactor.

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APPENDICES

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Appendix A

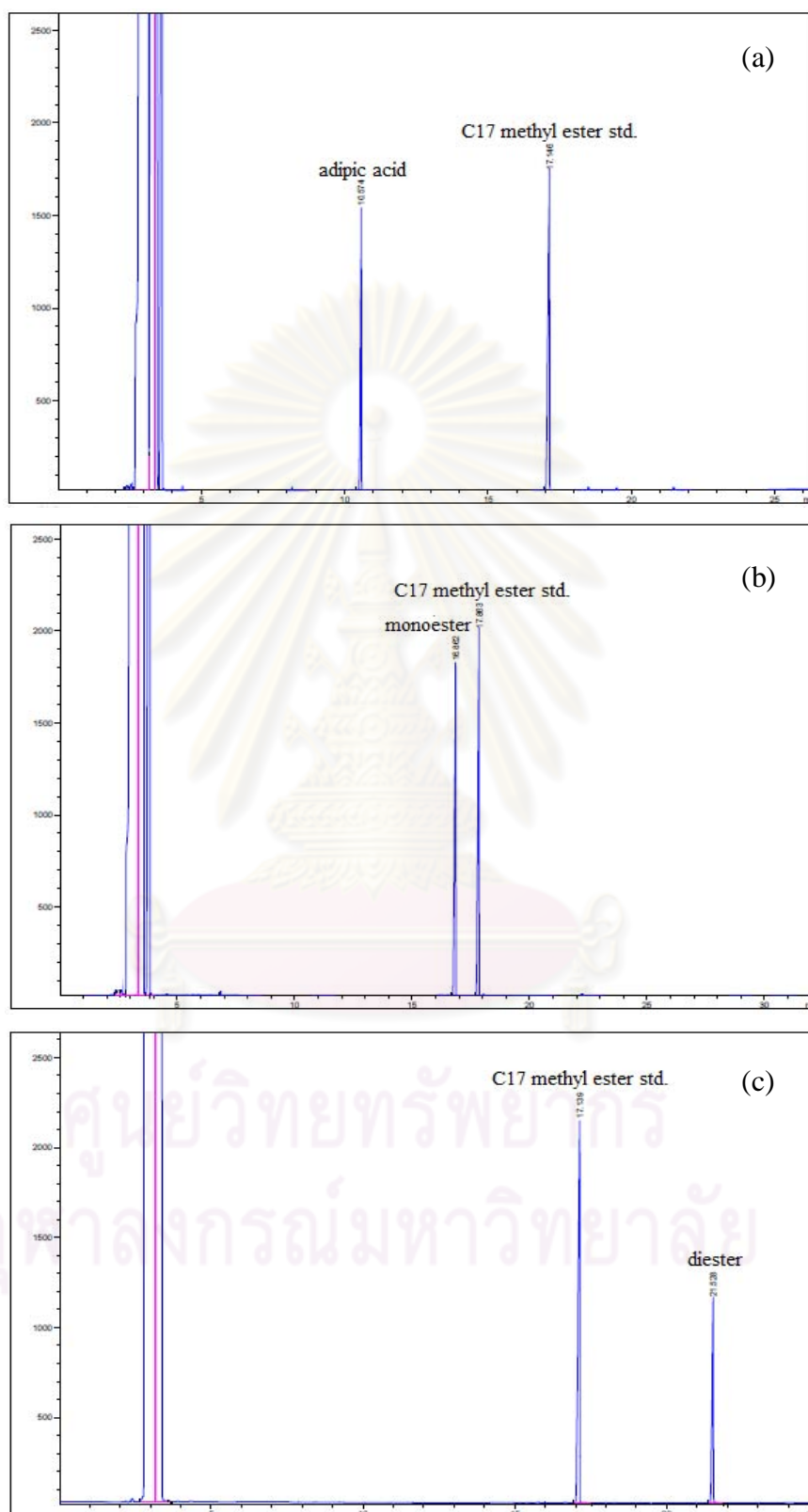


Figure A-1 The chromatograms of (a) adipic acid (b) 6-(2-ethylhexyloxy)-6-oxohexanoic acid and (c) bis (2-ethyl hexyl) adipate standards using methyl heptadecanoate as internal standard.

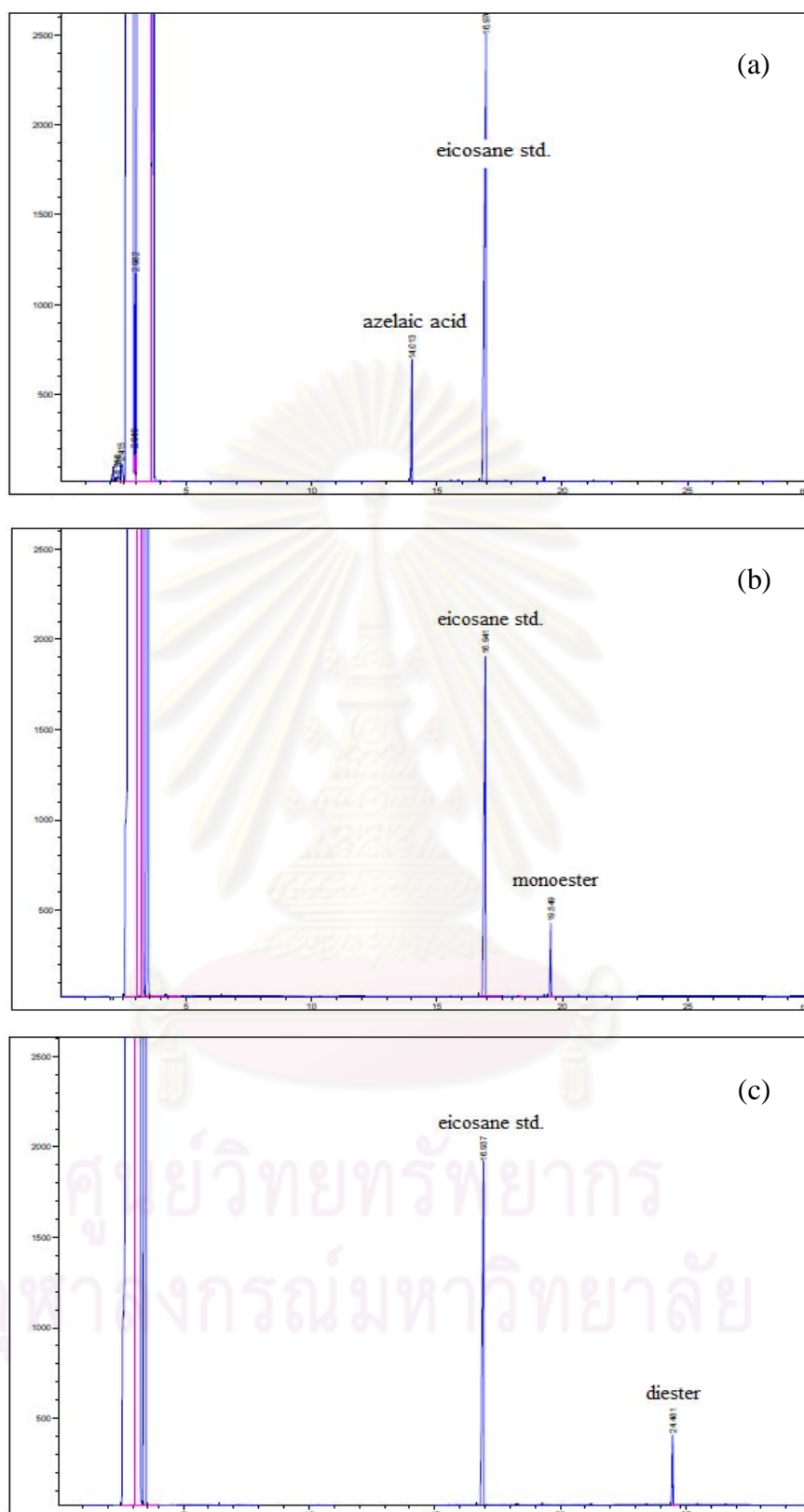


Figure A-2 The chromatograms of (a) azelaic acid (b) 9-(2-ethylhexyloxy)-9-oxononaic acid and (c) bis(2-ethyl hexyl) azelate using eicosane as internal standard.

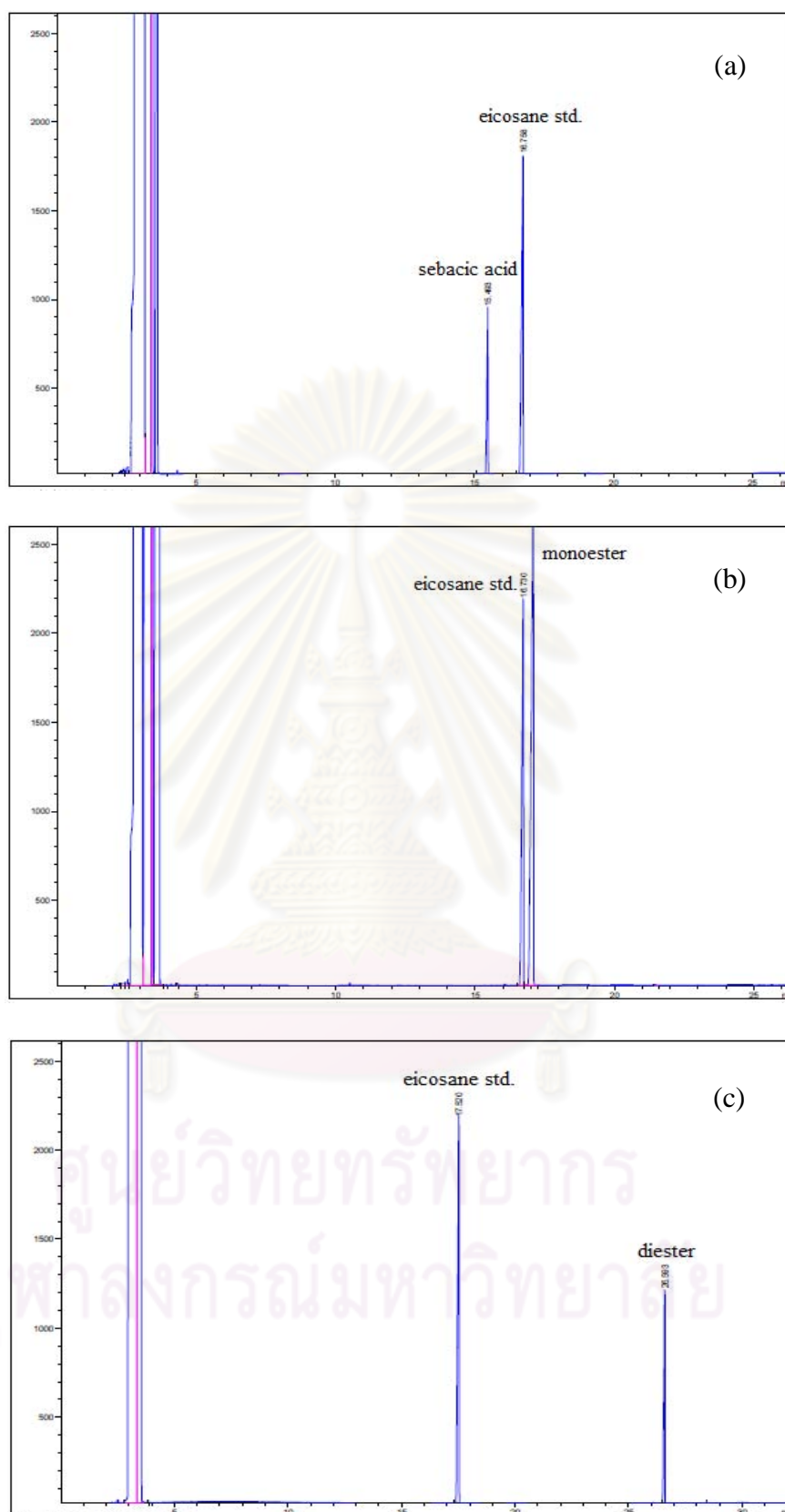


Figure A-3 The chromatograms of (a) sebacic acid (b) 10-(2-ethylhexyloxy)-10-oxodecanoic acid and (c) bis (2-ethyl hexyl) sebacate using eicosane as internal standard.

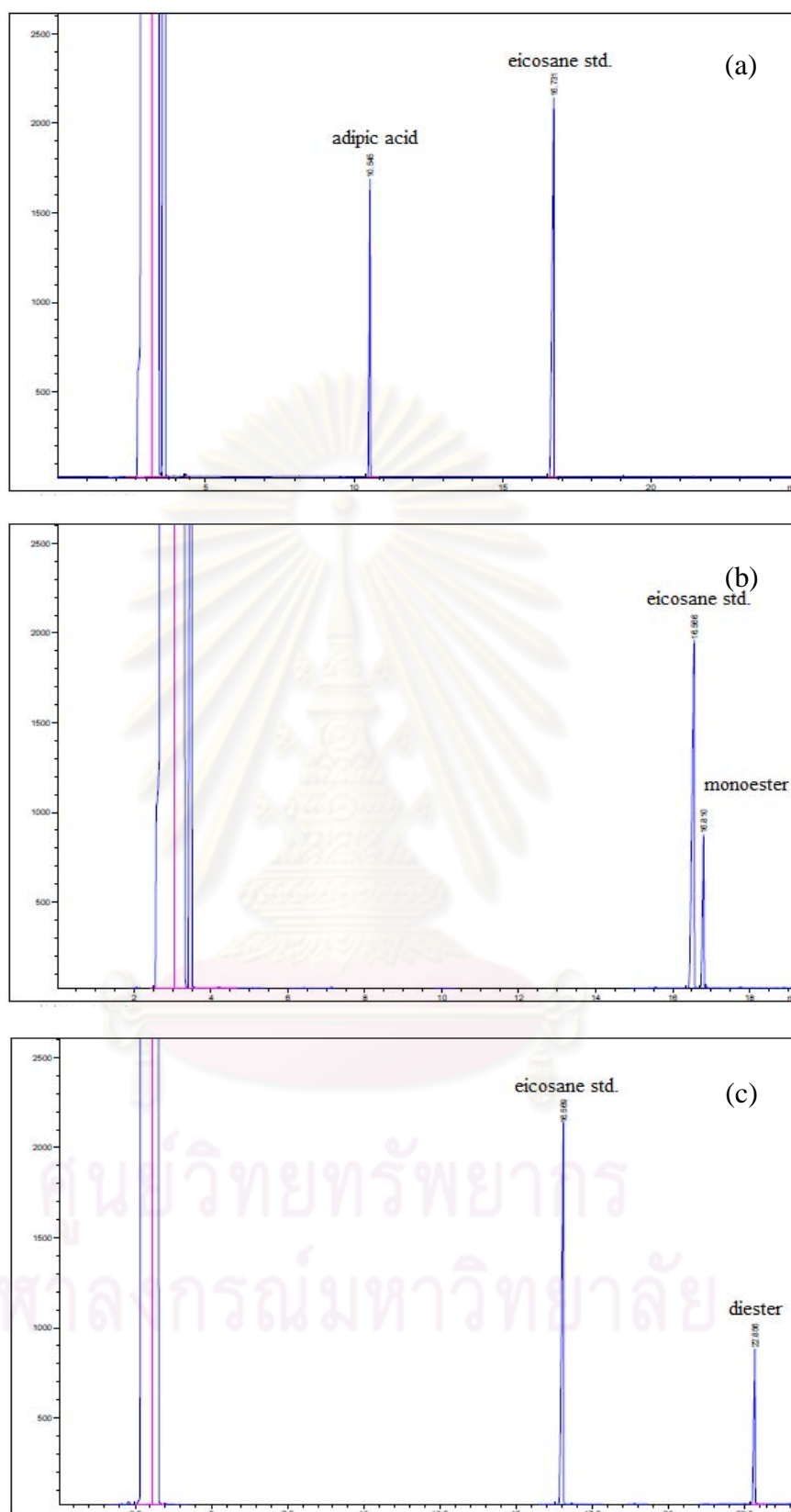


Figure A-4 The chromatograms of (a) adipic acid (b) 6-(octyloxy-6-oxohexanoic acid and (c) bis (octyl) adipate standards using eicosane as internal standard.

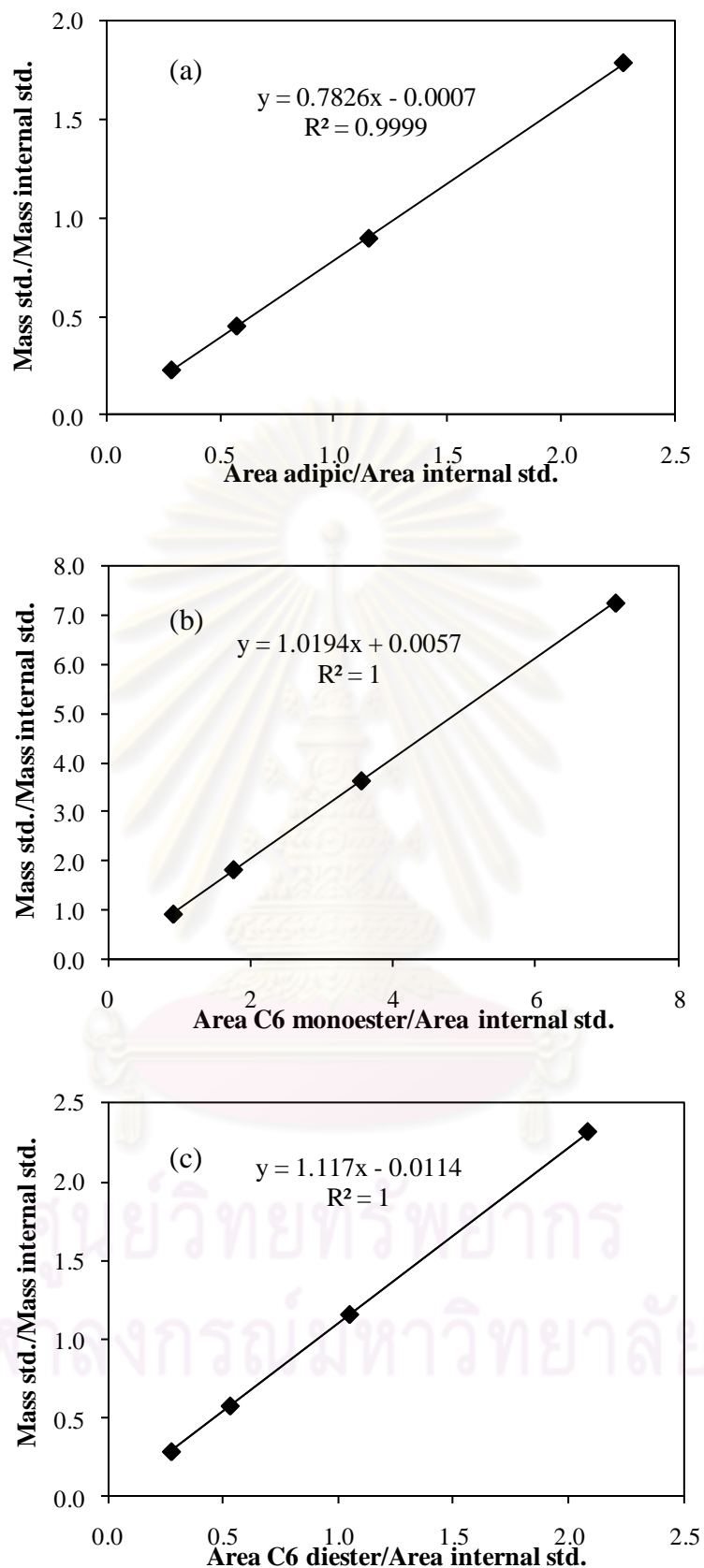


Figure A-5 The standard curves of (a) adipic acid (b) 6-(2-ethylhexyloxy-6-oxohexanoic acid and (c) bis (2-ethylhexyl) adipate standards using methyl heptadecanoate as internal standard.

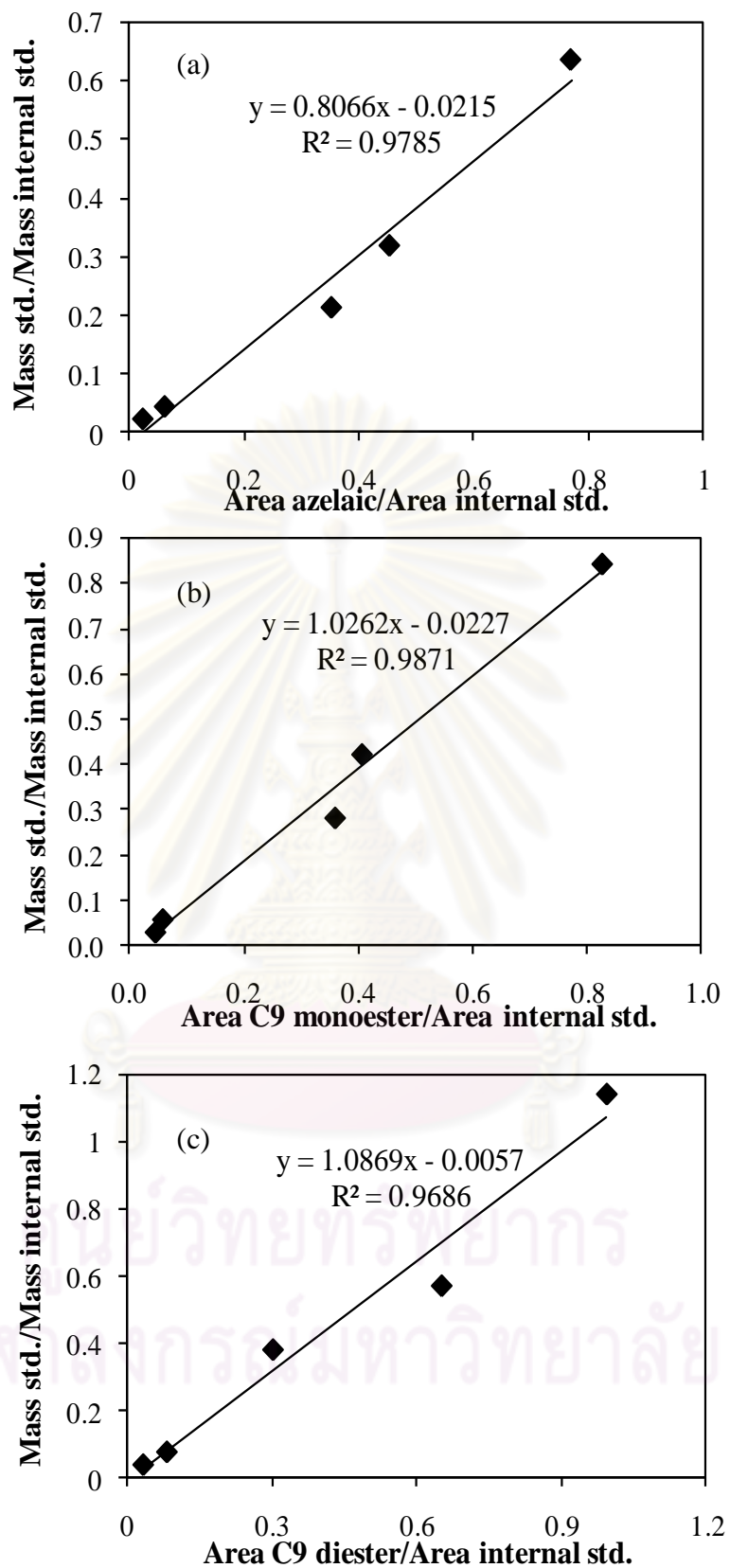


Figure A-6 The standard curves of (a) azelaic acid (b) 9-(2-ethylhexyloxy)-9-oxononaic acid and (c) bis (2-ethyl hexyl) azelate using eicosane as internal standard.

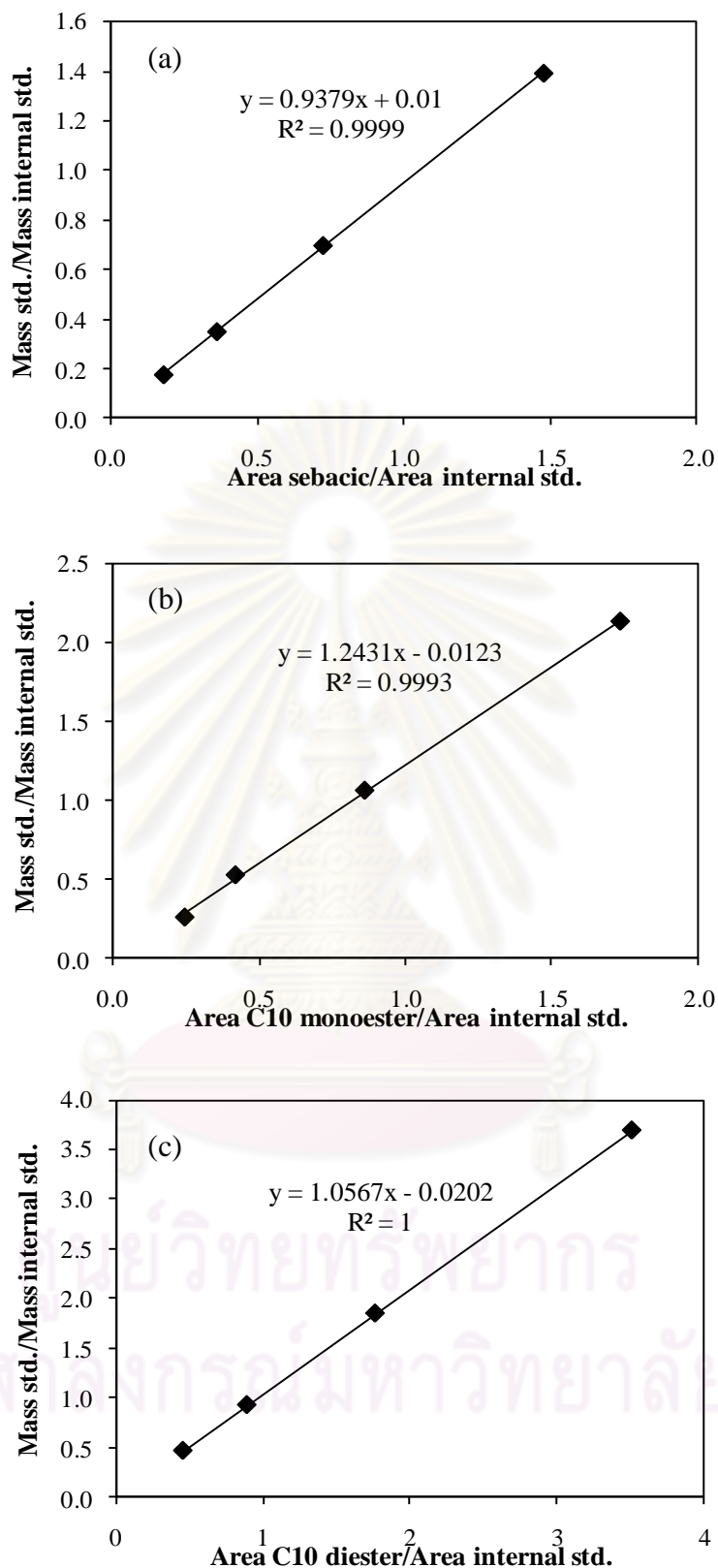


Figure A-7 The standard curves of (a) sebacic acid (b) 10-(2-ethylhexyloxy)-10-oxodecanoic acid and (c) bis (2-ethyl hexyl) sebacate using eicosane as internal standard.

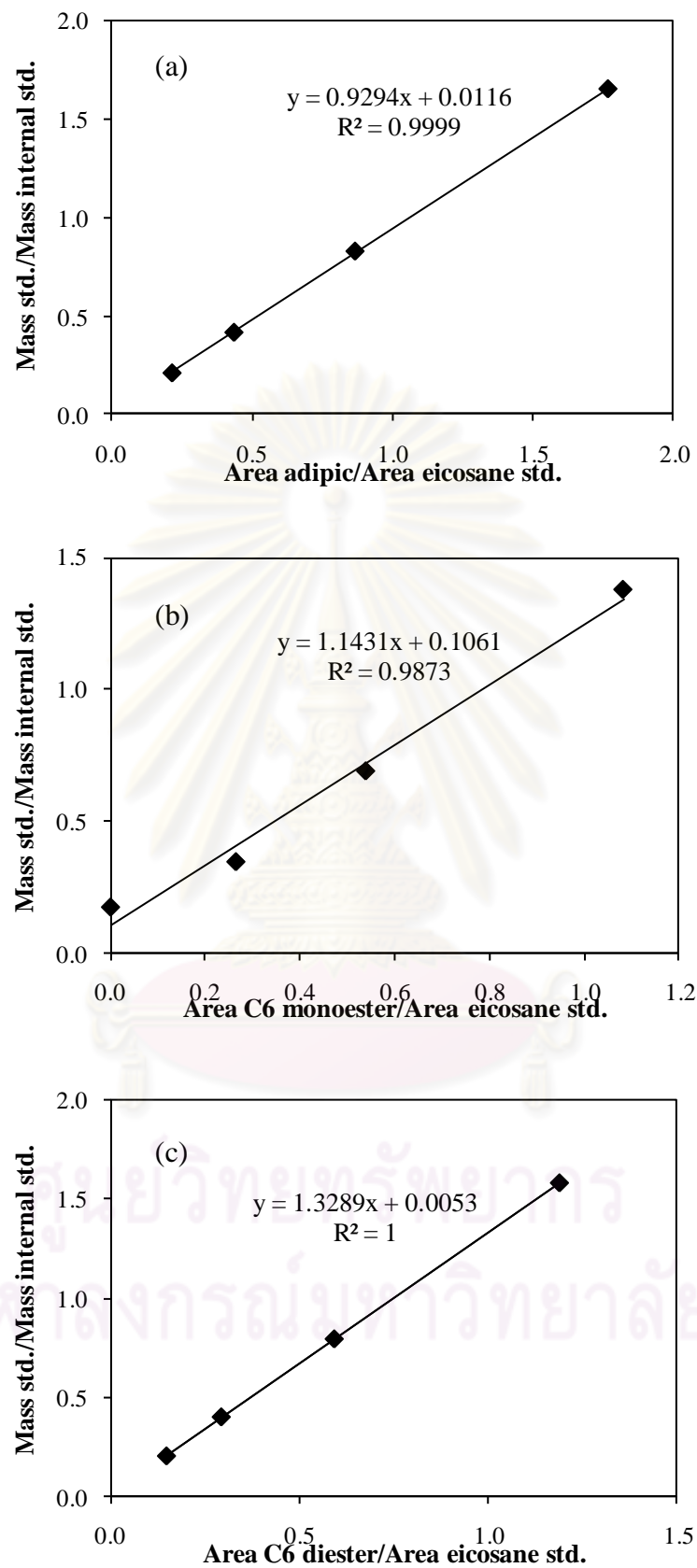


Figure A-8 The chromatograms of (a) adipic acid (b) 6-(octyloxy-6-oxohexanoic acid and (c) bis (octyl) adipate standards using eicosane as internal standard.

Appendix B

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

The percent yield was calculated based on the results obtained from gas chromatography. Methyl heptadecanoate (for adipic acid) and eicosane (for azelaic acid and sebacic acid) 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

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

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

$$= G \times D = H$$

The correction factor of the product can be calculated as:

$$= C/H = I$$

Thus, the percentage of product can be calculated as:

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

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

Appendix C

Table C-1 The degradation temperature and percentage of weight loss of the catalysts

Degradation temperature (°C) (onset – offset)	Percentage weight loss				
	Amberlyst15	Spent Amberlyst15			
		Hexane	THF	Acetone	Methanol
70 – 120	17	10	12	14	12
170 – 240	-	25	22	5	8
280 – 350	23	22	21	22	23
380 – 430	20	18	20	22	21
470 – 530	8	7	9	10	11

ศูนย์วิทยทรัพยากร
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VITAE

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