LUBE BASE SYNTHESIS FROM SORBITOL AND HEXANOIC ACID

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Abstract

The synthesis of lube base oil from sorbitol and hexanoic acid via esterification reaction was attempted. The degree of esterification was investigated over various reaction conditions which including the changes in the reaction temperature from 140°C to 130°C, the reaction time from 4 to 3 and 5 hours, and the ratio between sorbitol to hexanoic acid from 1:6 to 1:9. ^{1}H-NMR spectrometer and gas chromatograph – mass spectrometer (GC-MS), and thermogravimetric analyzer (TGA) were used to characterize the products. The optimum condition was found to be that using 1:6 ratio by mole of sorbitol to hexanoic acid at 140°C for 4 hours that resulting in the degree of esterification of 63.83%. The product from the optimum condition was found to be composed of 3 constituents; 3.78% of diesters, 10.96% of triesters, and 85.26% of tetra esters. Its properties; namely viscosity @40°C and @100°C, viscosity index, pour point, thermal stability, and total acid number were tested. These properties of synthetic ester product were close to those of base oil 500SN.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Motivation

Historically, it has been found from the earliest times that animal and vegetable oils were used as lubricants in transportation or machinery to reduce friction and wear. These lubricants, while still useful, are not adequate for our industrialized society, either in volume or in desirable properties. Two major problems with vegetable oils as based lubricants are low thermal stability and poor temperature properties. However, with the addition of additives, these properties can sometimes be improved, but only at the sacrifice of biodegradability, toxicity and cost. These problems can be solved by transesterification of vegetable oils to synthetic ester lubricants. Synthetic ester lubricants show superior biodegradability, viscosity indices and lubricating properties compared with mineral oils. Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and grease formulations. The inherent biodegradability of ester molecules offers additional benefits to their performance [1].

In 2005, the world demand of lubricating oil was about 36.5 million tons per year. It continuously increases [2]. Normally, lubricating oil is originated from crude oil that is non-renewable. Rising prices and environmental problem might be of a major concern in the near future. So, many researches use biomass as the source of lubricating oil which is renewable and good for environment.

Due to the fact that Thailand is an agricultural country that can produce approximately 5 million tons of sugar per year [3], which is very important as feedstock in industries such as food, drink, medicine and candy. Sugar can be classified into three different types: monosaccharide,

disaccharide and polysaccharide. Sorbitol is an important form of sugar which is obtained from glucose through hydrogenation reaction. L.Harvet and his team conducted an experiment which synthesized lubricating oil from sorbitol acetate with metallic alcohol to obtain sorbitol ester and acetic acid via transesterification [4]. However, the lubricating oil product from their research had low viscosity which cannot be used widely. To improve upon the previous result and make it possess higher viscosity over a wider range, the chain length of the product should be extended.

In this research, esterification reactions of sorbitol with hexanoic acid which can be found naturally in various animals fats and oils were attempted. The degree of esterification was investigated over various reaction temperatures and time. ^{1}H-NMR spectra and gas chromatogram of the synthetic ester were provided to find the optimized conditions. The viscosity, viscosity index, density, pour point, flash point, thermal stability and total acid number of the product were also tested.

1.2 Objectives

1) To synthesize an ester product from sorbitol and hexanoic acid

2) To study the properties of ester as a lube base oil.

1.3 Scope of study

1) Synthesis of the ester product via esterification

The reaction variables effecting the degree of esterification were studied as the following:

- The reaction temperature from 130^{o}C to140^{o}C
- The reaction time from 3 hours to 5 hours
- The ratio between sorbitol and hexanoic acid from 1:6 to 1:9

2) Characterization of ester products

- Nuclear Magnetic Resonance Spectrometer (NMR)
- Thermal Gravimetric Analyzer (TGA)
- Gas Chromatograph-Mass Spectrometer (GC-MS)

3) Testing of the properties of ester products

- Viscosity by ASTM D445
- Viscosity Index by ASTM D2270
- Density by ASTM D4052
- Pour point by ASTM D97
- Flash point by ASTM D92
- Thermal stability by ASTM D6203
- Total acid number (TAN) by ASTM D664

1.4 Expected results

The synthesized lube base oil would has a high degree of esterification. Its properties could be used as a replacement for some grades of lube base oil and provides a positive environmental effect as a renewable lubricant.

CHAPTER 2

THEORETICAL AND LITERATURE REVIEWS

2.1 Lubricants [5]

The most important function of lubricants is the reduction of friction and wear and in some case, the relative movement of two bearing surfaces is only possible if a lubricant is present. In time when saving energy and resources and cutting emission have become central environmental matters, lubricants are increasingly attracting public awareness. Scientific research has shown that 0.4% of gross domestic product could be saved in term of energy in Western industrialized countries if current tribiological knowledge, i.e. the science of friction, wear and lubrication, was just applied to lubricated processes.

Apart from important applications in internal combustion engines, vehicle and industrial gearboxes, compressors, turbines or hydraulic systems, there are a vast number of other applications which mostly require specifically tailored lubricants. This is illustrated by numerous types of greases or the different lubricants for chip-forming and chip-free metal working operations which are available. Between 5,000 and 10,000 different lubricant formulations are necessary to satisfy more than 90% of all lubricant applications.

2.2 fundamentals of lubrication [6]

2.2.1 General

This section provides an overview of the fundamentals of lubrication. Included are the basic properties and functions of a lubricant, and how a lubricant acts to reduce friction and wear, dissipate heat, and prevent corrosion.

2.2.2 Friction and wear

The surfaces of machinery components appear well-finished to the naked eye. When magnified, however, surface imperfections become readily apparent. These microscopic hills and valleys are called asperities. When dry surfaces move relative to one another, asperities may rub, lock together, and break apart. The resistance generated when these adjacent surfaces come in contact is called friction. The welding together and breaking apart of asperities is a form of adhesive wear. Another form of wear may occur when a hard contaminant particle becomes trapped between two opposing surfaces. When this occurs, the contaminant acts as a miniature lathe, cutting into the softer machinery surface. This process is termed abrasive wear. Another consequence of friction is that the energy created by resistance is converted into heat. The primary functions of a lubricant, then, are the formation of a protective film between adjacent surfaces to reduce wear, and the dissipation of heat generated at these wear surfaces.

2.2.3 Corrosion protection

A second role provided by a lubricant is the prevention of system corrosion. In environments where contamination of the system with water is likely, protection of machinery components from corrosion is of the utmost importance. Salt water is considerably more corrosive than fresh water; thus machinery must be well protected from this contaminant. Water molecules may also diffuse through the lubricant and enter surface microcracks, causing hydrogen embrittlement and subsequent surface failure. It is thus imperative that water contamination of machinery systems be minimized. To achieve corrosion protection, lubricants must form a protective barrier on machinery surfaces. Modern-day lubricants often contain corrosion inhibitors which chemically bond to the metallic surfaces of equipment components. Corrosion inhibitors are an example of a class of compounds called additives.

2.3 Important properties of lubricants [7]

2.3.1 Viscosity

The most important physical property of a lubricant is its viscosity. Viscosity, which may be defined as a fluid's resistance to flow, is the characteristic most frequently stipulated by equipment manufacturers when making lubricant recommendations. The selection of proper lubricant viscosity is often a compromise between selecting one high enough to prevent metal to metal (wear) contact, and one low enough to allow sufficient heat. In the past, viscosity was measured in such units as Saybolt Universal Seconds (SUS), Redwood No. 1 Seconds, and Engler Degrees. The preferred unit of measurement for the U.S. Navy is the centistokes (cSt). Kinematic viscosity in centistokes is obtained by measuring the time required for a specified volume of fluid to flow through a calibrated capillary tube at a specified temperature.

2.3.2 Viscosity index (VI)

The effect of temperature on a lubricant's viscosity is a measurement of its Viscosity Index (VI). When the VI scale was introduced in 1929, a reference paraffinic base stock was S9086-H7-STM-010/CH-262R4 262-2 assigned a VI of 100, and a naphthenic base stock a VI of 0. Most naval oils of paraffinic base stock have VI's in the 95-100 range. Naval oils prepared from synthetic stock, and multigrade engine oils typically have VI's in excess of 100. The higher the VI, the less a given lubricant's viscosity will change with a subsequent change in temperature.

2.3.3 Cloud point and pour point

Since petroleum stock consists of a mixture of molecular components, lubricants do not exhibit sharp freezing points. Rather, as a lubricant is cooled, certain components such as waxes will begin to precipitate out and become evident in the liquid as a cloud. The temperature at which this occurs is called the cloud point of the lubricant. If the product is

further cooled, a point will be reached at which the lubricant will no longer flow or be efficiently pumped. The temperature at which this occurs is termed the pour point of the lubricant. Both properties are related to the wax content of the base stock. The pour points of high-wax lubricants may be depressed by the addition of pour point depressant additives. Pour point behavior becomes important in applications such as refrigerant compressor lubrication where the oil is subjected to low temperatures.

2.3.4 Flash point and fire point

As a lubricant is heated, lighter components begin to vaporize. The temperature at which sufficient vapor concentration exists above the surface of the lubricant so that ignition with a test flame is possible is called the flash point of the product. Flash point is useful for both product storage requirements and for the detection of contamination of one product with another. The fire point of a lubricant is that temperature at which sufficient vapors are present above the surface of the lubricant to sustain combustion upon ignition. This parameter is useful for storage and safety considerations.

2.3.5 Neutralization number

As petroleum products are subjected to elevated temperatures, the process of oxidation occurs. Oxidation leads to the formation of organic acids in the lubricant. This increase in acidity reduces the water-separating ability of certain oils, and may also prove corrosive to certain alloys. The neutralization number measures the amount of acidity present in the lubricant. It is quantitatively defined as the amount of potassium hydroxide (KOH) required to neutralie the acid present in one gram of sample. This quantity is also referred to as the Total Acid Number (TAN).

2.3.6 Total base number

Internal combustion engine oils are formulated with a highly alkaline (base) additive package designed to neutralize the acidic byproducts of combustion. The Total Base Number (TBN) is a measure of this additive package, and it may be used as an indication of when diesel engine oil should be changed.

2.3.7 Water content

The most common contaminant in Naval lubricating systems is water. Common sources of water include lube oil cooler leaks, condensation, steam turbine gland seal leaks, and diesel engine piston blow-by and jacket water leaks. The acceleration of system corrosion by water contamination cannot be overemphasized. In addition, excessive water contamination increases the viscosity and decreases the fluid film strength of oil. This may result in accelerated wear due to rupture of the oil film and resultant surface-to surface contact. A qualitative assessment of the amount of water present in some lubricants may be made by inspecting the oils' appearance. Another method for determining water contamination levels is the Bottom Sediment & Water (B.S.& W.).

2.3.8 Demulsibility

Demulsibility refers to a lubricant's ability to readily separate from water. Oils used in force-feed lubrication systems should possess good water separability to prevent emulsification.

2.3.9 Hardness

Greases are classified according to a hardness scale developed by the National Lubricating Grease Institute (NLGI). According to this system, softer greases are assigned a low NLGI number, and stiffer greases a high NLGI number. The penetration numbers refer to the depth, in tenths of millimeters, that a weighted cone penetrates the grease. Most greases have NLGI numbers from 1 to 2, and are classified as medium consistency greases.

2.3.10 Dropping point

Greases exist in an essentially semi-solid form. The temperature at which changes from a semi-solid to a liquid is termed its dropping point. Dropping point provides some indication of the high temperature characteristics of grease.

2.3.11 Water wash out

Greases subjected to splashing or impinging water must possess good water washout resistance. Greases with good resistance will maintain an adequate lubricating film under excessive water contamination conditions.

2.3.12 Load carrying ability

The ability of a lubricant to maintain an effective lubricating film under high loads or pressures is a measure of its load carrying or extreme pressure (EP) characteristics. The load carrying ability of a lubricant may be enhanced by the addition of EP additives.

2.4 Classification of lubricants

The primary functions of lubricants are to reduce friction and wear, heat removal and contaminant suspension in an application. The number of applications is very large, requiring attention to develop specific formulations. Lubricants are often, as in the EEL, classified on the basis of their application. Despite their large number of applications lubricants consist of one or more base oils and one or more additives giving it its specific and unique properties. Wide variety of lubricants may be arranged according to the following methods:

2.4.1 Mineral lubricants

1. **Fluid lubricants (Oils)**

   Mineral fluid lubricants are based on mineral oils. Mineral oils (petroleum oils) are products of refining crude oil. There are three types of mineral oil: paraffinic, naphtenic and aromatic.

2. Paraffinic oils

Paraffinic oils are produced either by hydrocracking or solvent extraction process. Most hydrocarbon molecules of paraffinic oils have non-ring long-chained structure. Paraffinic oils are relatively viscous and resistant to oxidation. They possess high flash point and high pour point. Paraffinic oils are used for manufacturing engine oils, industrial lubricants and as processing oils in rubber, textile, and paper industries.

3. Naphtenic oils

Naphtenic oils are produced from crude oil distillates. Most hydrocarbon molecules of naphtenicnic oils have saturated ring structure. Naphtenic oils possess low viscousity, low flash point, low pour point and low resistance to oxidation. Naphtenic oils are used in moderate temperature applications, mainly for manufacturing transformer oils and metal working fluids.

4. Aromatic oils

Aromatic oils are products of refining process in manufacture of paraffinic oils. Most hydrocarbon molecules of aromatic oils have non-saturated ring structure. Aromatic oils are dark and have high flash point. Aromatic oils are used for manufacturing seal compounds, adhesives and as plasiticizers in rubber and asphalt production.

5. Semi-fluid lubricants (greases)

Semi-fluid lubricants (greases) are produced by emulsifying oils or fats with metallic soap and water at 400-600°F (204-316°C). Typical mineral oil base grease is vaseline. Grease properties are determined by a type of oil (mineral, synthetic, vegetable, animal fat), type of soap (lithium, sodium, calcium, etc. salts of long-chained fatty acids) and additives (extra pressure, corrosion protection, anti-oxidation, etc.). Semi-fluid lubricants (greases) are used in variety applications where fluid oil is not applicable and where thick lubrication film is required: lubrication of roller bearings in railway car wheels, rolling mill bearings, steam turbines, spindles, jet engine bearings and other various machinery bearings.

6. Solid lubricants

Solid lubricants possess lamellar structure preventing direct contact between the sliding Surfaces even at high loads. Graphite and, olybdenum disulfide particles are common solid lubricants, boron nitride, tungsten disulfide and polytetrafluorethylene (PTFE) are other solid lubricants. Solid lubricants are mainly used as additives to oils and greases. Solid lubricants are also used in form of dry powder or as constituents of coatings.

2.4.2 Synthetic lubricants

1. Polyalphaolefins (PAO)

Polyalphaoleins are the most popular synthetic lubticant. PAO's chemical structure and properties are identical to those of mineral oils. Polyalphaoleins (synthetic hydrocarbons) are manufactured by polymerization of hydrocarbon molecules (alphaoleins). The process occurs in reaction of ethylene gas in presence of a metallic catalyst.

2. Polyglycols (PAG)

Polyglycols are produced by oxidation of ethylene and propylene. The oxides are then polymerized resulting in formation of polyglycol. Polyglycols are water soluble. Polyglycols are characterized by very low coefficient of friction. They are also able to withstand high pressures without EP (extreme pressure) additives.

3. Ester oils

Ester oils are produced by reaction of acids and alcohols with water. Ester oils are characterized by very good high temperature and low temperature resistance.

4. Silicones

Silicones are a group of inorganic polymers, molecules of which represent a backbone structure built from repeated chemical units (monomers) containing Si=O moieties. Two organic groups are attached to each Si=O moiety: eg. methyl+methyl ($(CH_3)_2$), methyl+phenyl ($CH_3 + C_6H_5$), phenyl+phenyl ($(C_6H_5)_2$). The most popular silicone is polydimethylsiloxane (PDMS). Its monomer is $(CH_3)_2SiO$. PDMS is produced from silicon and methylchloride. Other examples of silicones are polymethylphenylsiloxane and

polydiphenylsiloxane. Viscosity of silicones depends on the length of the polymer molecules and on the degere of their cross-linking. Short non- crosslinked molecules make fluid silicone. Long cross-linked molecules result in elastomer silicone. Silicone lubricants (oils and greases) are characterized by broad temperature range: -100°F to +570°F (-73°C to 300°C).

2.4.3 Vegetable lubricants

Vegetable lubricants are based on soybean, corn, castor, canola, cotton seed and rape seed oils. Vegetable oils are environmentally friendly alternative to mineral oils since they are biodegradable. Lubrication properties of vegetable baseoils are identical to those of mineral oils.

The main disadvantages of vegetable lubricants are their low oxidation and temperature stabilities.

2.4.4 Animal lubricants

Animal lubricants are produced from the animals fat. There are two main animal fats: hard fats (stearin) and soft fats (lard). Animal fats are mainly used for manufacturing greases.

2.5 Synthetic ester lubricants [8]

Prior to early 19th century, the main lubricants were natural esters contained in animal fats such as sperm oil and lard oil, or in vegetable oils such as rapeseed and castor oil. During World War II, a range of synthetic oils was developed. Among these, esters of long chain alcohols and acids proved to be excellent for low temperature lubricant. Following World War II, the further development of esters was closely linked to that of the aviation gas turbine. In the early 1960s, neopolyol esters were used in this application because of their low volatility, high flash points and good thermal stabilities. Esters are now used in many applications including automotive and marine engine oils, compressor oil, hydraulic fluids, gear oil and grease formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance.

2.5.1 Ester type

The direct effect of the ester group on the physical properties of a lubricant is to low volatility and raise the flash point. This is due to strong dipole moments, called the London forces, binding the lubricant together. The presence of the ester group also affects other properties such as thermal stability, hydraulic stability, solvency, lubricity and biodegradability.The major types of esters and their feedstocks are reviewed in Table 2.1 summarizes the physical properties of these esters.

2.5.2 Manufacture of esters lubricants

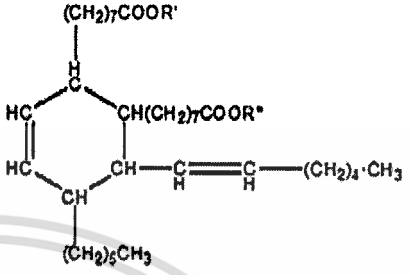
The manufacturing process of esters consists of three distinct processes: esterification, filtration and distillation. The fundamental reaction process is that of acid and alcohol to produce ester and water. This reaction is reversible, but is driven to completion by the use of excess alcohol and removal is optional. The acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reaction. Possible catalyst includes sulphuric acid, *p*-toluene sulphonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorus oxides and stannous octanoate. After the ester has been formed, unreacted acid is neutralized using sodium carbonate or calcium hydroxide and removal by filtration. Typical reaction conditions are 230°C and 50-760 mmHg pressure. A significant amount of alcohol vaporizes along with the water and must be recovered. This is accomplished by considering the reactor vapors and separating the resulting two-phase liquid mixture. The alcohol is then returned to the reactor. Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NGP), trimethylol propane (TMP), with a monobasic acid to give the desired ester. When making neopolyol esters, excess acid is used because the acid is more volatile than the neopoly esters, excess acid is used because the acid is more volatile than nepolyol and is therefore easy to recover from the ester product.

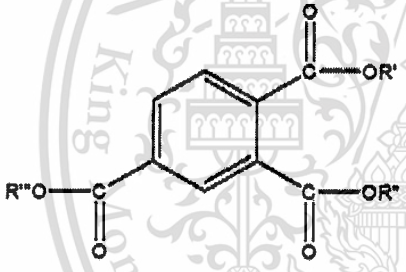
Table 2.1 The major types of ester lubricants [9]

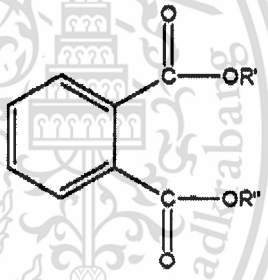
<table>
<tr>
<td>Diesters (dioates)

R'OOC(CH₂)_nCOOR"

R', R"= linear branched or mixed alkyl chain
n = 4 = adipates
n = 7 = azelates
n = 8 = sebacates
n = 10 = dodecanedioates</td>
<td>C₁₆ dimer acid esters

R', R"= linear branched or mixed alkyl chain</td>
</tr>
<tr>
<td>Trimellitate esters
(1,2,4-bezene tricarboxylate)
 

R', R", R'" = linear branched or mixed alkyl chain</td>
<td>Phthalate esters
(1,2-bezene dicarboxylate)
 

R', R"= linear branched or mixed alkyl chain</td>
</tr>
<tr>
<td colspan="2">Polyols (hindered esters)

C(CH₂OCOR)₄ Pentaerythritol esters

CH₃CH₂C(CH₂OCOR)₃ Trimethylolpropane esters

(CH₃)₂C(CH₂OCOR)₂ Neopentylglycol esters

R = linear branched or mixed alkyl chain</td>
</tr>
</table>

Table 2.2 Summarized properties of ester lubricants [10]

	Diesters	Phthalates	Trimellitates	C36dimer ester	Polyols	Polyoleates
Viscosity at 40oC	6 to 46	29 to 94	47 to 366	13 to 20	14 to 35	8 to 95
Viscosity at 100oC	2 to 8	4 to 9	7 to 22	90 to 185	3 to 6	10 to 15
Viscosity Index	90 to 170	40 to 90	60 to 120	120 to 150	120 to 130	130 to 180
Pour point (oC)	70 to 40	50 to 30	55 to 25	50 to 15	60 to 9	40 to 5
Flash point (oC)	200 to 260	200 to 270	270 to 300	240 to 310	250 to 310	220 to 280
Thermal stability	good	very good	very good	very good	exccellent	fair
%Biodegradability	75 to 100	46 to 88	0 to 69	18 to 78	90 to 100	80 to 100
Conradson carbon	0.01 to 0.06	0.01 to 0.03	0.01 to 0.40	0.2 to 0.7	0.01 to 0.1	0.01 to 0.4
Costs (PAO-1)	0.9 to 2.5	0.5 to 1.0	1.5 to 2.0	1.2 to 2.8	2.0 to 2.5	0.6 to 1.6

2.5.3 Physicochemical properties of ester lubricants

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the other hand are prepared from man-made base stocks having uniform molecular structures, and therefore well-defined properties that can be tailored to specific applications. Many lubricant requirements are translated into specific properties of 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 only be measured satisfactorily by elaborate and expensive rigs specially developed to simulate performance. A wide variety of raw material can be used for the preparation of ester type base fluids and this affect a number of lubricant properties including viscosity, flow properties, lubricity, thermal stability, hydrolytic stability, solvency and biodegradability.

1. Viscosity

The viscosity of an ester lubricant can be altered by:

- increasing the molecule 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 molecule backbone
- maximizing dipolar interactions

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

2. 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
- Molecular configuration-viscosity indices of polyol ester tend to be somewhat lower than their diester analogous due to more compact configuration of the polyol molecule

The pour point of the lubricant can be decrease by:

- Increasing the amount of the lubricant can be branching
- The positioning of the branch-branching in the centre of the molecule gives better pour points than branches near the end
- Decreasing the acid chain length
- Decreasing the internal symmetry molecule

As can be seen from the above lists, there is a natural trade-off between viscosity index and pour point. For instance by increasing the linearity of the ester the viscosity index improves but the pour point increase. Esters made from mixtures of normal and branched acid (having the same carbon numbers) have viscosity indices between those of the normal and branched acid esters, but have lower pour points than esters used from either branched or normal acids.

3. Lubricity

Ester groups are polar and will therefore affect the efficiency of anti-wear additives. When a too polar base fluids is used, and not the anti-wear additives, will cover the metal surfaces. This can result in higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives. Ester can be classified in term of their polarity, or non-polarity by using the following formula (Van der Waals, 1985):

$$Non-polarity\ index = \frac{\text{total number of C atom} \times \text{molecular weight}}{\text{Number of carboxylic group} \times 100}$$

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. Ester terminated by normal acids or alcohols have better lubricities than made form 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.

4. Thermal stability

The ester linkage is an exceptionally stable one; bond energy determinations predict that it is more thermally stable than C-C bond. Short linear chains generally have higher flash points than those made from branched acids. Increasing molecular weight also increase flash points.

5. 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 processing parameters include:

- Acid vale
- Degree of esterification
- Catalyst used during esterification and the remaining in the ester after processing

Esters must have acid value, a very high degree of esterification and a low ash level before the effects of molecular geometry will begin to assert themselves.

2.5.4 Applications of lubricants [11]

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 polyglygols. Experience from numerous laboratories of engine bench and vehicle test programmes conducted over the last ten years has shown that a blend of PAO and an excellent base fluid for the formulation of synthesized crankcase oils [13].

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 condition. 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 C_{36} 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 build-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 result in reduce oil emission which is a benefit in environmentally-sensitive application such as marine outboard engines and chainsaw motors. Third, in some applications, such as engines used to power snowmobile-type vehicles, low temperature performance is important. In these applications, esters with low pour point (down to -56°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 [14]. PAHs have been found to be one of the major contributors to the carcinogenic nature of exhaust emission. Esters can also 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 in compressor handling natural gas. In reciprocating compressors, where oils of rather higher viscosity are preferred, trimelliate esters can be used. Diesters and polyol esters may also be blended with PAOs fofr 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 vapor inhalation, ingestion and skin irritation, these properties make them considerably safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradabitities can also lessen their environmental impact. Diesters

generally have high viscosity indices, giving them a wide temperature range without the use

of generally have high viscosity indices, giving them a wide temperature range without the use of viscosity improves. (the latter can shear in this application) 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 temperature.

6. **Aviation oils**

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 (Type1) were diesters but over the last 25 years, these have slowly lost ground to the more expensive (Type2) 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 to 3 cSt.

2.6 Esterification [12]

The ester reaction Figure 2.1 shows the basic chemical reaction used to synthesize all esters: a carboxylic acid and an alcohol react to form an ester and water. Organic chemists call this a reversible reaction because water can react with ester groups and break the ester into its components. This is known as hydrolysis.

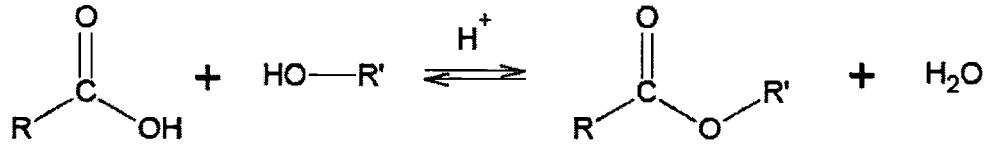


Figure 2.1 The esterification reaction

The raw materials used to make esters can be linear, branched, saturated, unsaturated, monofunctional, difunctional, or polyfunctional. There are hundreds of potential acid and alcohol building blocks, and the number of combinations is practically limitless. Attempts to classify esters in categories such as diesters and polyol esters, simple and complex esters, the technology is far ahead of the terminology and you know sometimes words have two meanings. The building blocks often define the maximum performance potential of an ester while the manufacturing savvy determines whether the ester reaches its potential. For example, a synthetic neopolyol (alcohol) can produce an ester with outstanding oxidative stability, but the oxidative stability of the ester may be diminished with inferior ingredients, contaminants or poor processing techniques.

2.7 Sugar [13]

Sugar is the generalised name for a class of sweet-flavored substances used as food. They are carbohydrates and as this name implies, are composed of carbon, hydrogen and oxygen. There are various types of sugar derived from different sources. simple sugars are called monosaccharides and include glucose, fructose and galactose. The table or granulated sugar most customarily used as food is sucrose, a disaccharide. Other disaccharides include maltose and lactose.

Sugars are found in the tissues of most plants but are only present in sufficient concentrations for efficient extraction in sugarcane and sugar beet. Sugarcane is a giant grass and has been cultivated in tropical climates in the Far East since ancient times. A great expansion in its production took place in the 18th century with the setting up of sugar plantations in the West Indies and Americas. This was

the first time that sugar became available to the common people who had previously had to rely on honey to sweeten foods. Sugar beet is a root crop and is cultivated in cooler climates and became a major source of sugar in the 19th century when methods for extracting the sugar became available. Sugar production and trade has changed the course of human history in many ways. It influenced the formation of colonies, the perpetuation of slavery, the transition to indentured labor, the migration of peoples, wars between 19th century sugar trade controlling nations and the ethnic composition and political structure of the new world. The world produced about 168 million tonnes of sugar in 2011. The average person consumes about 24 kilograms of sugar each year, equivalent to over 260 food calories per person, per day.

In modern times it has been questioned whether a diet high in sugars, especially refined sugars, is bad for health. Sugar has been linked to obesity and suspected of being implicated in diabetes, cardiovascular disease, dementia, macular degeneration and tooth decay. Numerous studies have been undertaken to try to clarify the position but the results remain largely unclear, mainly because of the difficulty of finding populations for use as controls that do not consume sugars.

2.7.1 Types of sugar

2.7.1.1 Monosaccharides

Glucose, fructose and galactose are all simple sugars, monosaccharides, with the general formula $C_6H_{12}O_6$. They have five hydroxyl groups (−OH) and a carbonyl group (C=O) and are cyclic when dissolved in water. They each exist as several isomers with dextro- and laevo-rotatory forms which cause polarized light to diverge to the right or the left.

Glucose, dextrose or grape sugar occurs naturally in fruits and plant juices and is the primary product of photosynthesis. Most ingested carbohydrates are converted into glucose during digestion and it is the form of sugar that is transported round the bodies of animals in the bloodstream. It can be manufactured from starch by the addition of enzymes or in the

presence of acids. Glucose syrup is a liquid form of glucose that is widely used in the manufacture of foodstuffs. It can be manufactured from starch by enzymatic hydrolysis.

Fructose or fruit sugar occurs naturally in fruits, some root vegetables, cane sugar and honey and is the sweetest of the sugars. It is one of the components of sucrose or table sugar. It is used as ahigh fructose syrup which is manufactured from hydrolized corn starch which has been processed to yield corn syrup, with enzymes then added to convert part of the glucose into fructose.

Galactose does not generally occur in the free state but is a constituent with glucose of the disaccharide lactose or milk sugar. It is less sweet than glucose. It is a component of the antigens found on the surface of red blood cells that determine blood groups.

2.7.1.2 Disaccharides

Sucrose, maltose and lactose are all compound sugars, disaccharides, with the general formula $C_{12}H_{22}O_{11}$. They are formed by the combination of two monosaccharide molecules with the exclusion of a molecule of water.

Sucrose is found in the stems of sugar cane and roots of sugar beet. It also occurs naturally alongside fructose and glucose in other plants, particularly fruits and some roots such as carrots. The different proportions of sugars found in these foods determines the range of sweetness experienced when eating them. A molecule of sucrose is formed by the combination of a molecule of glucose with a molecule of fructose. After being eaten, sucrose is split into its constituent parts during digestion by a number of enzymes known as sucrases.

Maltose is formed during the germination of certain grains, most notably barley, where it is the source of the malt used in the manufacture of beer. A molecule of maltose is formed by the combination of two molecules of glucose. It is less sweet than glucose, fructose or

sucrose. It is formed in the body during the digestion of starch by the enzyme amylase and is itself broken down during digestion by the enzyme maltase.

Lactose is the naturally occurring sugar found in milk. A molecule of lactose is formed by the combination of a molecule of galactose with a molecule of glucose. It is broken down when consumed into its constituent parts by the enzyme lactase during digestion. Children have this enzyme but some adults no longer form it and they are unable to digest lactose.

2.8 Sorbitol [14]

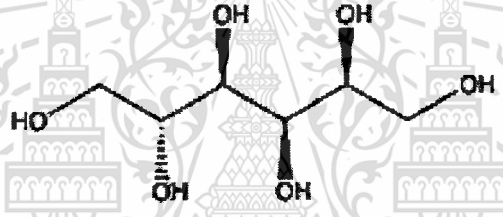


Figure 2.2 Sorbitol structure

Sorbitol, also known as **glucitol**, is a sugar alcohol that the human body metabolizes slowly. It can be obtained by reduction of glucose, changing thealdehyde group to a hydroxyl group. Sorbitol is found in apples, pears, peaches, and prunes. It is synthesized by sorbitol-6-phosphate dehydrogenase, and converted to fructose by succinate dehydrogenase and sorbitol dehydrogenase. Succinate dehydrogenase is an enzyme complex that participates in the citric acid cycle. As a hexahydric alcohol, sorbitol is a member of the polyhydric alcohol family, the lowest of which are ethylene glycol and glycerol. The close chemical relationship between sorbitol and the lower alcohols (like glycol and glycerol) is responsible for the similarity in their general physical properties and applications in industrial technology.

2.8.1 Properties

Sorbitol is soluble in water to approximately 83 parts Sorbitol in 100 parts of water by weight. Viscosity as well as specific gravity of Sorbitol 70% solution is higher than that of glycerine at the same concentration as can be seen in figure1 and Table1. Sorbitol is extremely useful as humectant. Because it is stable and non-volatile even with water vapour, there is no loss during heating or cooking or by evaporation. Unlike ethylene glycol, Sorbitol is non-toxic and non-irritant. The taste of sorbitol is mild, sweet, cooling, and unobtrusive. Sorbitol is more resistant to bacteriological degradation than sugar. This resistance also makes it less vulnerable to mould growth than most other humectant plasticising material. Sorbitol is chemically inert and compatible with many chemical substances. In general, the hexitols and particularly Sorbitol have the ability ti chelate iron, copper and aluminium ions in aqyeous solutions. Sorbitol undergoes several chemical reactions like oxidation, reduction, esterification and etherification, yielding such important products as ascorbic acid (Vitamin C), Sorbitan sorbides etc.

2.8.2 Application

In general, hexitols and their derivatives particularly Sorbitol, are used in diverse industries viz. pharmaceuticals, cosmetics, toothpastes, cigarettes, foods, textiles, adhesives, confectionery, printing ink, etc. One of the major uses of Sorbitol is as a humectant and conditioning agent. Many products under day-to-day atmospheric changes require the addition of a humectant to assist them to retain their freshness, softness and flexibility and to maintain ideal manufacturing condition. To summarise, the principal advantages which Sorbitol exhibits over other polyols are

- Sorbitol GIVES UP water very slowly to dry atmosphere
- Sorbitol TAKES UP water very slowly from a humid atmosphere

2.8.2.1 Confectionery:

In candy manufacture, sorbitol is used together with sugar to increase shelf life. The function of sorbitol is to retard the solidification of sugar often associated with staleness in candy. It also helps to improve softness, taste and texture. In butter creams additional benefit is enhanced 27umect. Sorbitol may be used in diabetic chocolates. Sorbitol is used as 27umectants and softener in shredded coconut, its decided advantage over invert sugar being that the darkening of the product does not occur. Sorbitol 70% added to peanut butter has been shown to reduce dryness and crumbliness and improve spreadability.

2.8.2.2 Textiles

Sorbitol functions in textile applications basically as a dispensing agent, humectant bodying agent and sequestering agent. In printing, a paste of 2% to 3% sorbitol solution 70% (on the weight of the gum in the dye paste) prevents levering of the paste, improves brightness and intensity of colour, assists penetration, prevents bleeding and promotes leveling. In textile sizing, sorbitol acts as a humectant and especially in winter it preserves the film of adhesive from becoming dry and maintain its plasticity. In finishing, it gives a soft feel, good drape and proven dimension stability to the fabric.

2.8.2.3 Tobacco

The moisture content of cigarettes is very important, and change in moisture content, due to change in humidity, is minimised if sorbitol is used as conditioner. Also sorbitol is non-volatile and hence there is no danger of losing the conditioner during drying and other pressing operations. Sorbitol is compatible with various ingredients used in tobacco mixture. Because of its sweetness and cooling taste, sorbitol contributes to the flavour of chewing tobacco besides conditioning the product.

2.8.2.4 Adhesives

Sorbitol is the ideal answer since it neither loses nor absorbs any appreciable quantity of water, unlike conventional humectants like glycerine or ethylene glycol. Sorbitol increases the viscosity of the glue composition so that more water is needed, resulting in

greater economy. Sorbitol functions as a moisture conditioning agent and its non-volatility ensures non-cracking labels and envelops with minimum of curling.

2.8.2.5 Pharmaceuticals

Sorbitol finds use as a bodying agent in pharmaceutical syrups and elixirs. The use of sorbitol in cough syrups reduces the tendency of the bottle caps to stick due to the crystallisation of the sugar present. Sorbitol is a good humectants and plasticiser and these properties make it useful in emulsion ointments, non-fat soluble ointments and gelatine capsules. Ointments, creams and pastes will show satisfactory spreading capacity with sorbitol as adjuvant. Aqueous sorbitol Solutions are not subjected to fermentative decomposition, and that is why sorbitol finds increasing use in the preparation of dental formulations for buckle cavity.

2.8.2.6 Cosmetics

Sorbitol is widely used in cosmetics, both as a humectant to retard loss of water from O/W type of creams and as an emollient. Sorbitol solution 70% has proved a useful additive for improving the aesthetic appeal of glycerine carbolic soap by imparting better transparency. Generally speaking, Sorbitol solution 70% can replace other humectants, by weight where the humectant percentage is less than 10%.

2.8.2.7 Foods

Sorbitol imparts to frozen desserts, body and texture, as well as some sweetness. Sorbitol is used in frozen desserts for diabetics because it is slowly absorbed from the intestine and is metabolised as fructose. In the manufacture of sugarless chewing gum, sorbitol provides water soluble solids; further a 70% solution of sorbitol resists fermentation of acids by micro-organisms in mouth and therefore it is believed not to contribute to the incidence of dental caries. In artificially sweetened canned fruits, the undesirable aftertaste of saccharine. In low-caloric soft drinks, sorbitol finds use as a bodying agent in addition to its use as a sequestering agent in canned soft drinks.

2.9 Hexanoic acid [15]

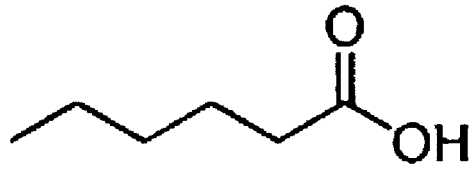


Figure 2.3 Hexnoic acid structure

Hexanoic acid (caproic acid), is the carboxylic acid derived from hexane with the general formula $C_5H_{11}COOH$. It is a colorless oily liquid with an odor that is fatty, cheesy, waxy, and like that of goats or other barnyard animals. It is a fatty acid found naturally in various animal fats and oils, and is one of the chemicals that give the decomposing fleshy seed coat of the ginkgo its characteristic unpleasant odor. The primary use of hexanoic acid is in the manufacture of its esters for artificial flavors, and in the manufacture of hexyl derivatives such as hexylphenols. The salts and esters of this acid are known as hexanoates or caproates. Two other acids are named after goats: caprylic (C8) and capric (C10). Along with hexanoic acid, these total 15% in goat milk fat. Caproic, caprylic, and capric acids (capric is a crystal- or wax-like substance, whereas the other 2 are mobile liquids) are not only used for the formation of esters but also commonly used "neat" in: butter, milk, cream, strawberry, bread, beer, nut, and other flavors.

2.10 Literature reviews

Carlos Marquez-Alvarez and his team [16] studied the partial esterification of polyols such as glycerol, polyglycerols and sorbitol which gave nonionic surfactants. It was found that solid catalyst based on MCM-41 and other mesostructures could give rise to development of new, more efficient process for the large-scale synthesis of fatty acid ester of polyols. These materials could be excellent catalysts for the esterification or tranesterification of sorbitol to obtain esters of high hydrophilic-

lipophilic balance (HLB), as they would produce esters with lower sorbitol anhydrization degree than those obtained with acid catalysts.

J. Giacometti and his team studied the kinetics of the esterification of sorbitol with lauric acid in the presence of p-TSA as a catalyst. A kinetic model of reversible second order reaction was purposed for the esterification. Parameters in the model were estimated by non-linear regression. The temperature dependence of the rate was calculated from the experimental constants estimated at various temperatures. The result showed that the optimum temperature was 160°C which the rate was sufficient, and in the presence of p-TSA catalyst the formation of undesirable by products was avoided. However, the lubricating oil product from these researches had either low viscosity or emulsion occurred.

S. Gryglewicz and his team [17] studied the possibility of using some natural fats; rapeseed oil, olive oil and lard, as starting material for the preparation of neopentyl glycol (NPG) and trimethylol propane (TMP) esters. The syntheses of final products were performed by alcoholysis of fatty acid methyl esters, obtained from natural fats studied, with the appropriate polyhydric alcohol using calcium methoxide as a catalyst. The basic physicochemical properties of the synthesized NPG and TMP esters were the following; viscosity at 40°C in the range of 13.5–37.6 cSt, pour point between 10.5 and 17.5 °C and very high viscosity indices, higher than 200. Generally, the esters of neopentyl alcohols were characterized by higher stability in thermo-oxidative conditions in comparison to native triglycerides. Due to the low content of polyunsaturated acids, the olive oil based esters showed the highest thermo-oxidative resistance. Also, methyl esters of fatty acids of lard would constitute a good raw material for the synthesis of lubricating oils, provided that their saturated acids content was lowered. This permits synthesis of NPG and TMP esters with a lower pour point (below 10 °C) than natural lard (+33 °C).

Jumat Salimon and his team [18] studied a new class of environmentally acceptable and renewable biolubricants based on plant oils. Even though plant oils possess excellent lubricant-related

properties, there are some concerns about using it as biolubricant base oil. In this work, a series of structures derived from oleic acid to be used as synthetic biolubricant basestocks was present. Measuring of pour point (PP), flash point, viscosity index (VI), oxidation onset temperature (OT) and signal maximum temperature (SMT) was carried out for each compound. Furthermore, the friction and wear properties were measured using a high-frequency reciprocating rig (HFRR). The resulting product structures were confirmed by NMR and FTIR spectroscopic analysis. The results showed that ethylhexyl 9-(octanoyloxy)-10-(behenoxy) octadecanoate with behenyl mid-chain ester exhibited the most favorable low temperature performance (PP -48°C) and ethylhexyl 9-(octanoyloxy)-10-(octyloxy)octadecanoate octyl mid-chain ester exhibited higher oxidation stability (OT 142°C) than the other synthetic ester oils. On the other hand, the highest ball wear scan diameter was obtained for ethylhexyl 9-(octanoyloxy)-10- (behenoxy)octadecanoate while the lowest value was obtained for 9-hydroxy-10-octyloxyoctadecanoic acid. Overall, it was concluded that these synthetic ester oils had potential for use in formulation of industrial fluids for different temperature applications.

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals

1) D-sorbitol 97%, 500 GR, from Acros Organic Co.Ltd
2) Hexanoic acid ($C_5H_{11}COOH$), commercial grade, from Sigma-Aldrich Co.Ltd
3) 0.2 M NaOH, AR, from Labscan asia Co.Ltd.
4) Anhydrous Na_2SO_4 from Carlo Erba
5) Distilled water
6) Silicone oil

3.2 Apparatus and equipments

1) Laboratory glasswares
2) Hot Plate Magnetic Stirrer : MR 3001 K, Heidolph
3) Analytical Balance (FY-2000)
4) Stand
5) Stirring Rod
6) Spatula
7) Condenser
8) Thermometer
9) Lamp Holder
10) O-ring
11) Utility Clamp
12) 2 cm Magnetic Bar

13) Tube Band

14) Buret

15) Separatory funnel

16) Oil Bath

17) Vial

18) ropper

19) Filter paper

20) Lid

21) Fourier Transform Nuclear Magnetic Resonance Spectrometer, (FT-NMR) : Advance DPX300, Bruker

22) Gas Chromatograph-Mass Spectrometer (GC-MS), 6890N, Agilent Technologies, equipped with Agilent DB-Wax Capillary column, 0.25 mm x 30 mm x 0.25 μm

23) Thermalgravimetric Analyzer, TGA : Pyris 1 TGA, Perkin Elmer

3.3 Method of study

3.3.1) Synthesis of an ester oil from sorbitol and hexanoic acid via esterification

3.3.2) Characterization of the product ester

- Nuclear Magnetic Resonance Spectrometer, ^{1}H-NMR
- Gas Chromatography, GC
- Thermalgravimetric Analyzer, TGA

3.3.4) Properties Testing (ASTM Standard)

- Viscosity (ASTM D 445)
- Viscosity Index (ASTM D 2270)
- Pour point (ASTM D 97)
- Total acid number (ASTM D 664)

3.4 Experimental Methods

3.4.1 Preparation of sorbitol hexanoate

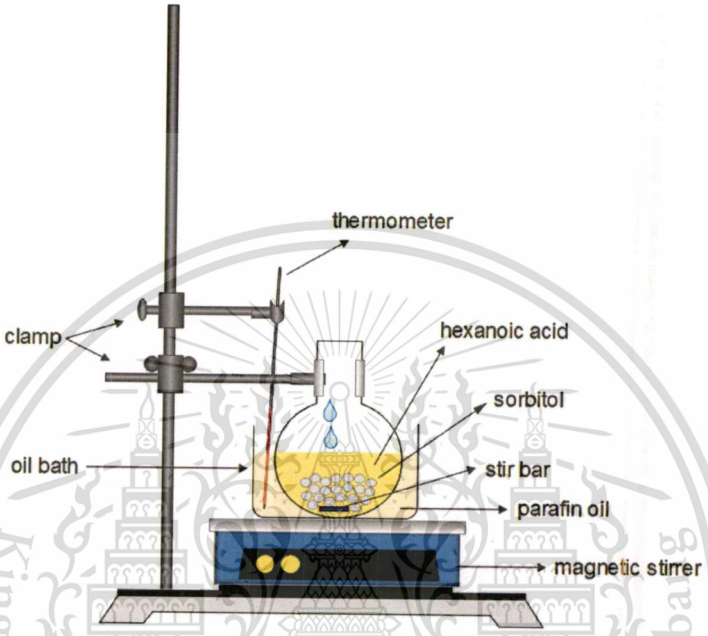


Figure 3.1 Typical apparatus for miniscale contents of reaction mixture using a heating source with magnetic stirring

1. The apparatus was set up as illustrated in Figure 3.1, the paraffin oil was heated to 140°C.
2. 23.68 g (0.13 mol) of sorbitol and 100 ml (0.09 mol, 1:6 ratio by mol) of hexanoic acid was poured into a 250-ml round bottom flask. The flask was then placed in an oil bath which was set on a hot plate with magnetic stirrer.
3. The mixture was heated at 140°C for 4 hours.
4. After the reaction was stopped, the mixture was cool down to room temperature.
5. Then 20 ml of the mixture from step 4 was pipetted into a 125 ml separatory funnel.
6. The remaining hexanoic acid was washed out for 15 times with 20 ml of 0.2 M NaOH as the lower layer from the upper organic layer. The aqueous layer was discarded.
7. The remaining base was washed for 15 times with 20 ml of distilled water.

8. The mixtures were poured into a beaker, and anhydrous Na_2SO_4 was added to dry the remaining water.
9. The ester product was filtered to separate the solid particles.
10. Step 1 to 9 was repeated by changing the reaction time from 4 hours to 3 and 5 hours.
11. Next, step 1 to 9 was repeated by changing the reaction temperature to 130°C.
12. Finally, step 1 to 9 was repeated by changing the ratio between sorbitol and hexanoic acid to 1:9.

3.4.2 Characterization of the ester product

3.4.2.1 Nuclear Magnetic Resonance Spectrometer, (NMR)

The ester products were characterised by Nuclear Magnetic Resonance Spectrometer at Faculty of Science, Chulalongkorn University. ^{1}H-NMR spectra in dueteriate chloroform ($CDCl_3$) were used to determine the degree of esterification. The measurement was performed on a Bruker ADVANCE DPX 300 NMR spectrometer with 300 MHz proton resonance frequency. The integral spectra was obtained in separated scans from 0 to 10 parts per million (ppm).

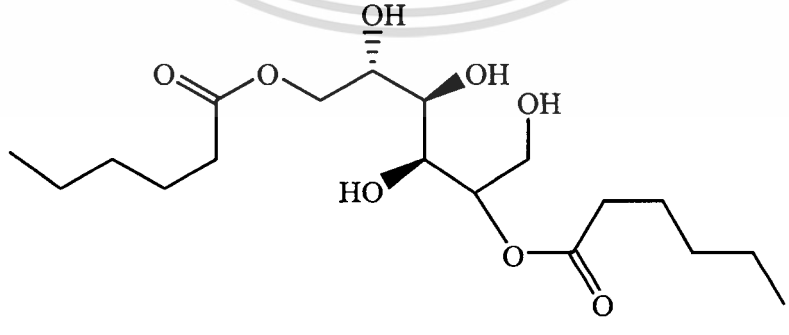


Figure 3.2 A structure of synthetic diester products from esterification of sorbitol and hexanoic acid

Figure 3.3 ^{1}H-NMR spectrum ($CDCl_3$) of an ester product synthesised from sorbitol and hexanoic acid via esterification reaction.

From Figure 3.2 and 3.3, the signals at δ 3.1-δ4.85 ppm are corresponded to the protons of (-C**H**-O-CO-) and (-C$\mathbf{H_2}$-O-CO-) groups. They appear in the sorbitol region of the spectrum. The signal at δ 0.75 ppm appears as singlet and is assigned to (-C$\mathbf{H_3}$) group in the hexanoic acid region of the spectrum. The number of –OH substitution could be calculated as following ;

$$\frac{No.\ of\ protons\ from\ (-C\underline{\boldsymbol{H_3}})\ group}{No.\ of\ proton\ from\ (-C\underline{\boldsymbol{H}}-O-CO-)and\ (-C\underline{\boldsymbol{H_2}}-O-CO-)\ groups} = \frac{integration\ at\ \delta 0.75\ ppm}{integration\ at\ \delta 3.1-\delta\ 4.85\ ppm}$$

Theoretically, the ratio of protons from (-C$\underline{H}_3$) group by those of (-C$\underline{H}$-O-CO-) and (-C$\underline{H}_2$-O-CO) groups can be calculated when the degree of esterification changes as shown in Table 3.1. A standard curve can then be made as illustrated in Figure 3.4. It was used to determine the degree of esterification and number of –OH group substitution from the reactions in this work using the proton ratio of those groups from ^{1}H-NMR spectrum.

Table 3.1 Number of –OH group substitution and degree of esterification of synthetic ester from sorbitol and hexanoic acid

$\frac{\text{No. of proton from } (-C\underline{H}_3) \text{ group}}{\text{No. of proton from } (-C\underline{H}-O-CO-) \text{ and } (-C\underline{H}_2-O-CO-) \text{ groups}}$		Degree of esterification (%)	Number of -OH group substitution
3/8	0.375	16.67	1
6/8	0.750	33.33	2
9/8	1.125	50.00	3
12/8	1.500	66.67	4
15/8	1.875	83.33	5
18/8	2.250	100.00	6

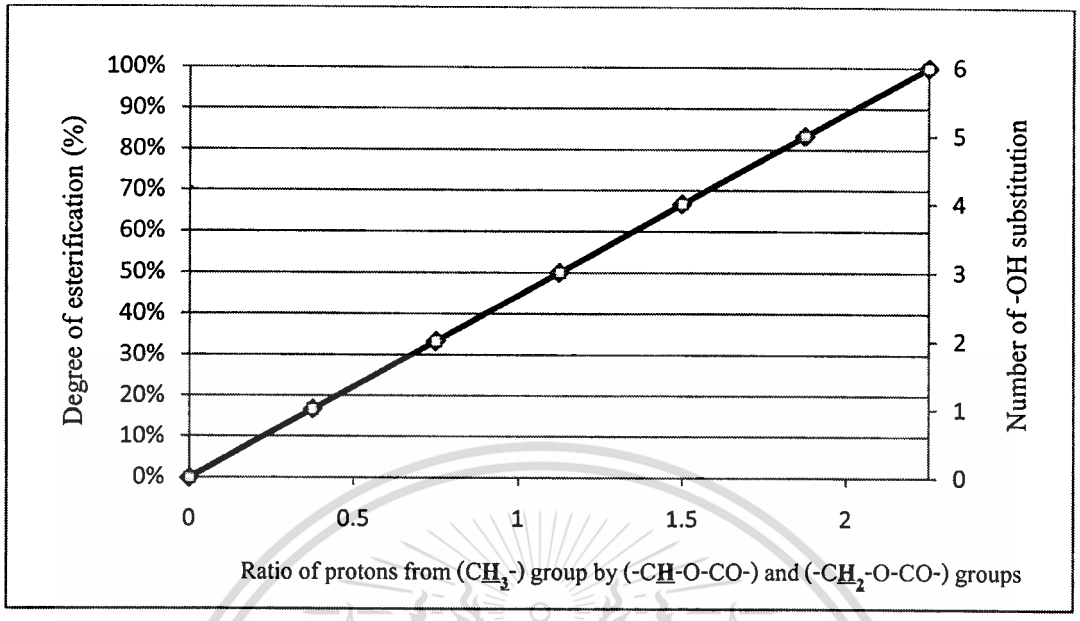


Figure 3.4 Standard curve illustrates the degree of esterification and the number of –OH group substitution versus the ratio of protons from (C**H**$_3$-) group by those from (-C**H**-O-CO) and (-C**H**$_2$-O-CO-) groups

3.4.2.2 Gas Chromatograph-Mass Spectrometer, (GC-MS)

Composition of ester products was determined by Gas Chromatograph-Mass Spectrometer (GC-MS) at Thai Plastic and Chemicals Public Company Limited. Gas chromatograph 6890N, Agilent Technologies, equipped with Agilent DB-Wax Capillary column, 0.25 mm x 30 mm x 0.25 μm, was used to determine the composition of ester product. The atmosphere used for all the experiments is a dry mixture of 5% H_2 in a balance of N_2. The gas mixture is flown from the gas cylinder through a Teflon® PTFE tubing, at a rate of 80 mL·min^{-1} controlled by a mass flow controller, to a quartz reactor tube. During the experiments, the outer zones of the furnace are maintained at a constant temperature of 120°C, heated linearly from 80°C to 500°C.

3.4.2.3 Thermal gravimetric Analyzer, TGA :

Thermal Stability of ester products was determined by Thermal gravimetric Analyzer at Thai Plastic and Chemicals Public Company Limited. A model Pyris 1 TGA, Perkin Elmer thermal gravimetric analyzer was used to measure the thermal stability of the samples. Each sample of 10 mg was heated at 10°C min^{-1} up to a temperature of 500°C. The sample was maintained in a nitrogen environment with a nitrogen gas flow rate of 40 $cm^3 \cdot min^{-1}$.

3.4.3 Determination of the physical properties of ester products

Determination of the physical properties of ester products were tested by PTT Research and Technology Institute (Fuels & Lubricants Research Department). These properties include:

1. Viscosity @40°C (ASTM D 445) by using Viscometer
2. Viscosity @100°C (ASTM D 445) by using Viscometer
3. Viscosity Index (ASTM D2270) by using numerical evaluation of the property of resistance to change in viscosity due to change in temperature
4. Pour point (ASTM D97) by using pour point test cabinet, std. thermometer
5. Total acid number (ASTM D664)

Chapter 4

Results and Discussion

The results shown in this chapter are divided into three parts. The first part is the synthesis and characterization of ester product by Gas Chromatograph-Mass Spectrometer (GC-MS), Thermogravimetric Analyzer (TGA) and Nuclear Magnetic Spectrometer (NMR). The variables such as reaction temperature and reaction time that affect on degree of esterification will also be explained in the second part. Finally, determination of the properties of products are discussed in the third part.

4.1 Synthesis and characterization of synthetic ester product

The purpose of this research is to synthesise an ester lubricant base oil. The preparation of synthetic ester was attempted from the esterification reaction of sorbitol with hexanoic acid.

The reaction variables effecting the degree of esterification were studied as the following:

- The reaction temperature from 130^{o}C to140^{o}C
- The reaction time from 3 hours to 5 hours
- The ratio between sorbitol and hexanoic acid from ratio 1:6 to 1:9

Some of the reactions that occur during the esterification are shown in Figure 4.1

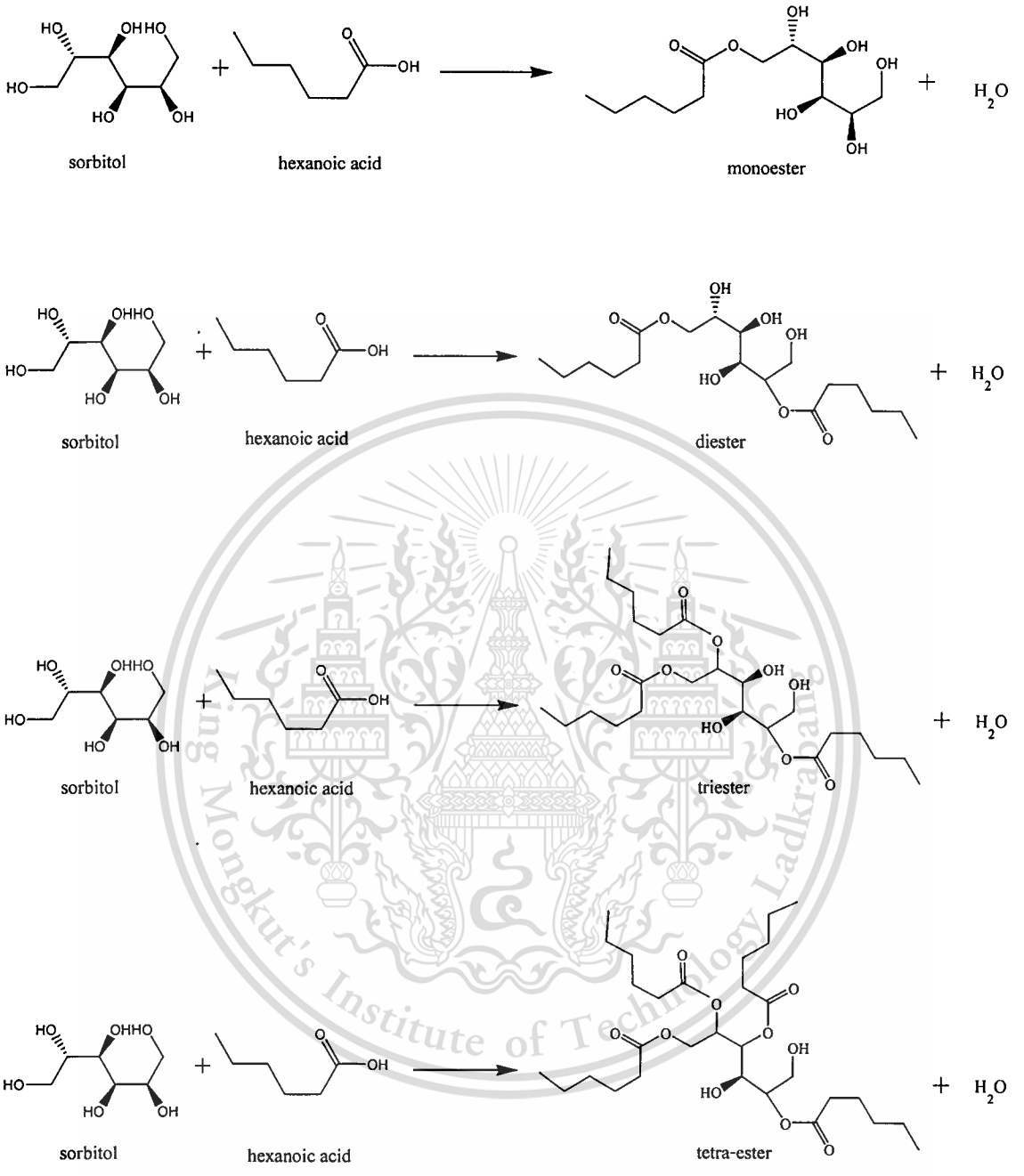


Figure 4.1 Esterification reactions between sorbitol and hexanoic acid

4.1.1 Characterization by ^{1}H-NMR spectroscopy

^{1}H-NMR spectra of sorbitol and hexanoic acid are shown below in Figure 4.2 and 4.3, respectively. ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 mole ratio of sorbitol to hexanoic acid at 140°C for 4 hours is illustrated in Figure 4.4.

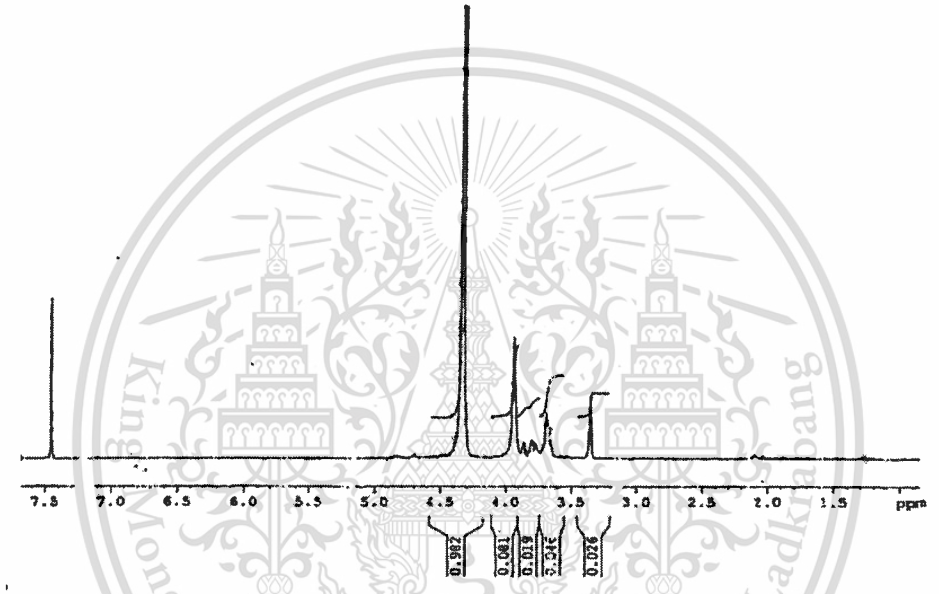


Figure 4.2 ^{1}H-NMR spectrum of sorbitol in D_2O

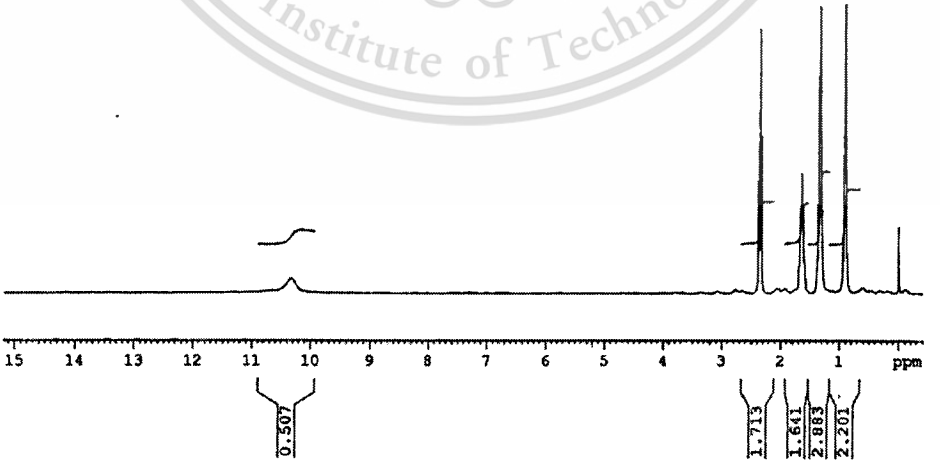


Figure 4.3 ^{1}H-NMR spectrum of hexanoic acid in $CDCl_3$

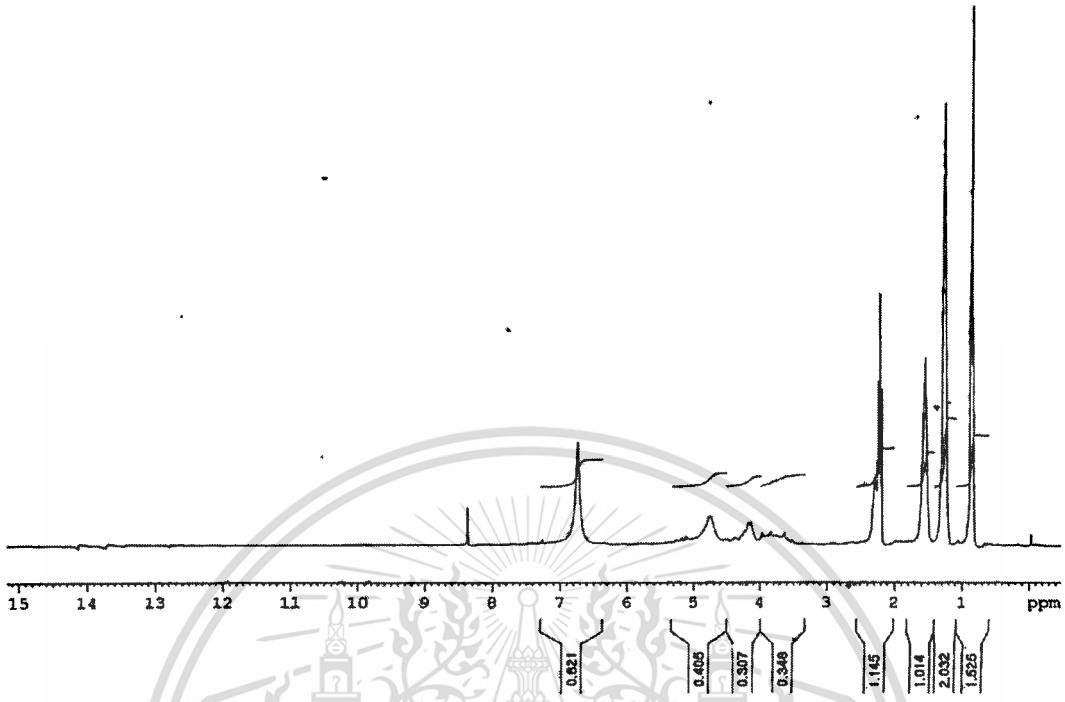


Figure 4.4 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 mole ratio of sorbitol to hexanoic acid at 140°C for 4 hours in $CDCl_3$

From Figure 4.4, it shows the broad peaks of (-C**H**-O-CO-) and (-C**H**$_2$-O-CO-) groups, which appear in the sorbitol region of the spectrum at δ 3.37 – 4.81 ppm. They are slightly shifted from (-C**H**-OH) and (-C**H**$_2$-OH) groups of sorbitol. This could prove that the reaction between sorbitol and hexanoic acid did occur. The other signals from ^{1}H-NMR spectra of products from the esterification reactions are also listed in Table 4.1.

Table 4.1 The signals from ^{1}H-NMR spectrum of products from the esterification reactions of sorbitol and hexanoic acid.

δ (ppm)	Signals
0.96	(C**H**$_3$-)
1.33	(-C**H**$_2$-)
1.56	(-C**H**$_2$-) at β (-C(=O)O-)
2.23	(-C**H**$_2$-) at α (-C(=O)O-)
3.37- 4.81	(-C**H**-O-CO-) and (-C**H**$_2$-O-CO-)
6.8	-O**H**

^{1}H-NMR spectra of products acquired from the reactions using the other conditions are present in Appendix B. From all spectra, number of –OH group substitution and degree of esterification were determined according to the calculation and method previously described in Chapter 3. The results are shown in Table 4.2 and 4.3

Table 4.2 Number of -OH group substitution of sorbitol from the reactions of sorbitol with hexanoic acid under various conditions

Times (hour)	1:6 mole ratio of sorbitol to hexanoic acid		1:9 mole ratio of sorbitol to hexanoic acid
	130°C	140°C	140°C
3	2.42	2.97	3.7
4	2.79	3.83	4.05
5	3.04	3.96	-

Table 4.3 Degree of esterification from the reactions of sorbitol with hexanoic acid under various conditions

Times (hour)	1:6 mole ratio of sorbitol to hexanoic acid		1:9 mole ratio of sorbitol to hexanoic acid
	130°C	140°C	140°C
3	40.33%	49.50%	61.67%
4	46.50%	63.83%	67.50%
5	50.67%	66.00%	-

The effect of reaction temperature, reaction time, and mole ratio between sorbitol and hexanoic acid on the esterification reaction were determined and the results are discussed in section 4.2.

4.1.2 Characterization by Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS), was used to determine the composition of ester product and also used for further investigates the quantitative and qualitative analysis of the esterification reaction product. During the experiments, the outer zones of the furnace are maintained at a constant temperature of 120°C, heated linearly from 80°C to 500°C.

Chromatogram of the synthetic ester product illustrated in Figure 4.5 shows the three compositions of product at retention time of 4.725, 6.930 and 9.640 minutes. Mass spectra of these three compositions are shown in Figure 4.6, 4.7, and 4.8, respectively.

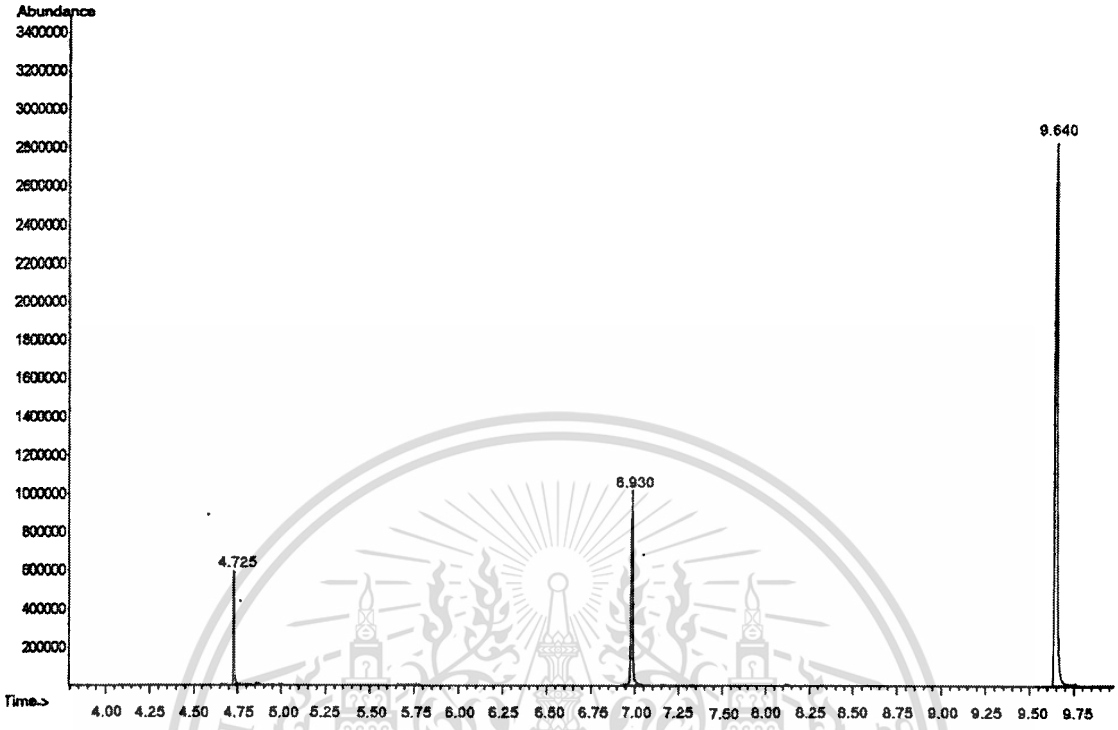


Figure 4.5 Gas chromatogram of the synthetic ester product from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours

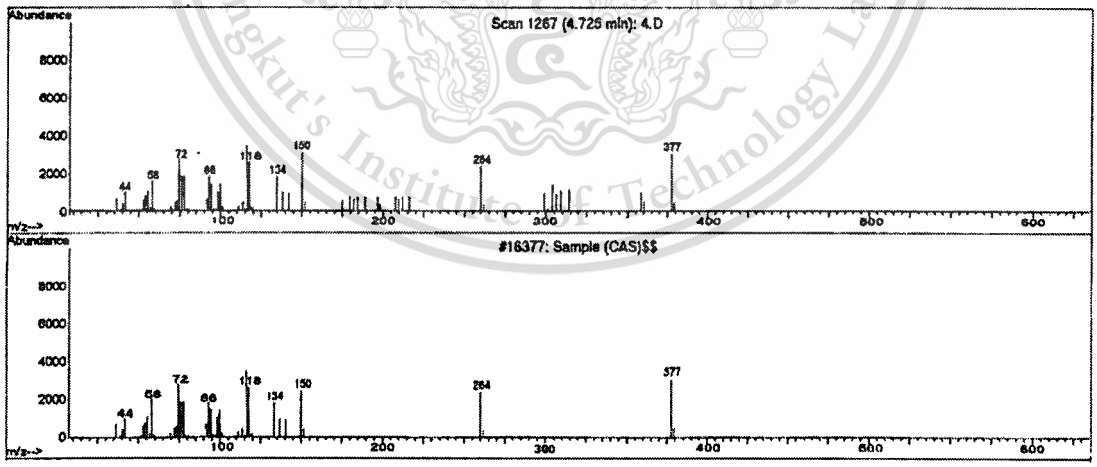


Figure 4.6 Mass spectrum of the first composition of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours; the retention time = 4.725 minutes

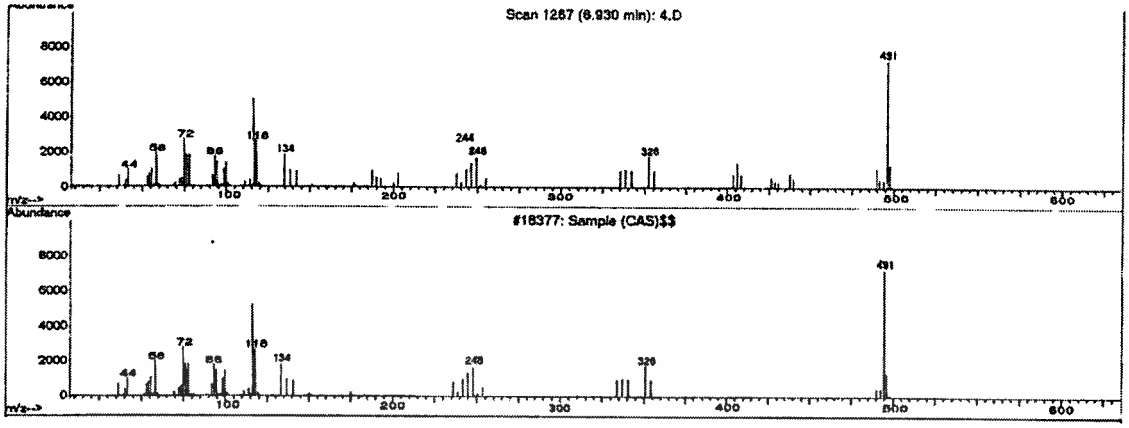


Figure 4.7 Mass spectrum of the second composition of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours; the retention time = 6.930 minutes

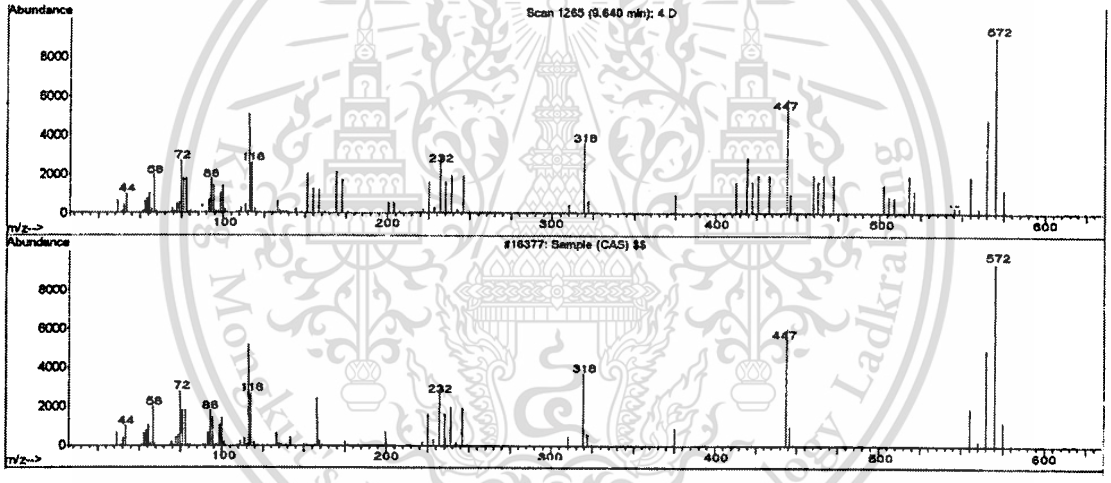


Figure 4.8 Mass spectrum of the third composition of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours; the retention time = 9.640 minutes

Theoretically, the molecular mass of sorbitol dihexanoate, sorbitol trihexanoate and sorbitol tetrahexanoate are 378, 476, and 574, respectively. From Figure 4.6 – 4.8, Mass spectra of the three compositions of synthetic ester product show their molecular ion peaks at m/z = 377, 491, and 572, respectively. This indicates that these three components are indeed the di-, tri- and tetra esters. These results are also supported by the degree of esterification and the number of –OH substitution calculated from ^{1}H-NMR spectra. However, according to the gas chromatogram of hexanoic acid

shown in Figure 4.9 which have a single peak appears at the same retention time as the third component, a trace of hexanoic acid could be left unreacted in the ester product.

Figure 4.9 Gas chromatogram of hexanoic acid

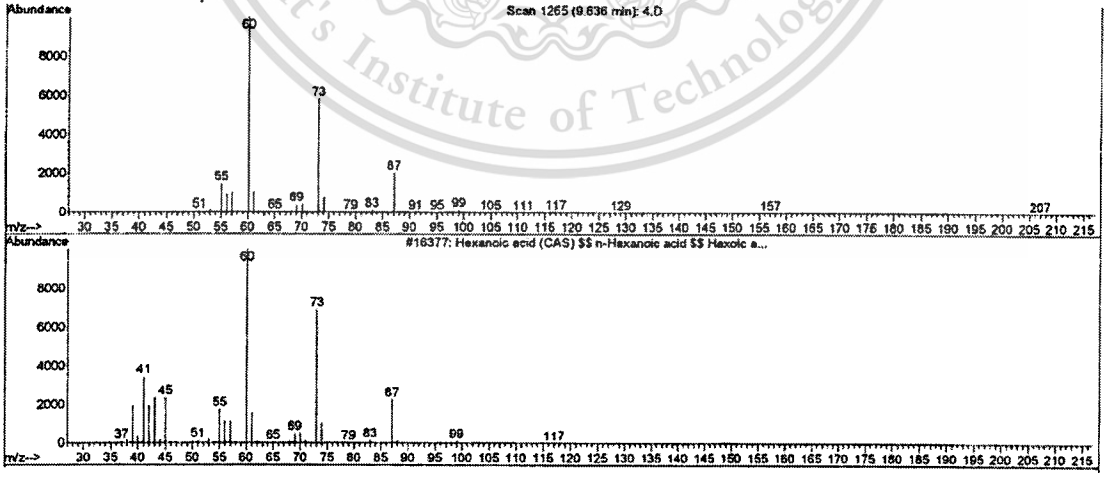


Figure 4.10 Mass spectrum of hexanoic acid

To confirm that the ester product was completely purified without hexanoic acid left in the product, the addition of hexanoic acid as internal standard is required. Figure 4.11 shows the gas chromatogram of the product mixed with hexanoic acid. It clearly shows an additional peak of hexanoic acid at the retention time of 9.640 minutes, completely separated from that of the tetraester. This proves that the synthetic ester product was completely purified without hexanoic acid left in the product.

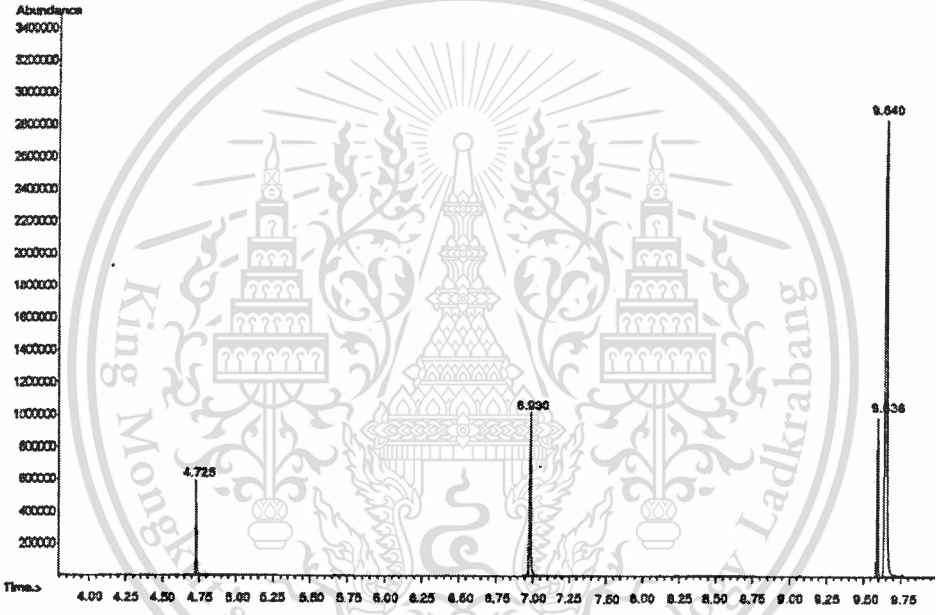


Figure 4.11 Gas chromatogram of a mixture between hexanoic acid and synthetic ester product

The percent selectivities towards each components were calculated using the peak area of each components from gas chromatogram (GC-MS) as shown in Appendix B-2. It can be concluded as relative amounts of product that the product is composed of 85.26% of tetraesters, 10.96% of triesters, and 3.78% of diesters.

4.1.3 Characterization by Thermal Gravimetric Analyzer (TGA)

Thermogravimetric analyzer was used to determine the thermal stability of the product ester. The result was also used to confirm that hexanoic acid was indeed not in the product. Figure 4.12 shows that hexanoic acid decompose at 175°C whereas the thermogram of ester product in Figure 4.13 shows the only onset temperature at 252°C. The result indicates that the ester product is stable up to 252°C.

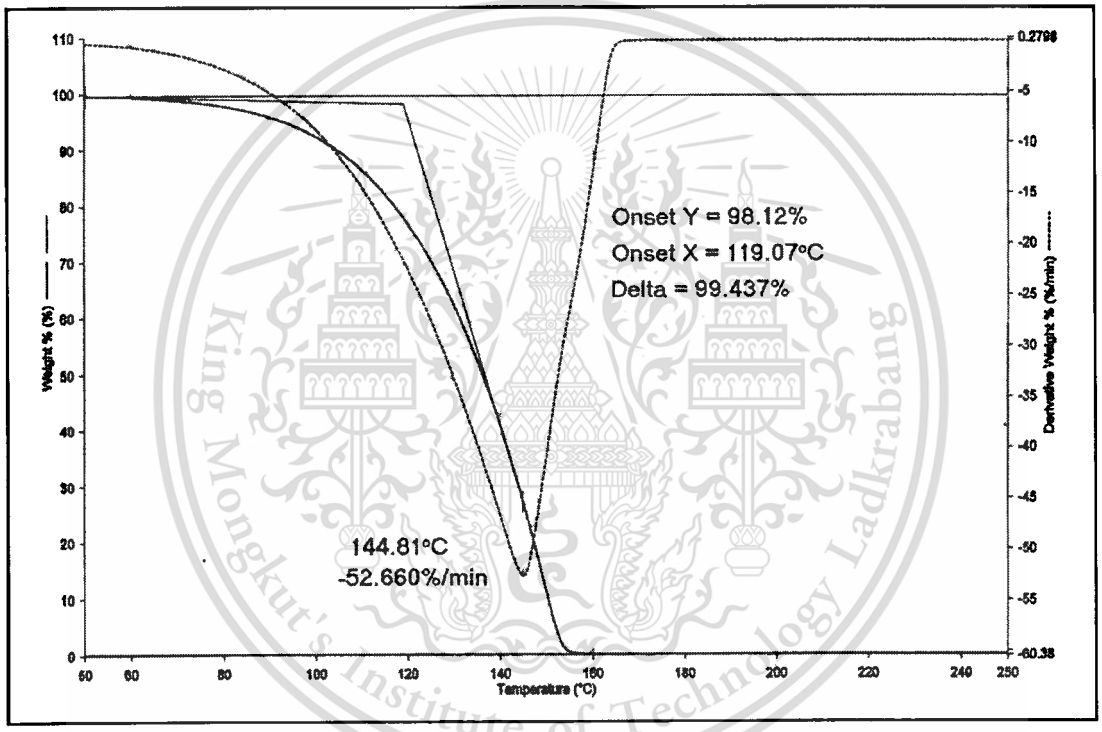


Figure 4.12 Thermogram analysis showing percent weight lost of hexanoic acid as a function of temperature

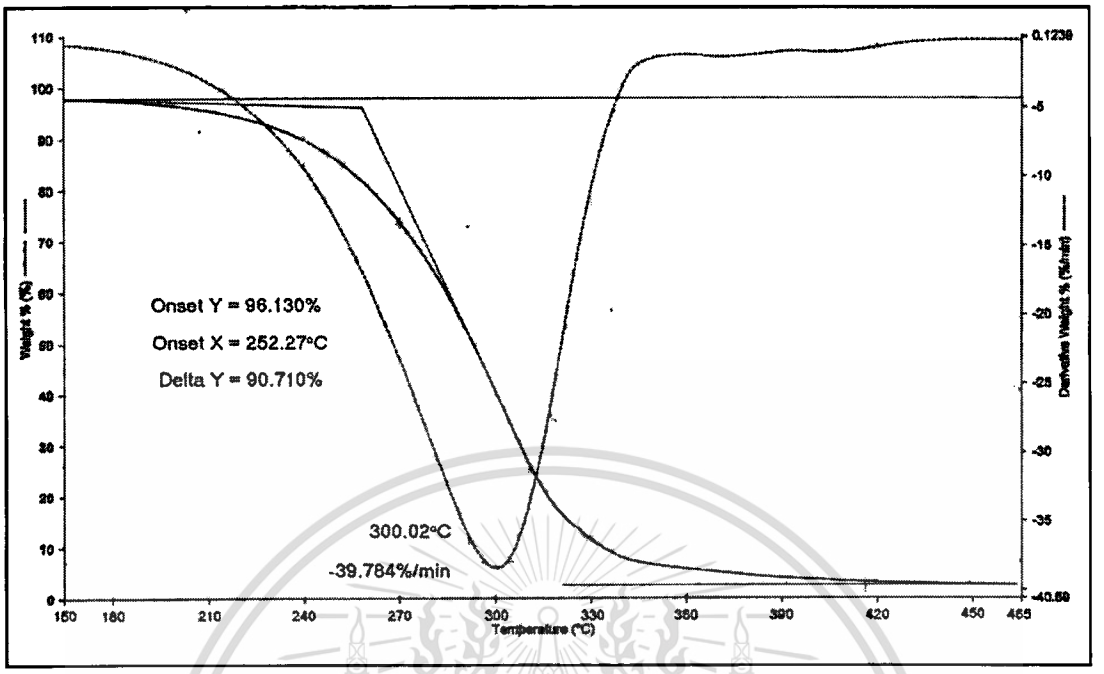


Figure 4.13 Thermogram analysis showing percent weight lost of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mol at 140 °C for 4 hours as a function of temperature

4.2 The effect of various conditions on esterification.

The effect of reaction temperature, reaction time, and mole ratio between sorbitol and hexanoic acid for the esterification reaction were determined and the results are discussed below.

4.2.1 Effect of reaction temperature and time

Temperature has a significant effect on the overall reaction. The esterification reactions were carried out at 130°C and 140°C and were run for 3, 4, and 5 hours using the mole ratio of sorbitol to hexanoic acid equal to 1:6.

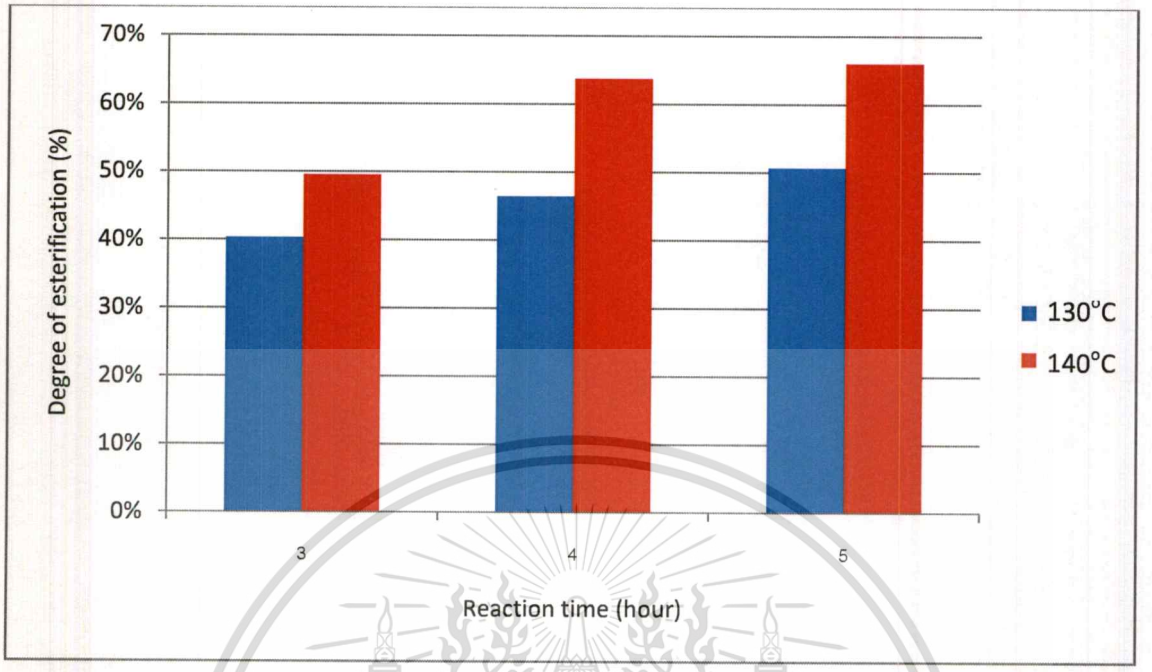


Figure 4.14 Effect of temperature and time on the degree of esterification of synthetic ester using mole ratio of sorbitol to hexanoic acid equal to 1:6

From Figure 4.14, the effect of temperature on the degree of esterification is shown. As the reaction temperature increases from 130°C to 140°C, the degree of esterification also increases as expected, since the reaction rate increases with temperature. The maximum degree of esterification of 66% were reached at 140°C for 5 hours. The temperature at 140°C was then chosen for the next study.

The reaction time also has an effect on the degree of esterification to the synthetic ester product. The esterification reactions were carried out at 3, 4, and 5 hours and were run at 130°C and 140°C. It was found that the degree of esterification increases with the reaction time. However, changing the time from 4 to 5 hours showed insignificant effect on the degree of esterification. This is presumably because water was not completely expelled from the reaction and the equilibrium was reached. The maximum degree of esterification was about 64% at 140°C for 4 hours.

4.2.2 Effect of ratio between sorbitol to hexanoic acid

It was observed that the ratio between sobitol and hexanoic acid also had an effect on the degree of esterification. The esterification reactions were carried out by using the mole ratio of sorbitol to hexanoic acid equal to 1:6 and 1:9 and were run at fixed temperature at 140°C for 3 and 4 hours. The degree of esterification versus reaction time are plotted in Figure 4.16 shown below.

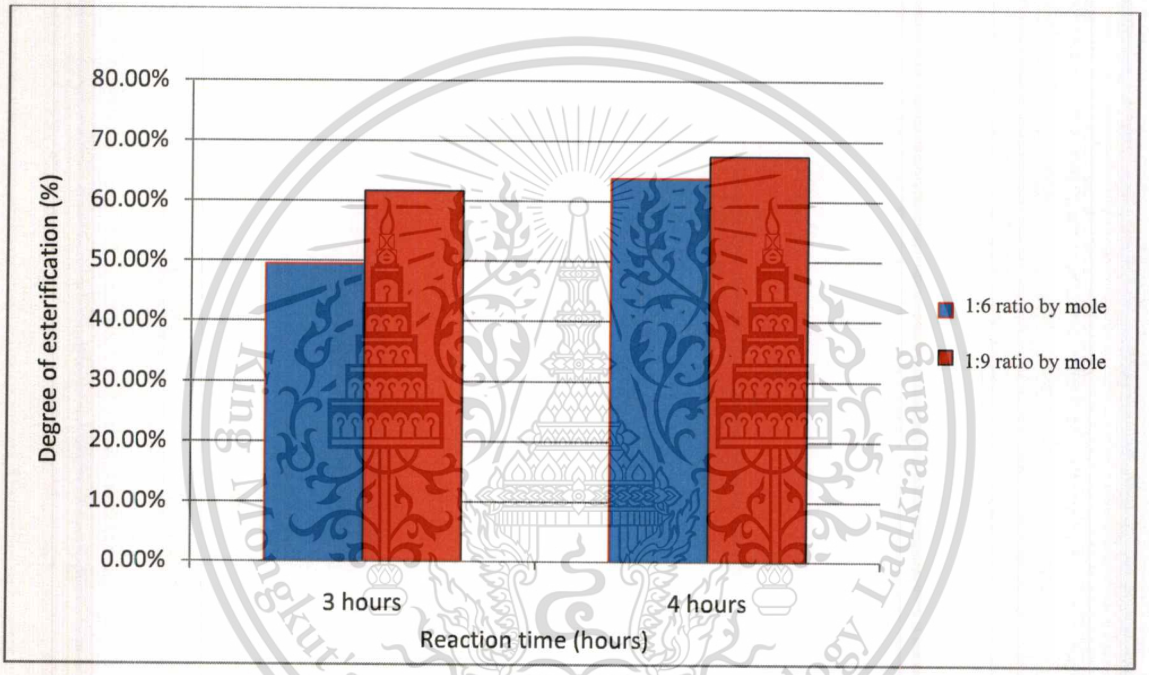


Figure 4.15 Effect of ratio between sorbitol to hexanoic acid on the degree of esterification at 140°C

From Figure 4.15, increasing the amount of hexanoic acid from the stoichiometric ratio of 1:6 can raise the degree of esterification. However, the differences were not much, especially after 4 hours of reaction. This is probably because the remaining –OH groups were more difficult to react due to the steric hindrance, and an equilibrium was also reached. The condition using 1:6 mole ratio of sorbitol to hexanoic acid at 140°C for 4 hours was then chosen as the optimum condition in this work.

4.3 Determination of the properties of synthetic ester product

The properties of product synthesized from the optimum condition were tested at Faculty of Science, Chulalongkorn University which are listed in Table 4.4. Considering for the possible applications, the properties of ester product from sorbitol and hexanoic acid were compared with those of lube base oil 500SN The solubility test is also reported in Table 4.5.

Table 4.4 Properties of synthetic ester from sorbitol and hexanoic acid via esterification reaction by using 1:6 ratio by mol for 4 hours at 140°C with base oil 500SN [19]

Properties	Synthetic ester	Specification limits of lube base oil 500SN	
		Min	Max
Viscosity @40°C, cSt	46.37	-	-
Viscosity @100°C, cSt	9.131	-	11-11.25
Viscosity Index	174	88	-
Density @20°C, kg/m^3	913	-	-
Pour point (°C)	-3	-3	-9
Flash point COC (°C)	274.15	210	-
Thermal stability (°C)	252.27	-	-
Total Acid Number (mg/KOH/g)	0.052	-	0.05

Table 4.5 Solubility test of synthetic ester from sorbitol and hexanoic acid via esterification reaction by using 1:6 ratio by mol for 4 hours at 140°C

Solvent	Solubility
Water	insoluble
Hexane	insoluble
Methanol	partly soluble
Diethyl ether	soluble
Hydrocarbon lube	insoluble

From the results obtained, it can be found that the synthetic ester which run under the optimum conditions using mole ratio of sorbitol to hexanoic acid equal to 1:6 for 4 hours at 140°C gives the viscosity @40°C and @100°C, and total acid number close to the values measured for 500SN. Its viscosity index and flash point are higher than those of 500SN. These properties seem to be within the specification limits of lube base oil 500SN. Furthermore, from the solubility test, it cannot be washed out by both hydrocarbon and water. This proves to be the advantage since the loss will be minimum used as engine oil. As a result, the synthetic ester product might be used as a replacement for 500SN. However, the low thermal stability is to be concerned because it could be too low to use in the engine.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The goal of this research is to prepare a lubricating base oil from the esterification reaction of sorbitol and hexanoic acid. Parameters that affect on the degree of esterification such as reaction temperature and time were investigated. The composition of products were characterized using Nuclear Magnetic Resonance Spectrophotometer (NMR), Thermogravimetric Analyzer (TGA), and Gas Chromatograph-Mass Spectrometer (GC-MS). It was found that the product was composed of 3 constituents; the di-, tri-, and tetraesters. They were present in product as relative amounts from GC-MS by 4%, 11%, and 85%, respectively. The rise of reaction temperature, reaction time, and the ratio between sorbitol to hexanoeic acid all led to higher degree of esterification. The optimum condition was found to be the one using 1:6 mole ratio of sorbitol to hexanoic acid at 140°C for 4 hours.

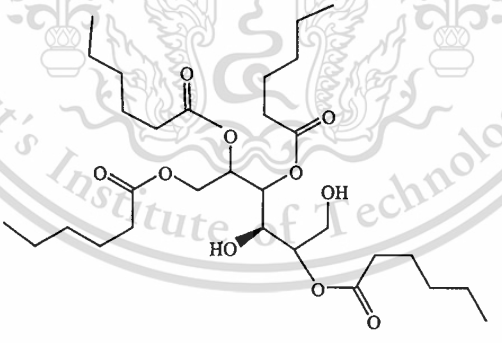


Figure 5.1 Structure of tetraester

The properties of product such as viscosity at 40°C and 100°C, viscosity index, density at 20°C, pour point, flash point, thermal stability and total acid number were determined. It was found that the product could be a candidate as a lube base 500SN replacement.

5.2 Suggestions

1. Adjustment of the chain length of carboxylic acid could be attemped to improve the properties or to adjust the oil grade.
2. To improve the degree of esterification, the second esterification step could be attempted using a smaller acid and this product as starting materials.
3. Since the product does not dissolved in both hydrocarbon and water, it would be interesting to study on the possible application of this synthetic ester as surfactant.

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APPENDICES

APPENDIX A

REACTANT CALCULATION

1. The average molecular weight of sorbitol at the ratio between sorbitol and hexanoic acid of 1:6

Molecular weight of sorbitol	= 182.17 g/mol
Molecular weight of hexanoic acid	= 116.16 g/mol
Density of hexanoic acid	= 0.920 g/cm^3
Hexanoic acid 100 ml	= 100x0.920
	= 92.0 g
So, hexanoic acid 100 ml	= 92.0/116.16
	= 0.7920 mol
At 1:6 mole ratio of sorbitol to hexanoic acid	
Weight of sorbitol	= 0.7920/6
	= 0.13 mol
	= 0.13x182.17
	= 23.68 grams

2. The average molecular weight of sorbitol at the ratio between sorbitol and hexanoic acid of 1:9

Molecular weight of sorbitol	= 182.17 g/mol
Molecular weight of hexanoic acid	= 116.16 g/mol
of hexanoic acid	= 0.920 g/cm^3
Hexanoic acid 100 ml	= 100x0.920
	= 92.0 g
So, hexanoic acid 100 ml	= 92.0/116.16
	= 0.7920 mol

At 1:6 mole ratio of sorbitol to hexanoic acid

Weight of sorbitol	= 0.7920/9
	= 0.09 mol
	= 0.09x182.17
	= 16.03 grams

APPENDIX B

PRODUCT CALCULATION

B-1 Analysis by ^{1}H-NMR spectra

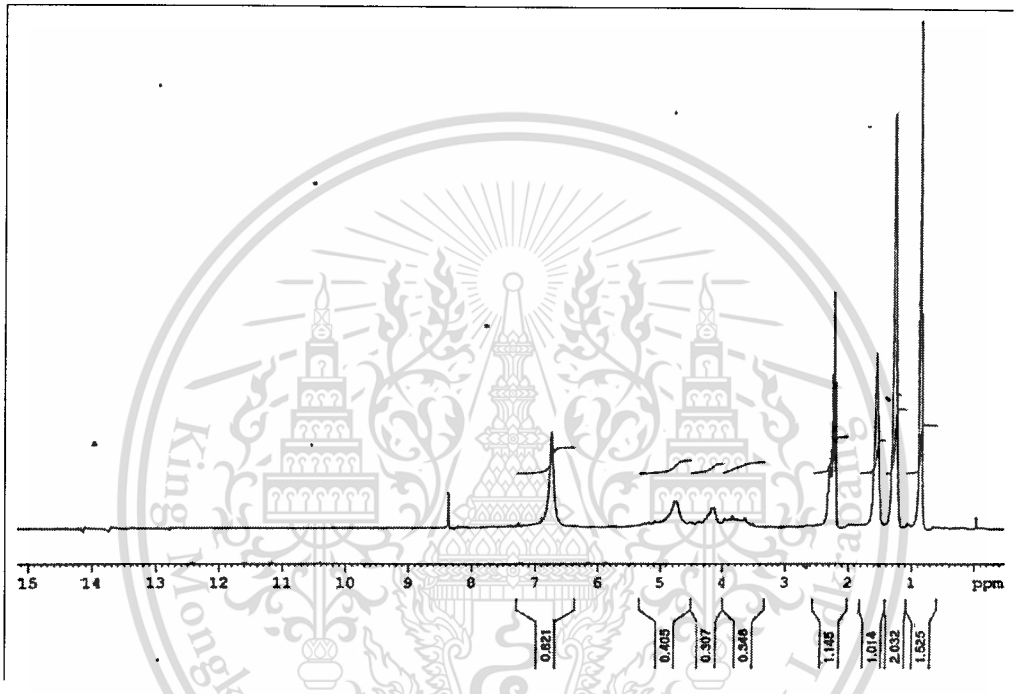

Figure B-1 ^{1}H-NMR spectrum of synthetic ester product in $CDCl_3$

From Figure B-1, the signals at δ 3.1-δ4.85 ppm are corresponded to the protons of (-C**H**-O-CO-) and (-C$\underline{\mathbf{H}}_2$-O-CO-) groups. They appear in the sorbitol region of the spectrum. The signal at δ 0.75 ppm appears as singlet and is assigned to (-C$\underline{\mathbf{H}}_3$) group in the hexanoic acid region of the spectrum. The number of –OH substitution could be calculated as following;

$$\frac{No.\,of\ protons\ from\ (-C\underline{H_3})\ group}{No.\,of\ protons\ from\ (-C\underline{H}-O-CO-)and\ (-C\underline{H_2}-O-CO-)\ groups} = \frac{integration\ at\ \delta 0.75\ ppm}{integration\ at\ \delta 3.1-\delta\ 4.85\ ppm}$$

$$= \frac{1.525}{1.06}$$

$$= 1.44$$

Theoretically, the ratio of protons from (-C$\underline{H}_3$) group by those of (-C$\underline{H}$-O-CO-) and (-C$\underline{H}_2$-O-CO) groups can be calculated when the degree of esterification changes as shown in Table B-1. A standard curve can then be made as illustrated in Figure B-2. It was used to determine the degree of esterification and number of –OH group substitution from the reactions in this work using the proton ratio of those groups from ^{1}H-NMR spectrum.

Table B-1 Number of –OH group substitution and degree of esterification of synthetic ester from sorbitol and hexanoic acid

$\frac{\text{No. of proton from } (-C\underline{H}_3) \text{ group}}{\text{No. of proton from } (-C\underline{H}-O-CO-) \text{ and } (-C\underline{H}_2-O-CO-) \text{ groups}}$		Degree of esterification (%)	Number of -OH group substitution
3/8	0.375	16.67	1
6/8	0.750	33.33	2
9/8	1.125	50.00	3
12/8	1.500	66.67	4
15/8	1.875	83.33	5
18/8	2.250	100.00	6

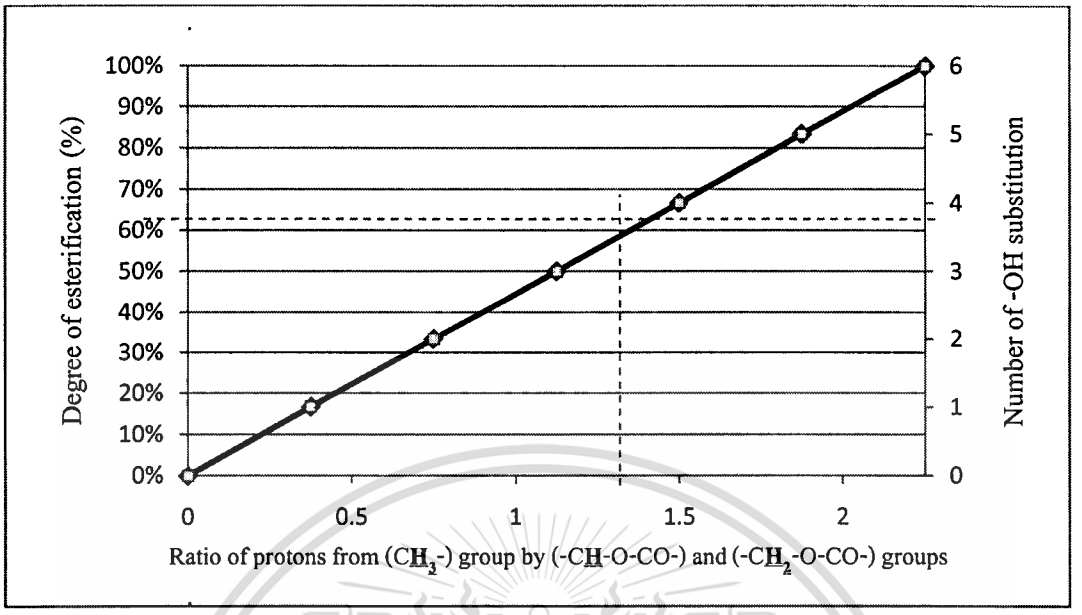

Figure B-2 Standard curve illustrates the degree of esterification and the number of –OH group substitution versus the ratio of protons from (C**H**$_3$-) group by those from (-C**H**-O-CO) and (-C**H**$_2$-O-CO-) groups

B-2 Analysis by Gas Chromatograph

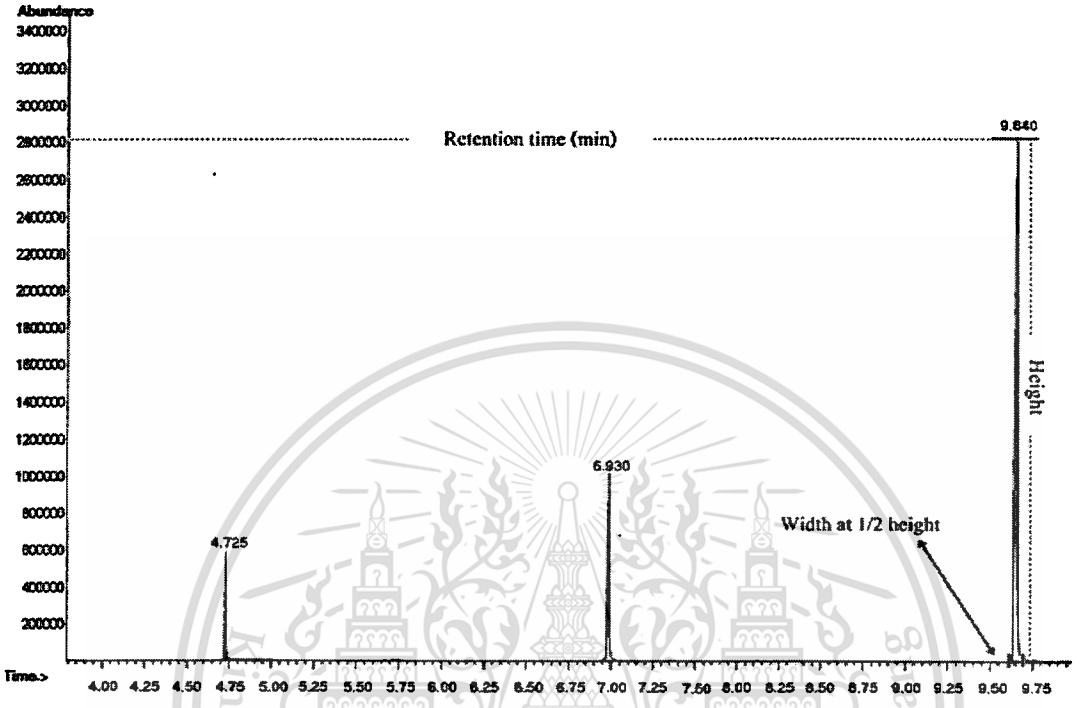

Figure B-3 Gas chromatogram of the synthetic ester product from sorbitol and hexanoic acid

$$Area = (height) \times (width\ at\ {}^{1}/_{2}\ height)$$

Assume that each component of the mixture causes the same response in the detector. Therefore, the areas under the curves can be used to calculate percent composition of the mixture. (This is a reasonable assumption when the components of the mixture are very similar in structure, as diester, triester, and tetraester).

$$\%Component = \left[\frac{area\ under\ peak}{total\ area}\right] \times 100$$

APPENDIX C

CHARACTERIZATION DATA

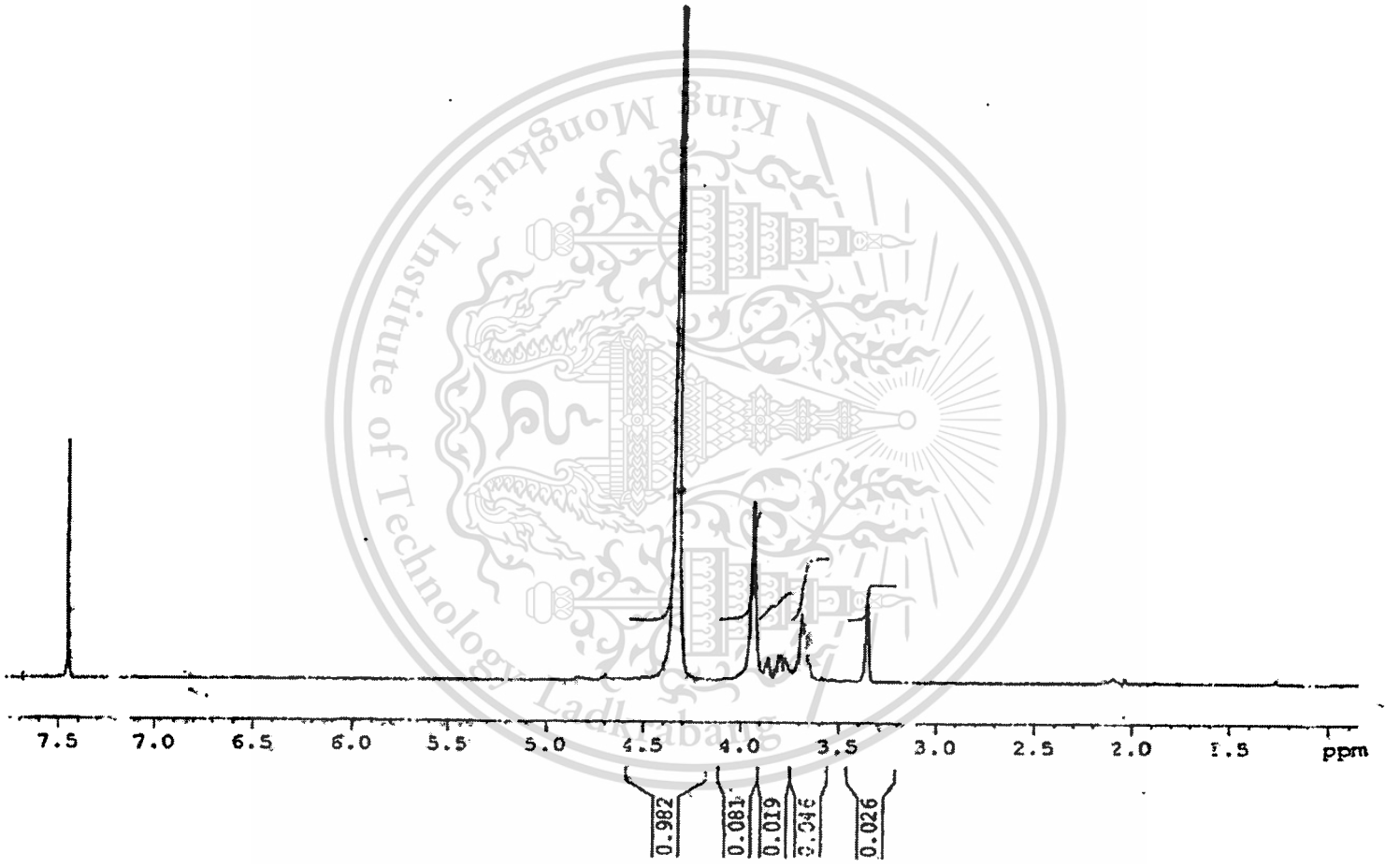

Figure C-1 ^{1}H-NMR spectrum of sorbitol in D_2O

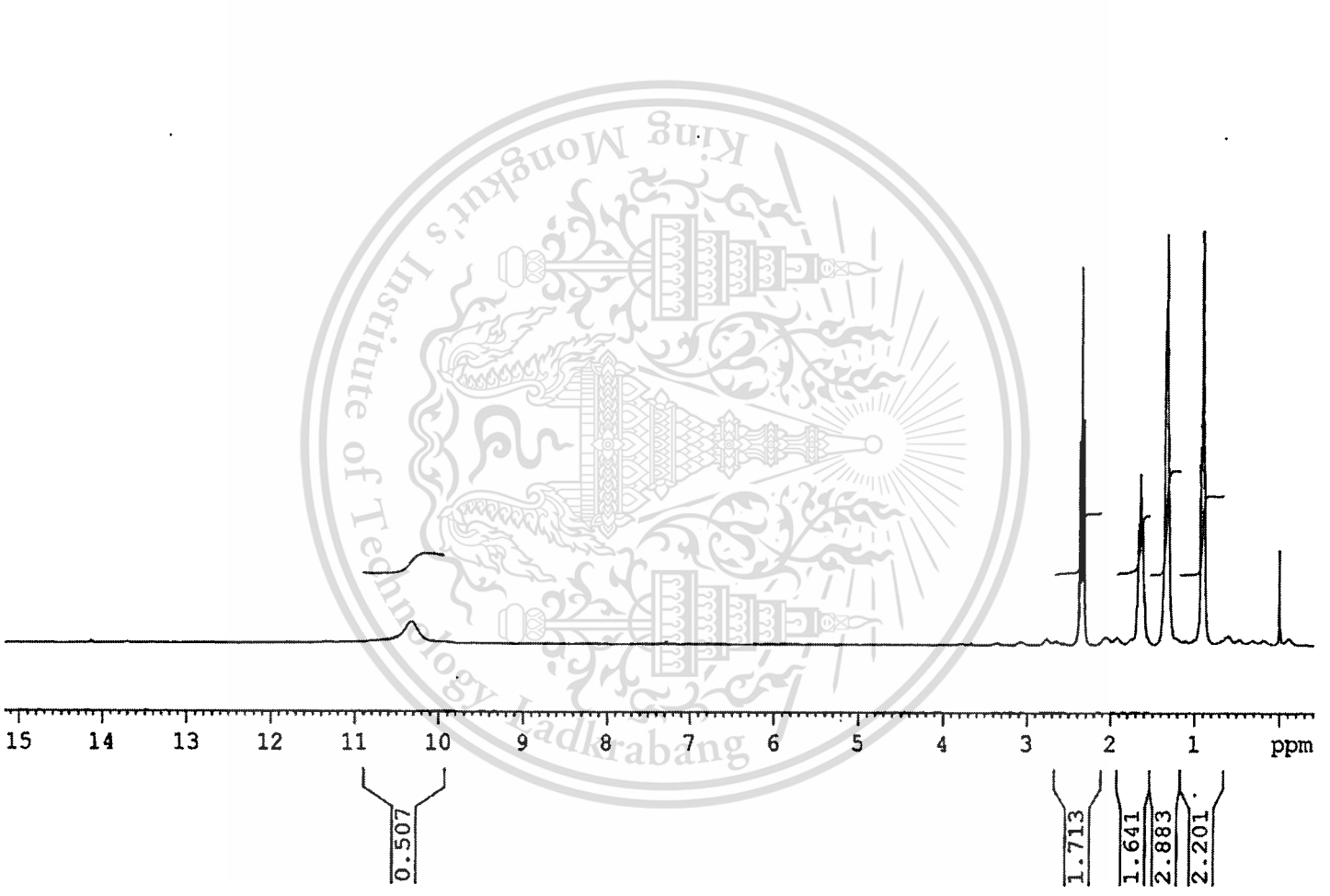

Figure C-2 ^{1}H-NMR spectrum of hexanoic acid in $CDCl_3$

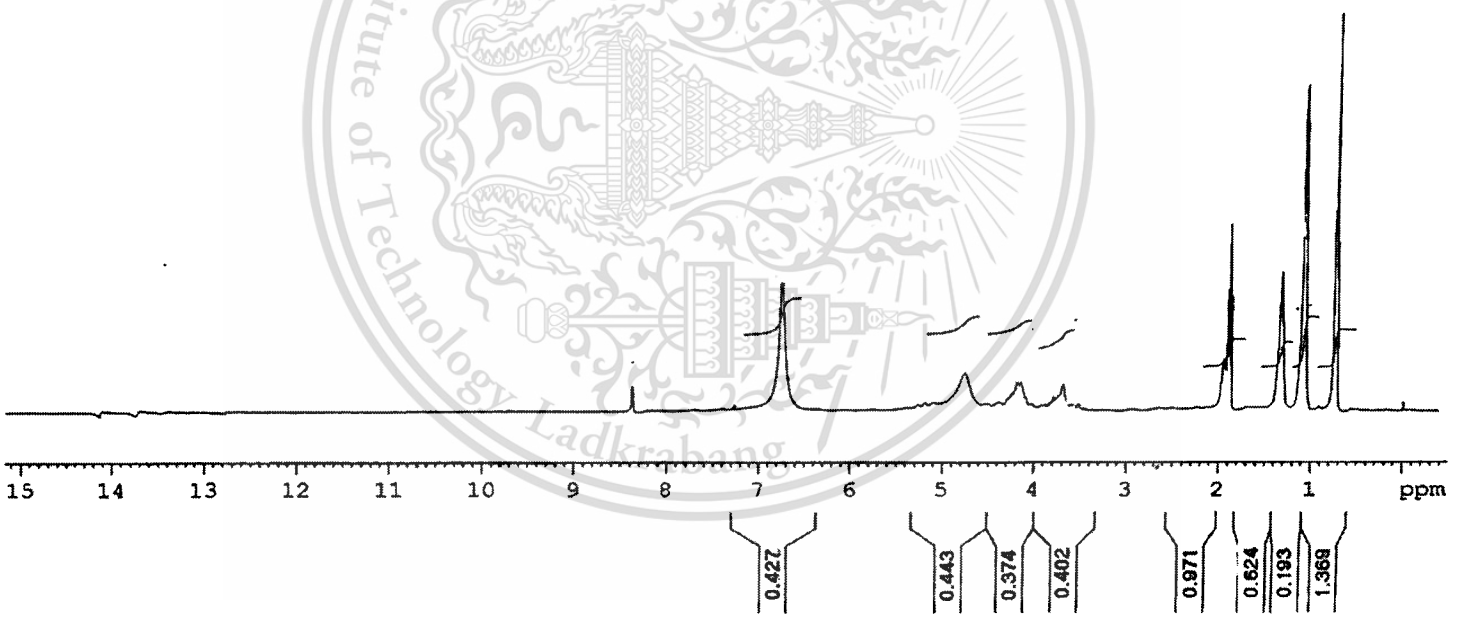

Figure C-3 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 ratio by mol of sorbitol to hexanoic acid at 130°C for 3 hours in $CDCl_3$

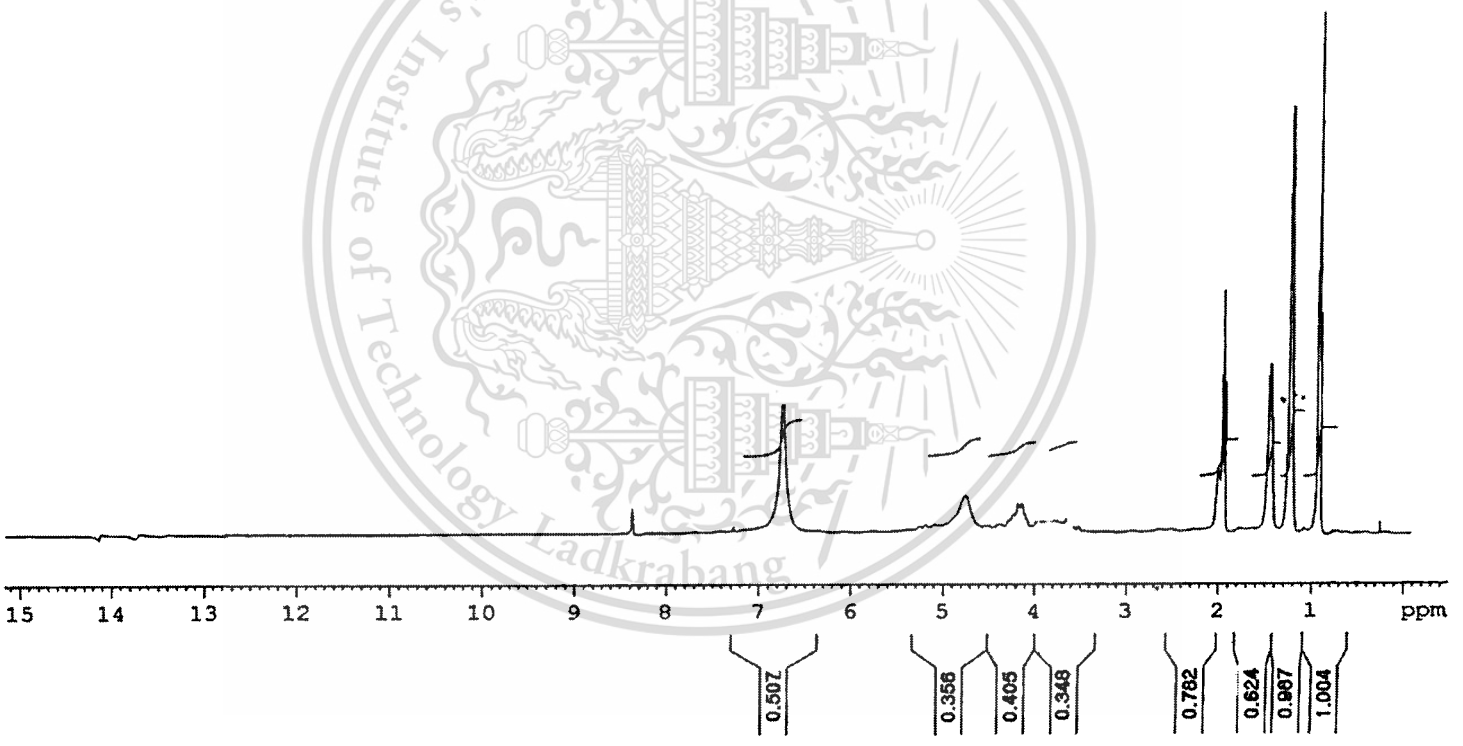

Figure C-4 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 ratio by mol of sorbitol to hexanoic acid at 130°C for 4 hours in $CDCl_3$

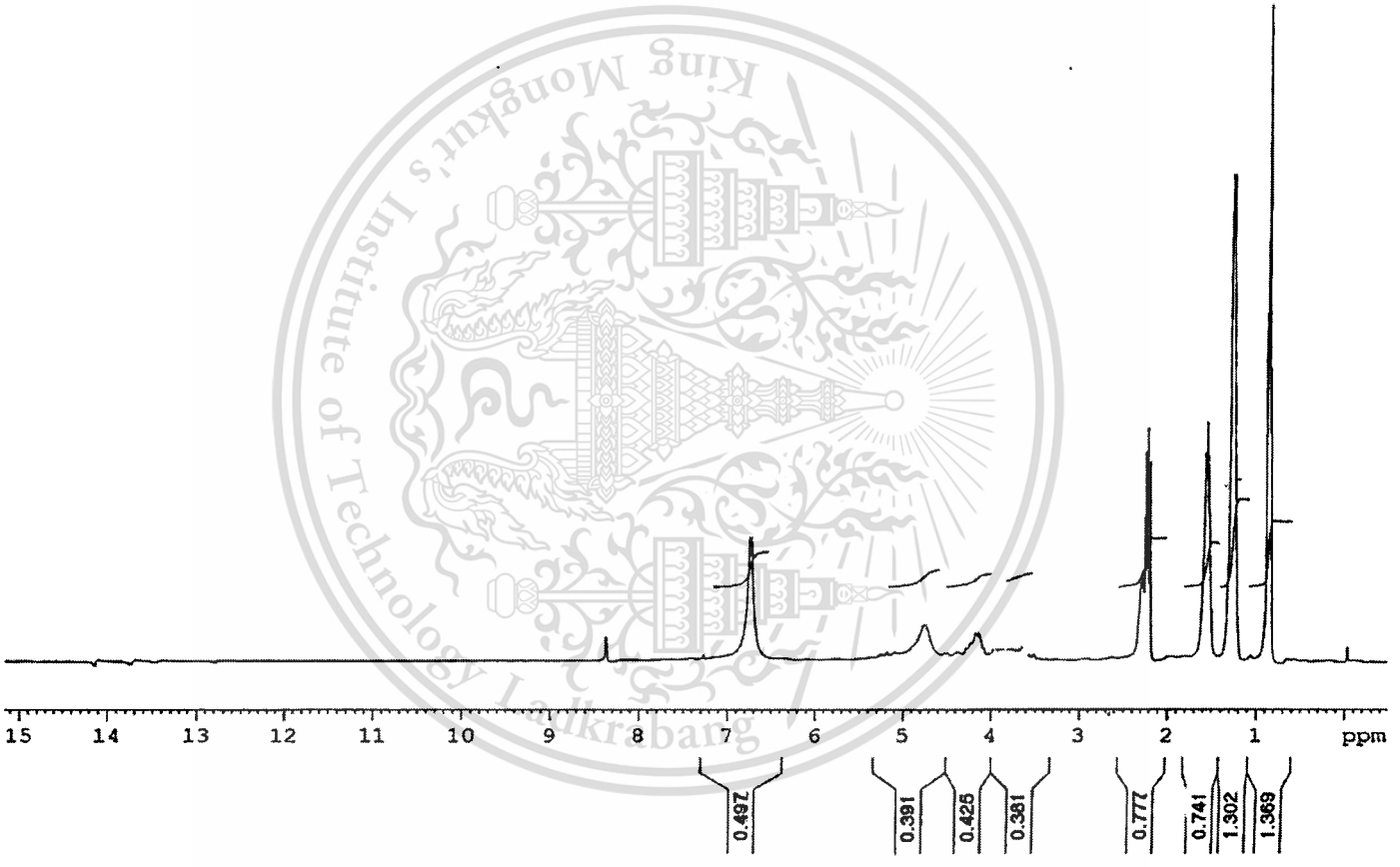

Figure C-5 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 ratio by mol of sorbitol to hexanoic acid at 130°C for 5 hours in $CDCl_3$

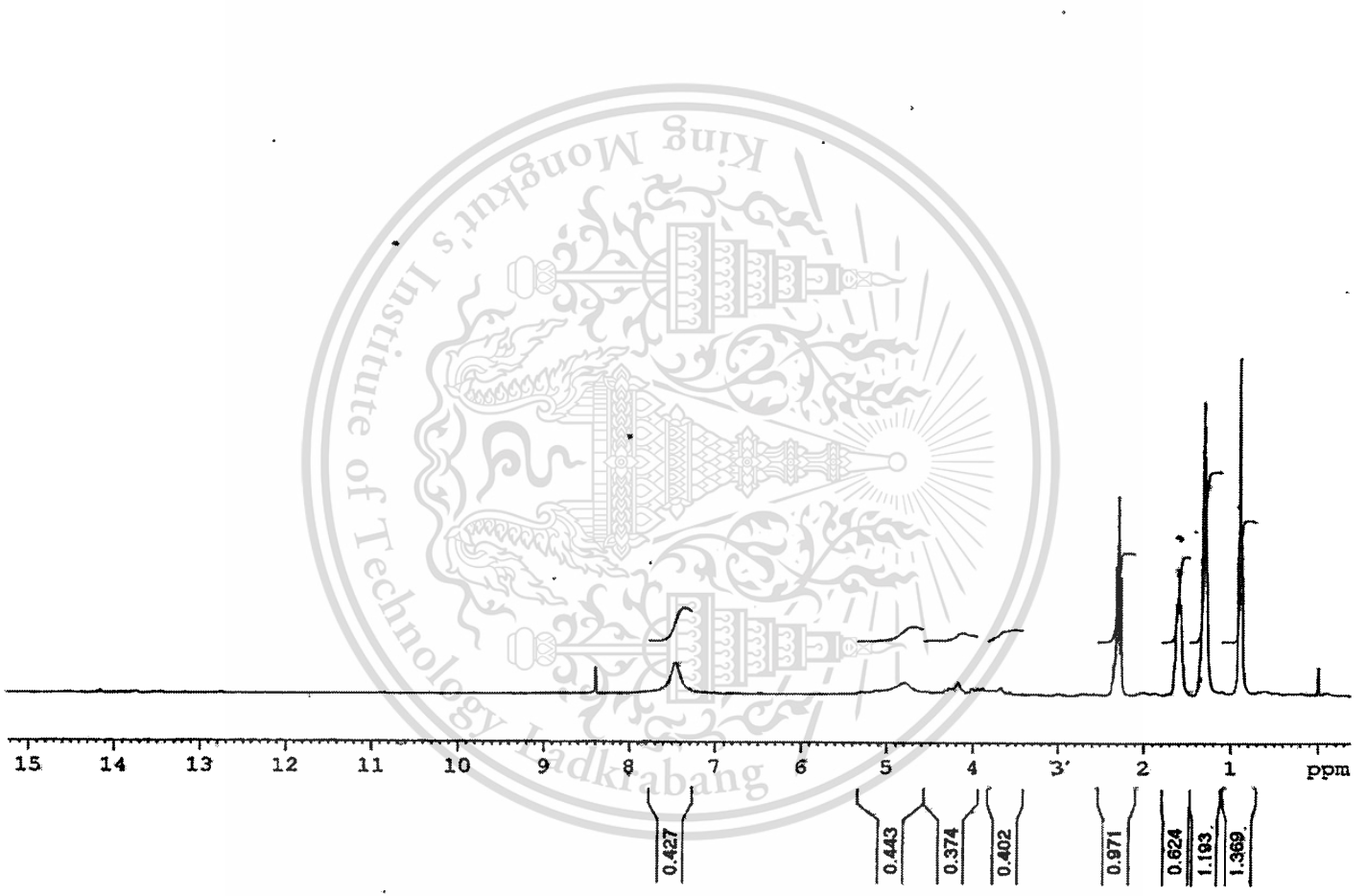

Figure C-6 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 ratio by mol of sorbitol to hexanoic acid at 140°C for 3 hours in $CDCl_3$

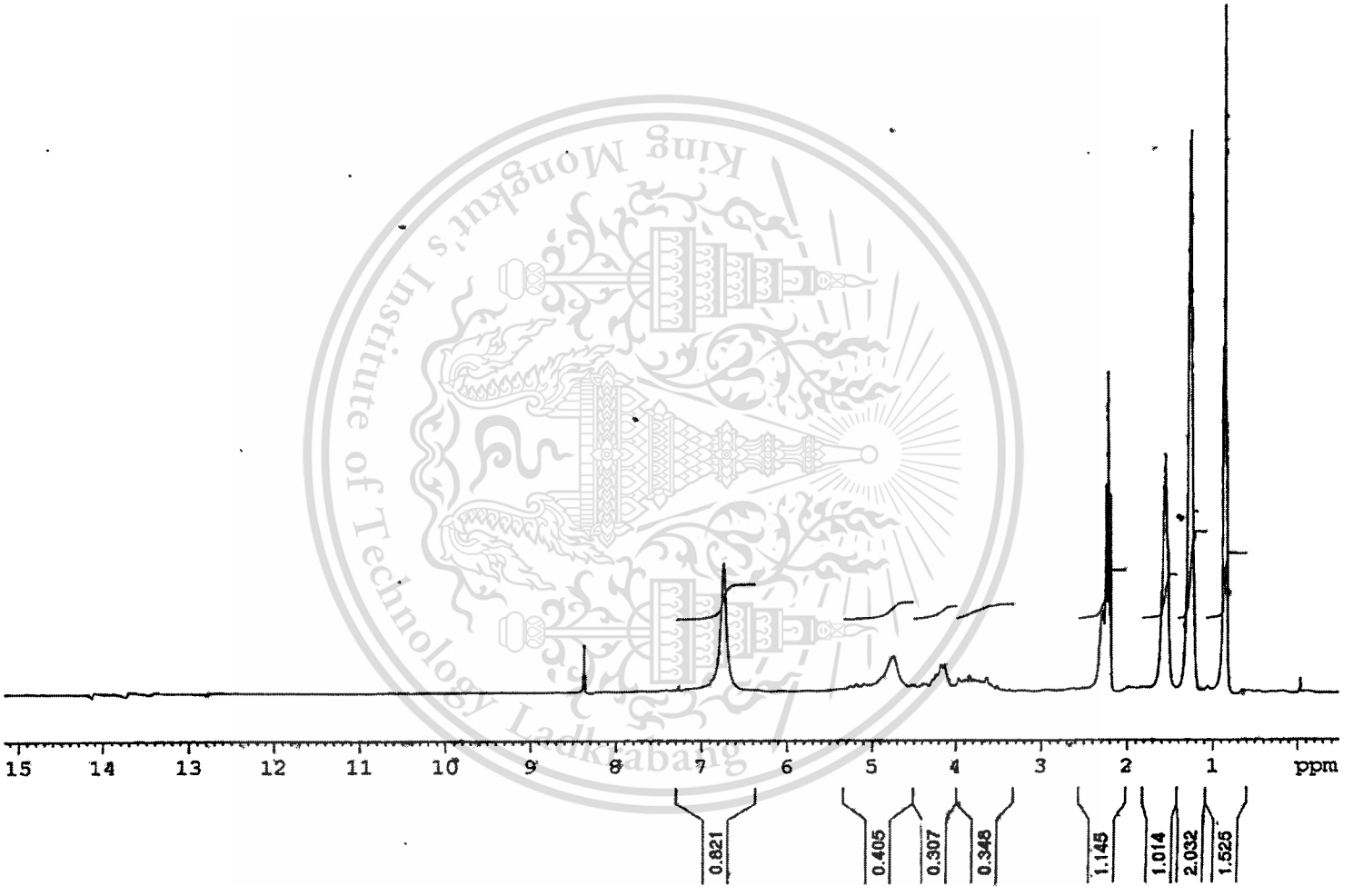

Figure C-7 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 ratio by mol of sorbitol to hexanoic acid at 140°C for 4 hours in $CDCl_3$

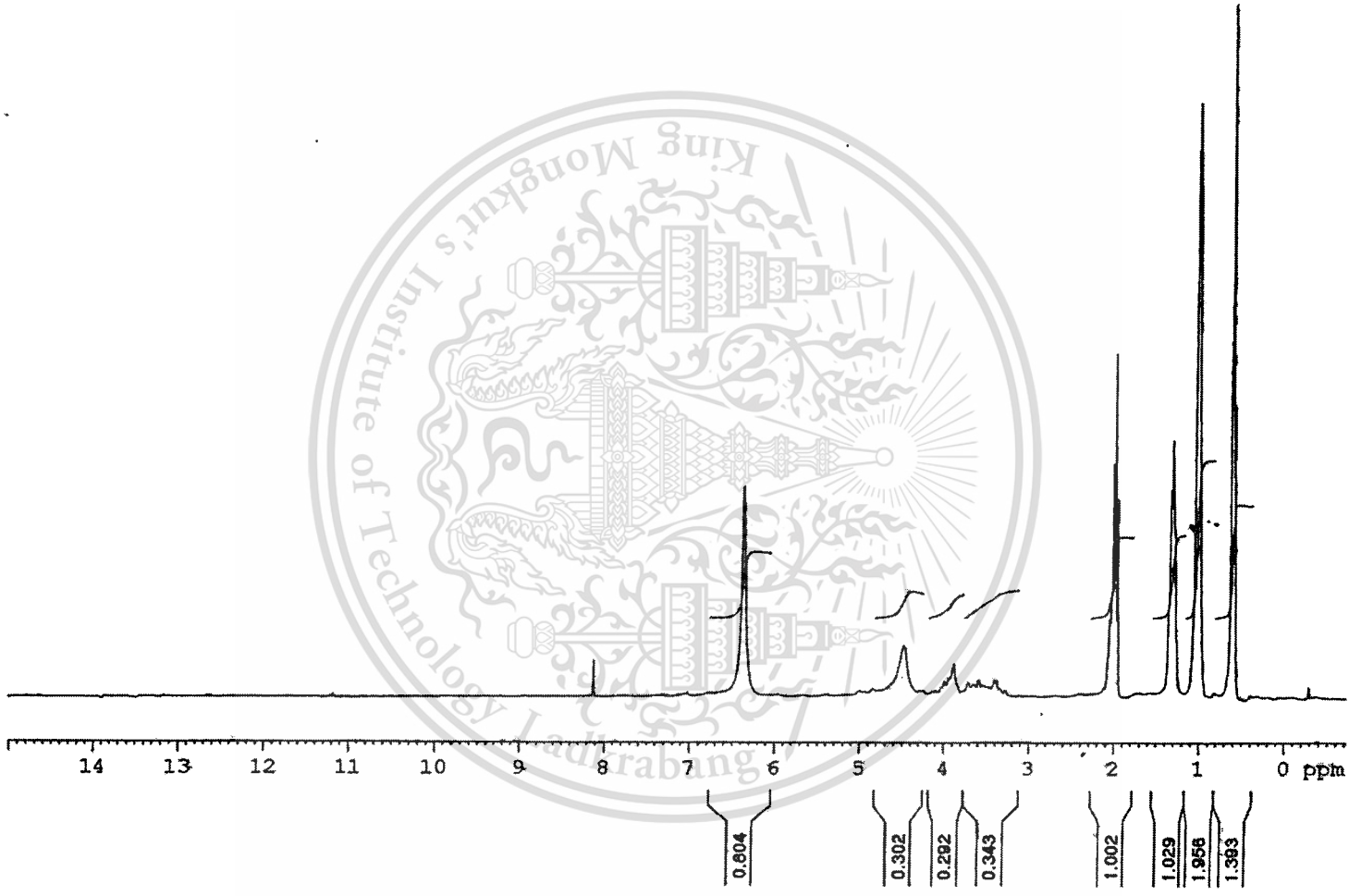

Figure C-8 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:6 ratio by mol of sorbitol to hexanoic acid at 140°C for 5 hours in $CDCl_3$

Figure C-9 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:9 ratio by mol of sorbitol to hexanoic acid at 140°C for 3 hours in $CDCl_3$

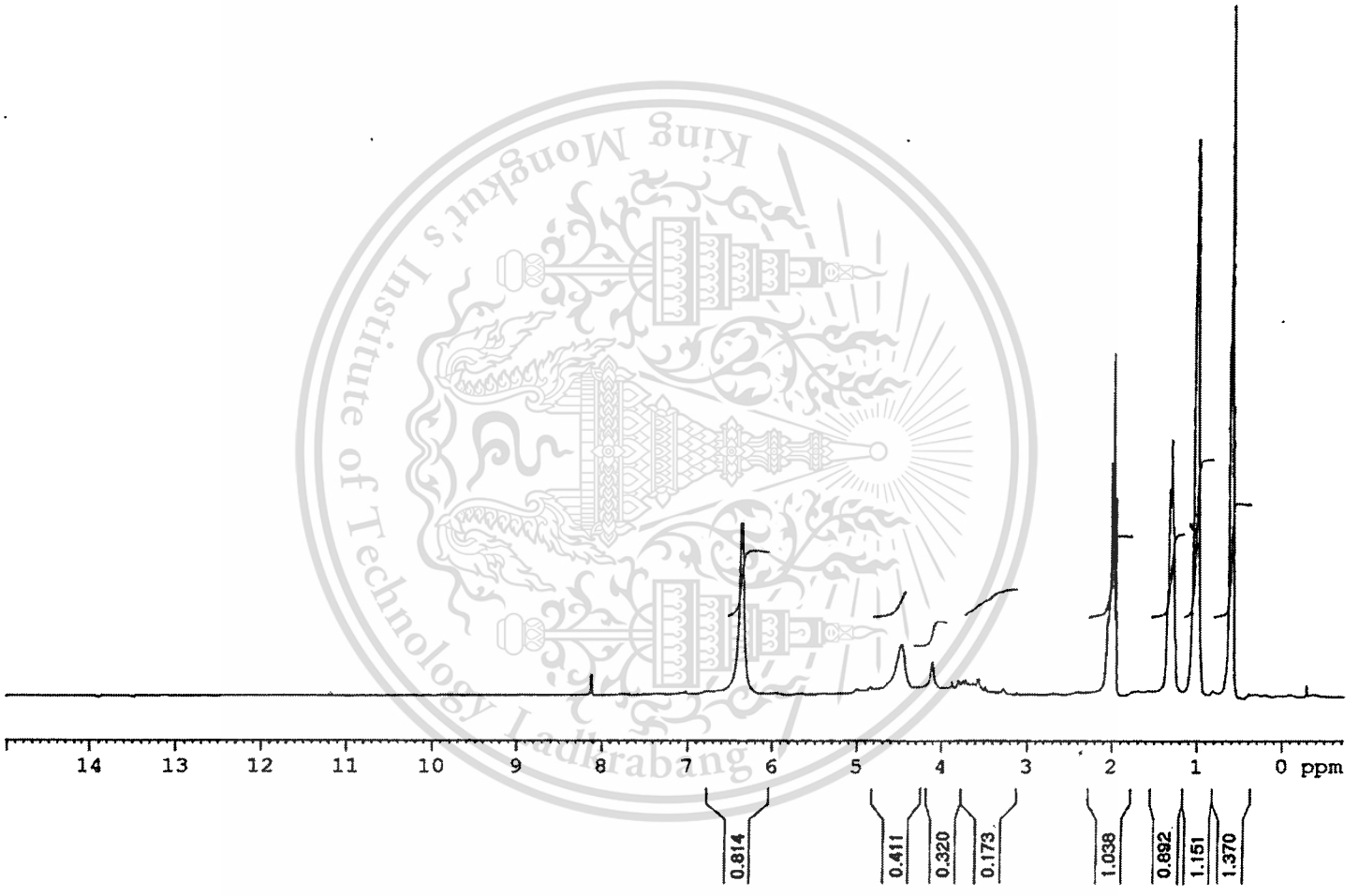

Figure C-10 ^{1}H-NMR spectrum of synthetic ester product from the reaction using 1:9 ratio by mol of sorbitol to hexanoic acid at 140°C for 4hours in $CDCl_3$

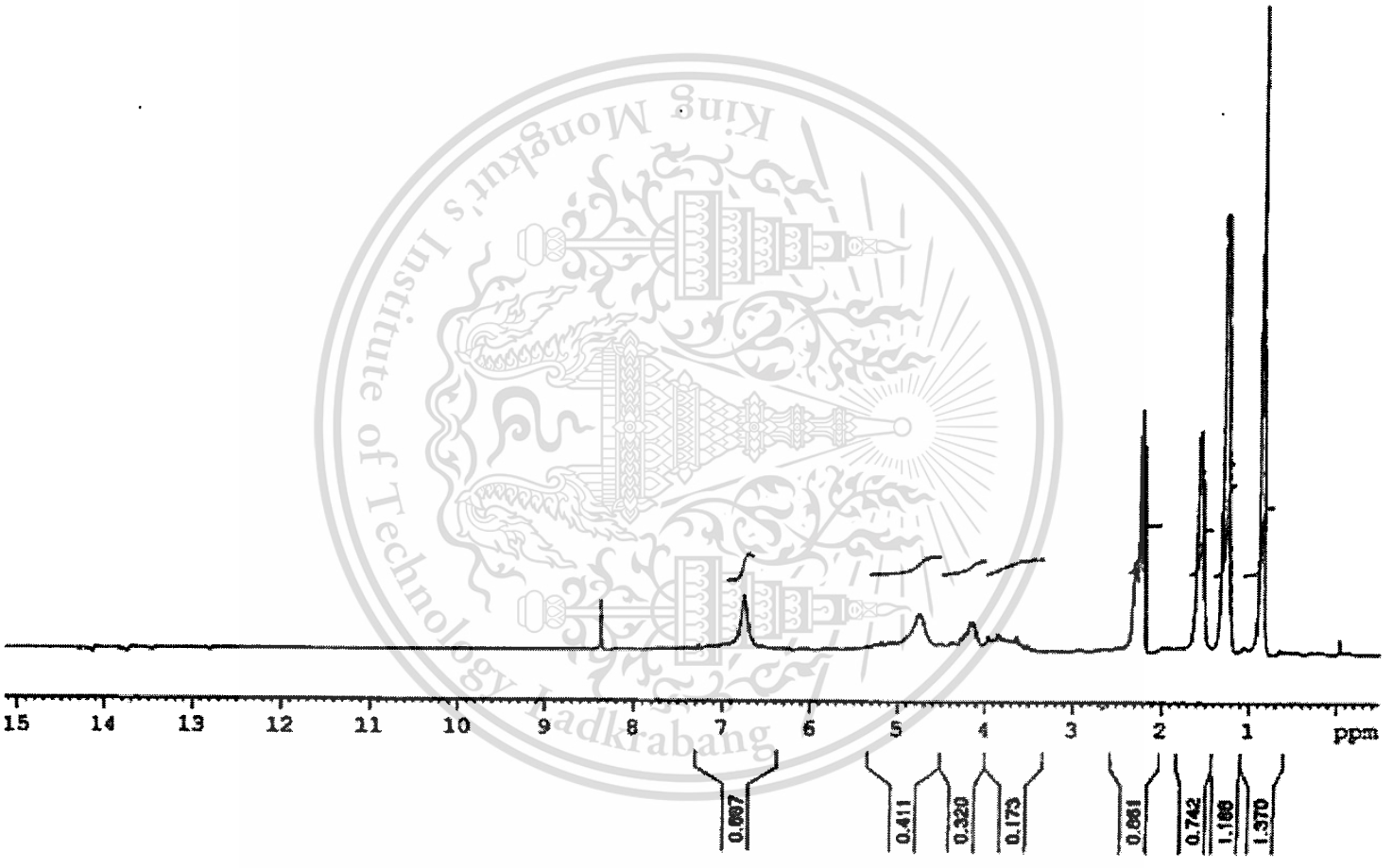

Figure C-11 ^{1}H-NMR spectrum for a larger scale synthesis of synthetic ester product using 1:6 ratio by mol of sorbitol to hexanoic acid at 140°C for 4 hours in $CDCl_3$

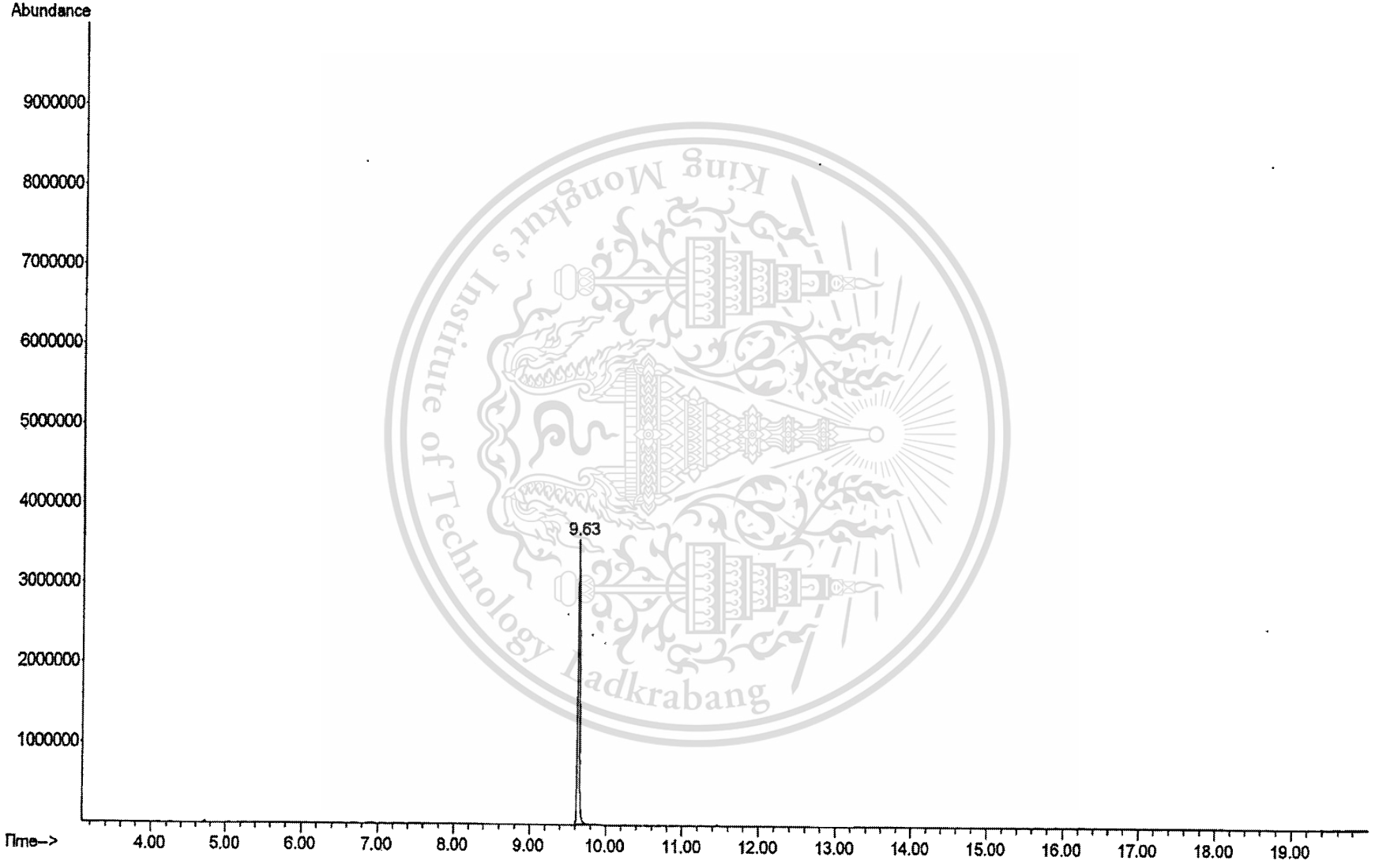

Figure C-12 Gas chromatogram of hexanoic acid

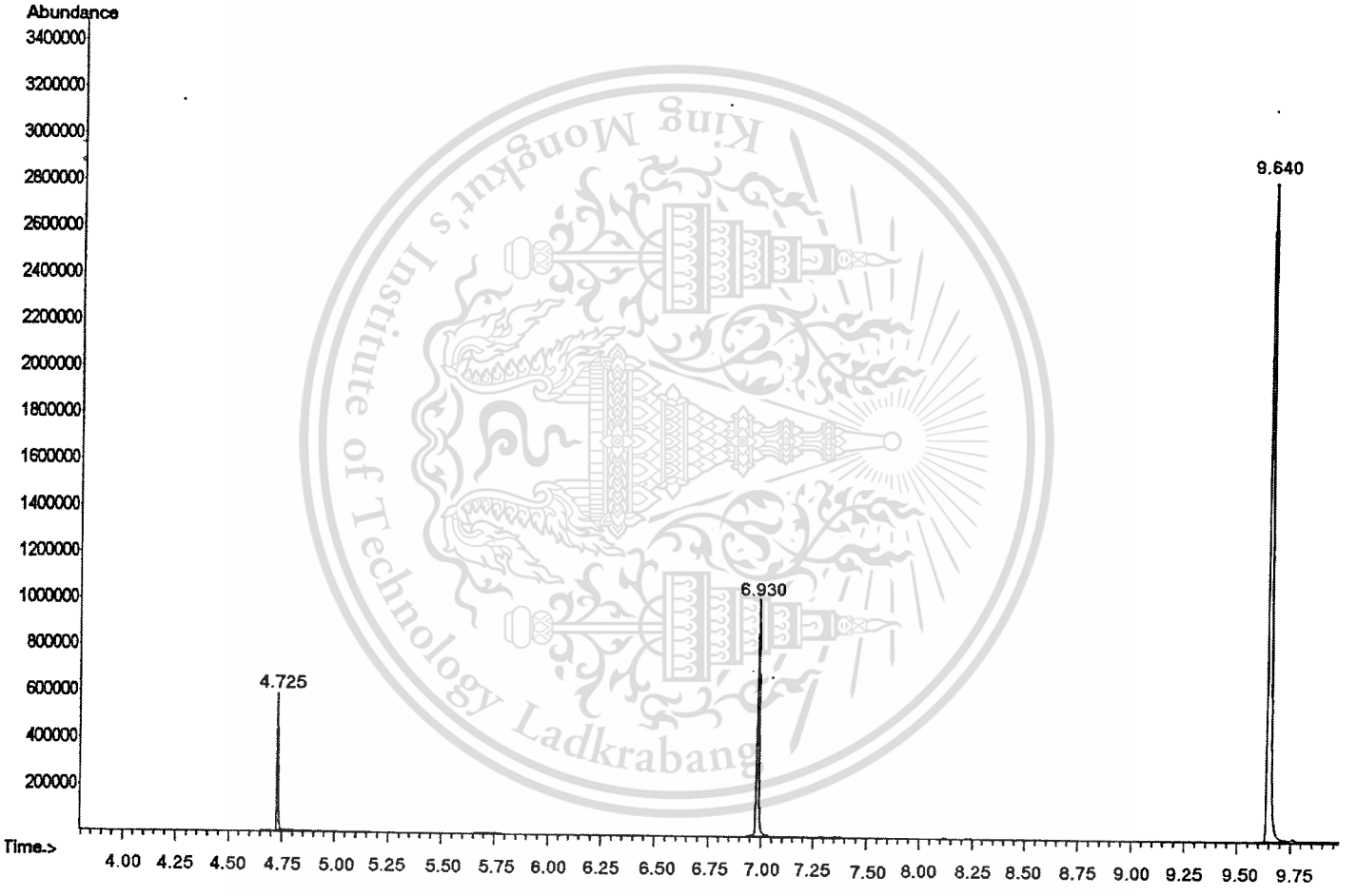

Figure C-13 Gas chromatogram of the synthetic ester product from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours

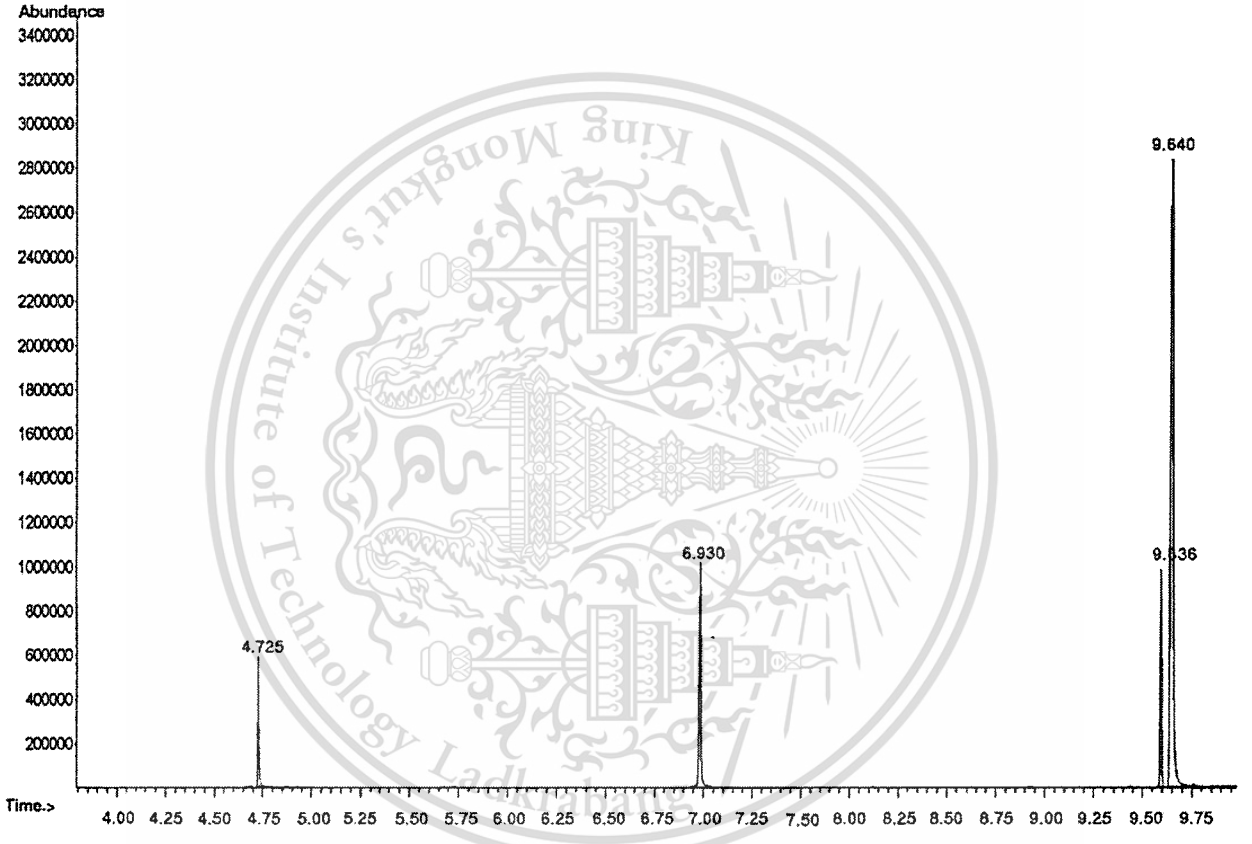

Figure C-14 Gas chromatogram of a mixture between hexanoic acid and synthetic ester product

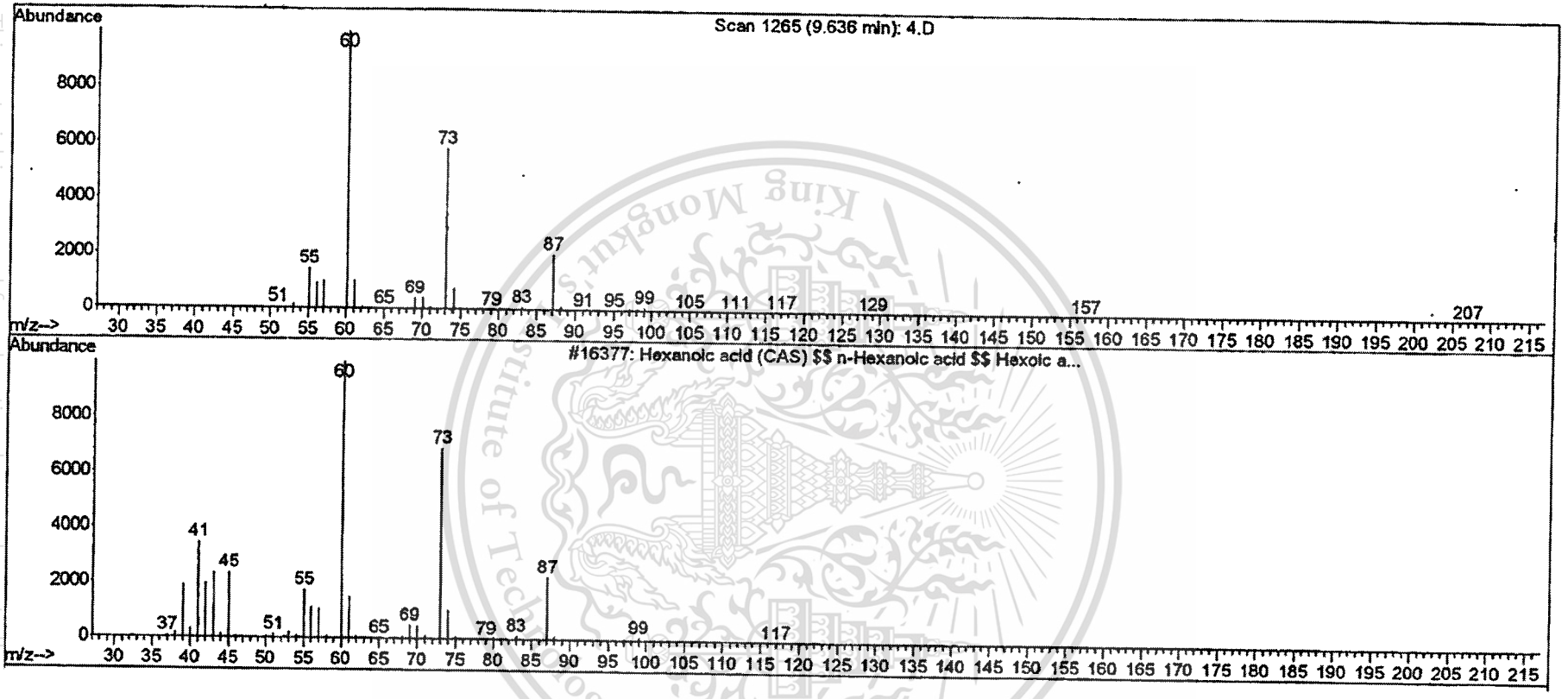

Figure C-15 Mass spectrum of hexanoic acid

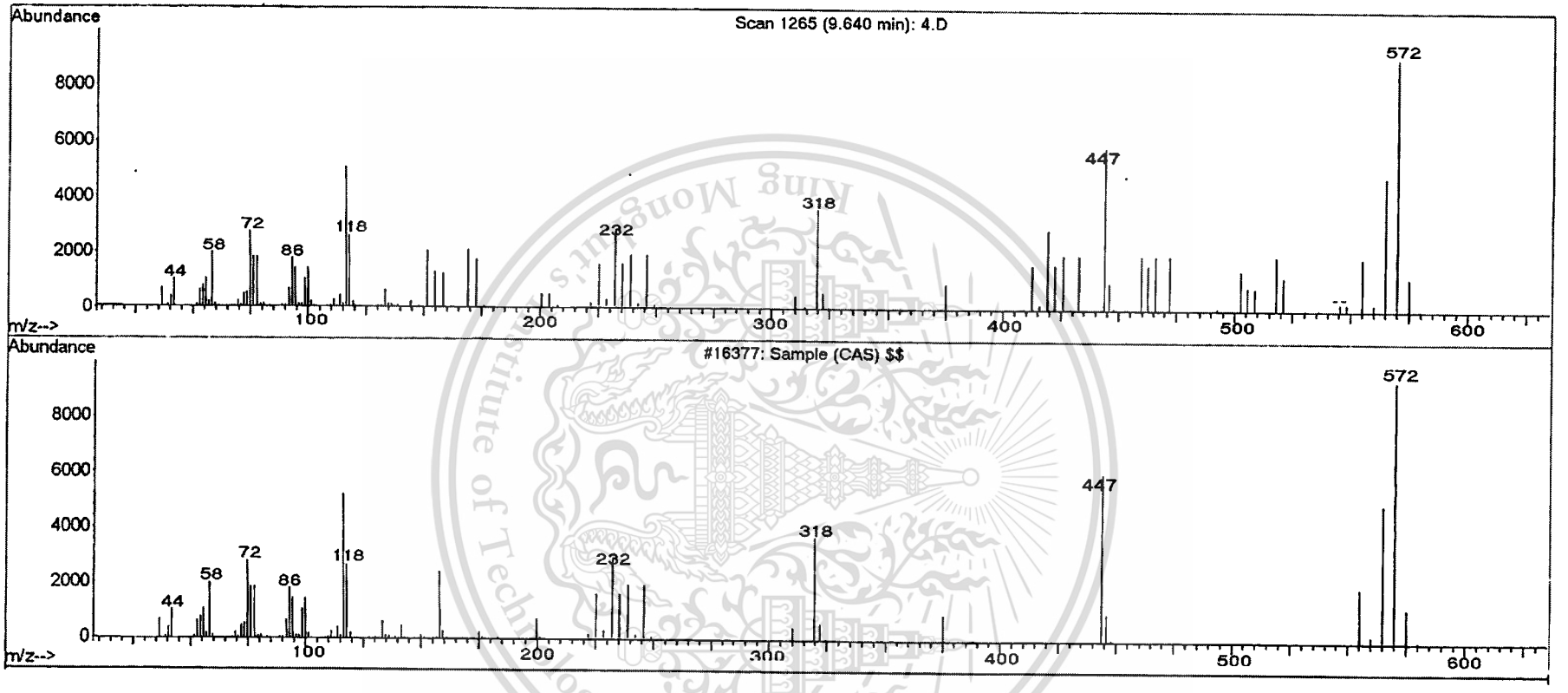

Figure C-16 Mass spectrum of the third composition of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours ; the retention time = 9.640 minutes

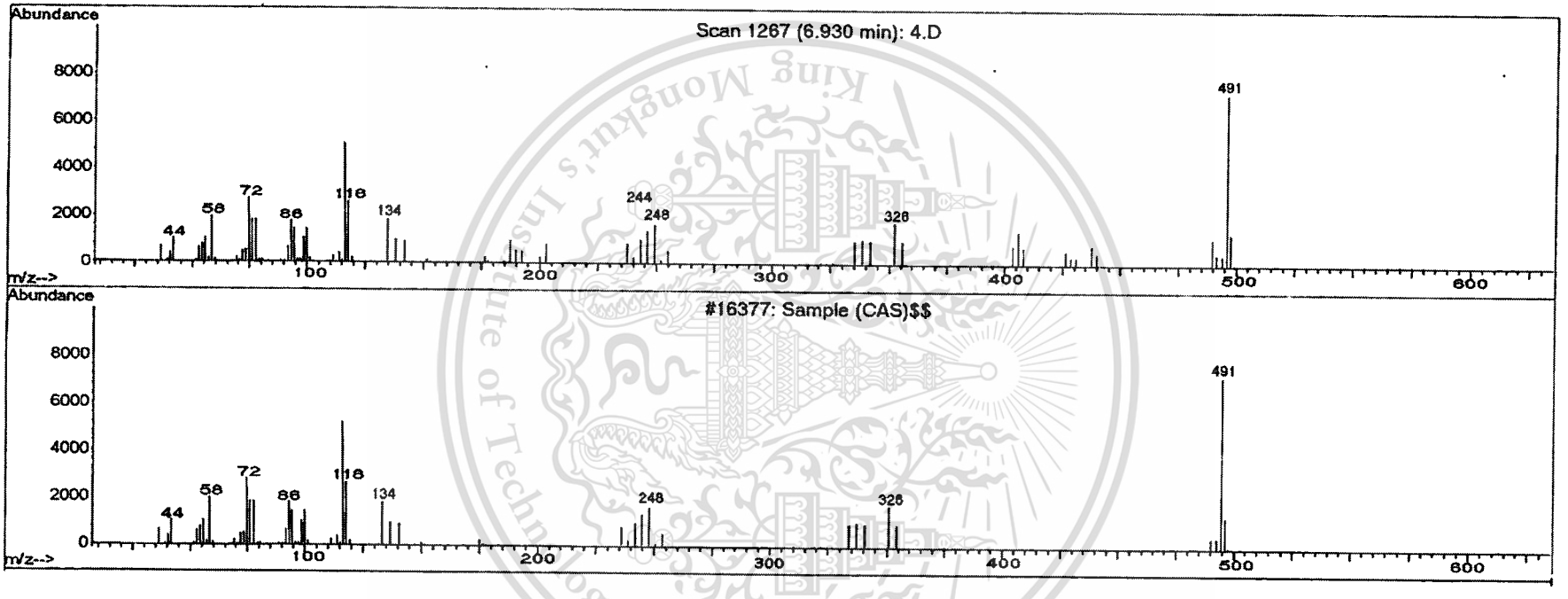

Figure C-17 Mass spectrum of the second composition of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours ; the retention time = 6.930 minutes

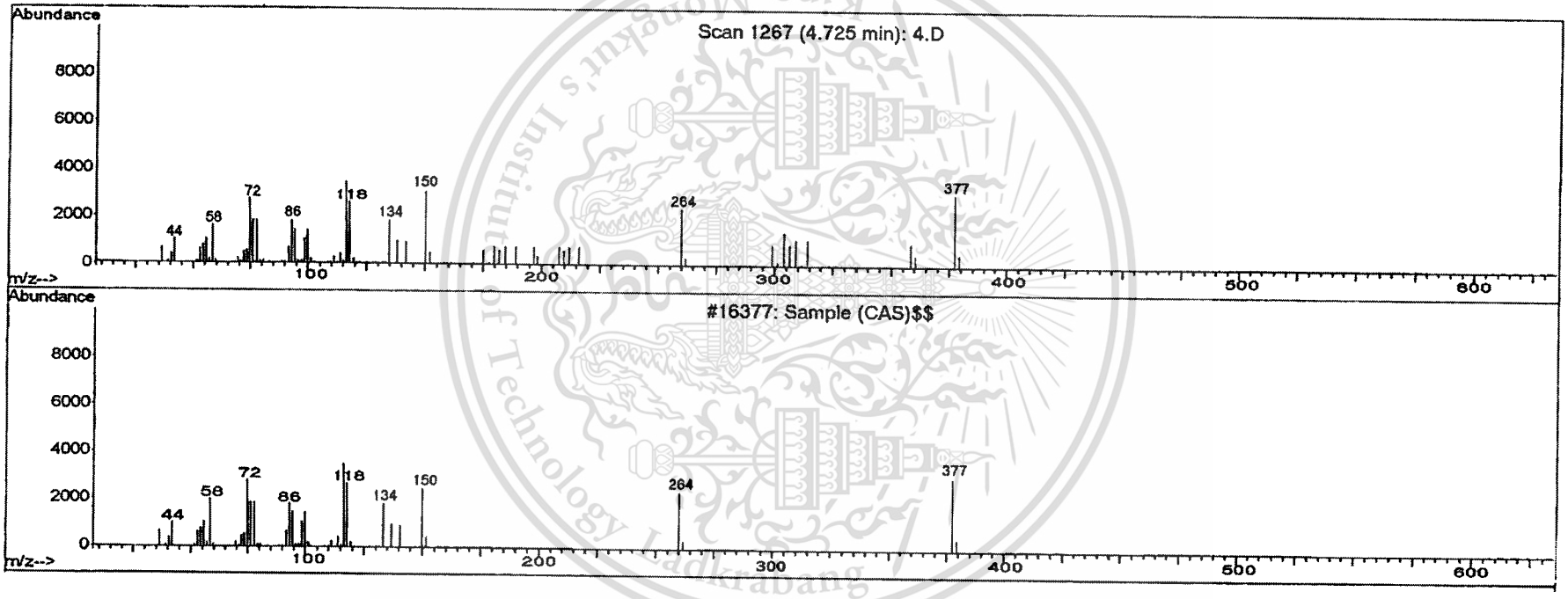

Figure C-18 Mass spectrum of the first composition of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mole at 140°C for 4 hours ; the retention time = 4.725 minutes

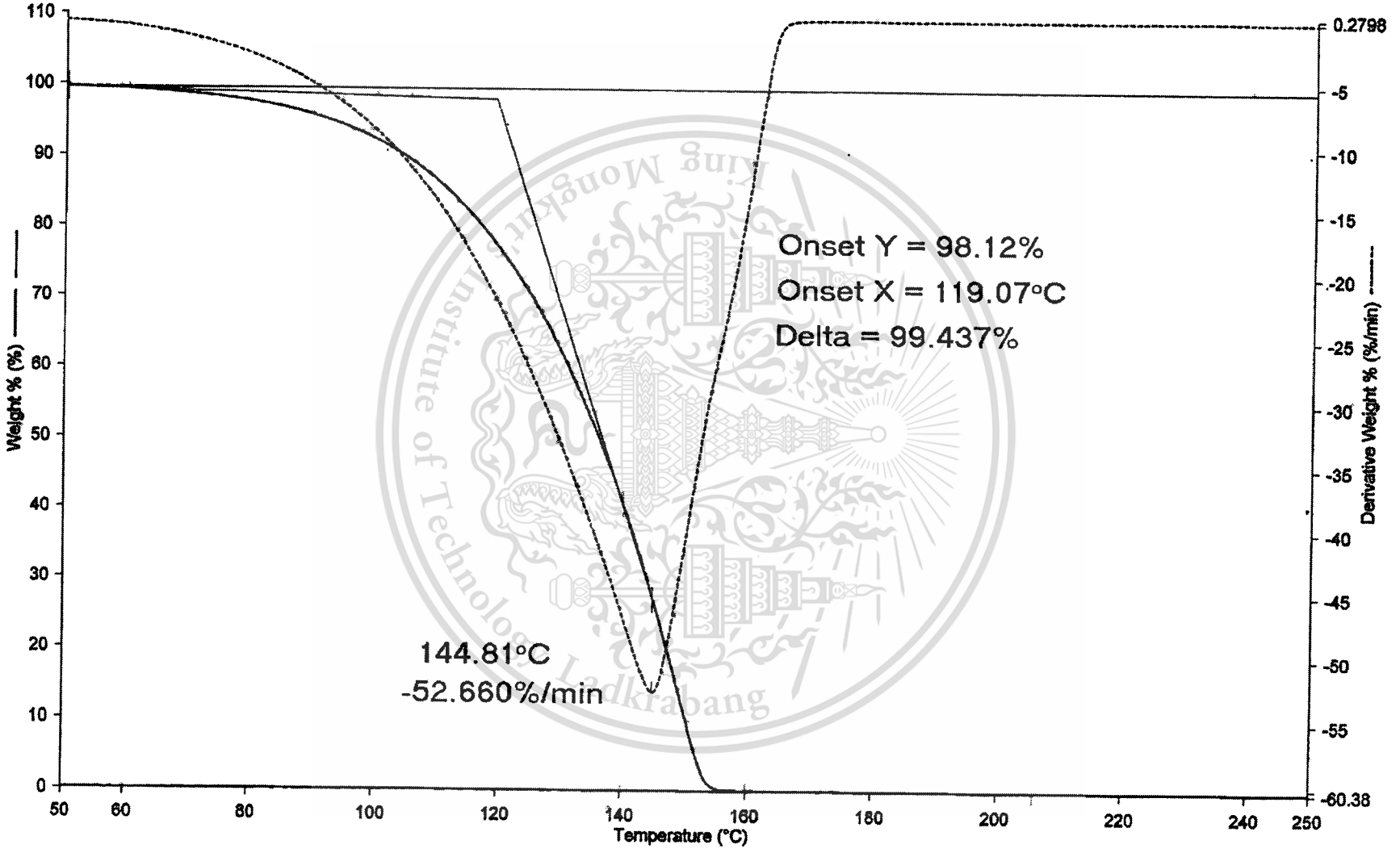

Figure C-19 Thermogram analysis showing percent weight lost of hexanoic acid as a function of temperature

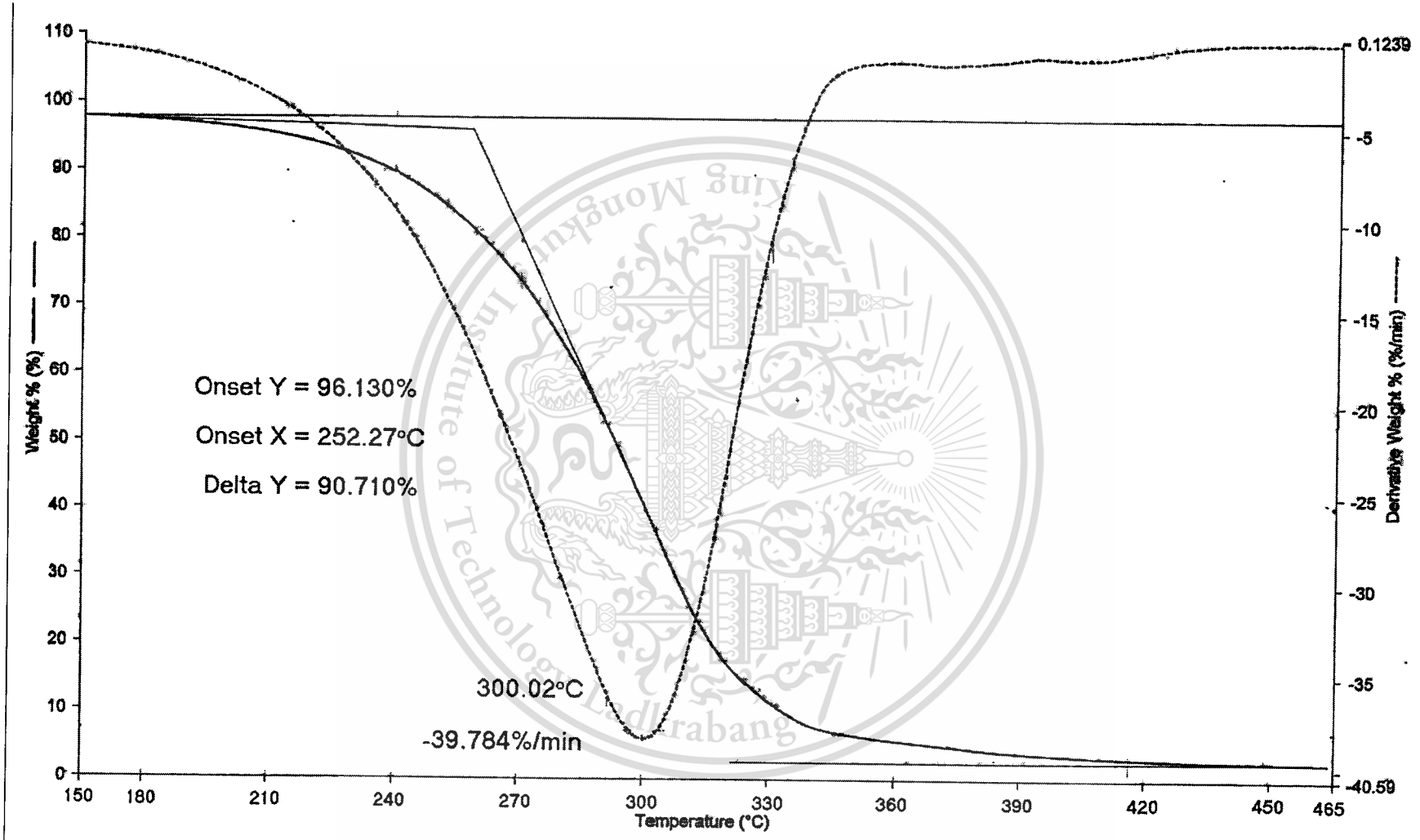

Figure C-20 Thermogram analysis showing percent weight lost of synthetic ester from sorbitol and hexanoic acid using 1:6 ratio by mol at 140 °C for 4 hours as a function of temperature