

**SYNTHESIS AND PROPERTIES OF 9,10-EPOXYSTEARIC ACID
DERIVATIVES WITH VARIOUS ALCOHOLS**

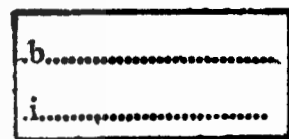


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หัวข้อวิทยานิพนธ์	การสังเคราะห์และสมบัติของอนุพันธ์ของ กรด 9,10-อีพอกซีสเตอริกกับแอลกอฮอล์ต่างชนิด
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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการเปลี่ยนกรดโอเลอิก ซึ่งเป็นตัวแทนของกรดไขมันไม่อิ่มตัวที่มีในน้ำมันพืช เป็นกรด 9,10-อีพอกซีสเตอริก โดยปฏิกิริยาอีพอกซิเดชันด้วยกรดเปอร์อะซิติกเมื่อใช้กรดซัลฟิวริกเป็นตัวเร่งปฏิกิริยา ทำการทดสอบหาสภาวะที่เหมาะสมสำหรับปฏิกิริยาอีพอกซิเดชัน โดยการเปลี่ยนปริมาณไฮโดรเจนเปอร์ออกไซด์ กรดอะซิติก และกรดซัลฟิวริก เวลาและอุณหภูมิในการทำปฏิกิริยา ยิ่งไปกว่านั้นได้มีการเปรียบเทียบวิธีการสังเคราะห์สองแบบ คือ การสังเคราะห์แบบสองขั้นตอน (กรดเปอร์อะซิติกถูกเตรียมขึ้นมาก่อนแล้วจึงทำปฏิกิริยาอีพอกซิเดชัน) และการสังเคราะห์ขั้นตอนเดียว (กรดเปอร์อะซิติกถูกเตรียมขึ้นในระหว่างการทำปฏิกิริยาอีพอกซิเดชัน) พบว่าการสังเคราะห์แบบสองขั้นตอนจะทำให้ได้ร้อยละการเปลี่ยนแปลงของกรดโอเลอิกและร้อยละผลผลิตอีพอกไซด์มากกว่าการสังเคราะห์แบบขั้นตอนเดียว นอกจากนี้ น้ำและกรดอะซิติกในสภาวะที่มีกรดซัลฟิวริกมากจะทำให้เกิดผลิตภัณฑ์พลอยได้เป็นสารประกอบไดออกไซด์และสารประกอบไฮดรอกซี-อะซิโตนซึ่งเกิดจากปฏิกิริยาการเปิดวงอีพอกไซด์ ผลการทดลองแสดงให้เห็นว่าสภาวะที่เหมาะสมในการเตรียมกรดเปอร์อะซิติกคือ ไฮโดรเจนเปอร์ออกไซด์ 0.6 โมล กรดอะซิติก 0.2 โมล กรดซัลฟิวริก 0.007 โมล ที่อุณหภูมิ 50 องศาเซลเซียส เป็นเวลา 4 ชั่วโมง และสภาวะในการทำปฏิกิริยาอีพอกซิเดชันคือ กรดโอเลอิก 0.1 โมล ที่อุณหภูมิ 30 องศาเซลเซียส เป็นเวลา 15 ชั่วโมง จะได้ร้อยละการเปลี่ยนแปลงของกรดโอเลอิกเป็น 76 และได้ร้อยละผลผลิตอีพอกไซด์เป็น 70.64

จากนั้นจึงทำการศึกษาการสังเคราะห์สารอนุพันธ์จากกรด 9,10-อีพอกซีสเตอริก ด้วยปฏิกิริยาการเปิดวงอีพอกไซด์ ควบคู่กับปฏิกิริยาเอสเทอร์ฟิเคชันที่หมู่คาร์บอกซิลด้วยแอลกอฮอล์ ซึ่งได้แก่ นอร์มอล-บิวทานอล ไอโซ-บิวทานอล นอร์มอล-เฮกซานอล นอร์มอล-เดคานอล ไชโคลเฮกซานอล และ เบนซิลแอลกอฮอล์ พบว่าหมู่อีพอกไซด์ของกรด 9,10-อีพอกซีสเตอริกสามารถเปลี่ยนเป็นผลิตภัณฑ์ที่เกิดจากการเปิดวง (Ring-opening product) ได้อย่างสมบูรณ์ในทุกแอลกอฮอล์ อย่างไรก็ตามการเปลี่ยนแปลงของหมู่คาร์บอกซิลิกของกรด 9,10-อีพอกซีสเตอริกไป

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เป็นผลิตภัณฑ์ที่เกิดจากปฏิกิริยาเอสเทอร์ฟิเคชัน (Esterified-product) ขึ้นอยู่กับชนิดของ แอลกอฮอล์ โดยสมบัติของสารอนุพันธ์สังเคราะห์ที่เตรียมได้ในงานวิจัยนี้เป็นดังนี้ ความหนืดที่ 40 องศาเซลเซียสมีค่าในช่วง 31.1 – 119.1 เซนติสโตก, ความหนืดที่ 100 องศาเซลเซียสมีค่าในช่วง 4.8 – 14.6 เซนติสโตก, ดัชนีความหนืดมีค่าในช่วง 113 – 172, จุดไหลเทมีค่าในช่วง -18 – -39 องศาเซลเซียส, ค่าความเป็นกรดมีค่าในช่วง 1.03 – 3.56 มิลลิกรัมของโพแทสเซียมไฮดรอกไซด์ต่อกรัม, ค่าการทนความร้อนมีค่าในช่วง 205 – 295 องศาเซลเซียส, ค่าการทนต่อปฏิกิริยาออกซิเดชันมีค่าในช่วง 200 – 287 องศาเซลเซียส โดยขึ้นกับลักษณะโครงสร้างและความยาวของสายโซ่ แอลกอฮอล์ นอกจากนี้ยังพบว่าผลิตภัณฑ์ที่ได้จากการ ปรับปรุงสมบัติทางกายภาพ และสมบัติการ ทนความร้อนและปฏิกิริยาออกซิเดชันของกรดโอเลอิกด้วยวิธีที่ใช้ในงานวิจัยนี้ มีสมบัติทาง ประการที่ดีกว่า และน่าจะสามารปรับใช้ร่วมกันได้กับน้ำมันหล่อลื่นพื้นฐานที่ใช้ในอุตสาหกรรม



Thesis Title	Synthesis and properties of 9,10-epoxystearic acid derivatives with various alcohols
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ABSTRACT

This thesis aims to study the conversion of oleic acid, the model compound representing unsaturated fatty acids in vegetable oils, to 9,10-epoxystearic acid via epoxidation with peracetic acid using sulfuric acid as catalyst. The suitable epoxidation condition was investigated by the variation of hydrogen peroxide, acetic acid and sulfuric acid content, reaction time, and reaction temperature. Moreover, two synthetic procedures, namely two-step synthesis (a generation of peracetic acid prior to epoxidation) and single-step synthesis (a generation of peracetic acid during epoxidation) were compared. It was found that the two-step synthesis provided a relatively higher conversion of oleic acid and higher yield of epoxidised product, as compared to the single-step synthesis. In addition, water and acetic acid in the presence of high H_2SO_4 content produced the by-products, namely diol and hydroxy-acetoxy compounds, from the ring-opening of epoxidised product. Experimental results showed that 76 % conversion of oleic acid and 70.64 % yield of epoxidised product were obtained by using 0.6 mol of hydrogen peroxide, 0.2 mol of acetic acid, 0.1 mol of oleic acid and 0.007 mol of H_2SO_4 . The optimised reaction temperature for peracetic acid preparation and for epoxidation were 50 °C and 30 °C whereas the optimised reaction time for peracetic acid preparation and for epoxidation were 4 and 15 hours, respectively.

The 9,10-epoxystearic acid derivatives were consecutively prepared by an acid-catalysed ring-opening reaction of the epoxide ring followed by esterification of the carboxyl group using different type of alcohols, namely *n*-butanol, isobutanol, *n*-hexanol, *n*-decanol, cyclohexanol, and benzyl alcohol. A 100 % conversion of oxirane ring of 9,10-epoxystearic acid can completely convert to ring opening products using each alcohol. However, the conversion of carboxylic group of 9,10-epoxystearic acid forming esterified-product depends largely on the type of

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alcohols. The properties of these derivatives were as follows: viscosity@40 °C, 32.1 – 119.1 cSt; viscosity@100 °C, 4.8 – 14.6 cSt; viscosity index (VI), 113 – 172; pour point, -18 – -39 °C, total acid number (TAN), 1.03 – 3.56 mgKOH/g; onset temperature under N₂, 205 – 295 °C; onset temperature under O₂, 200 – 287 °C. The differences in properties were due to the structure and chain-length of alcohols. Moreover, it was found that such chemically modified epoxidised oleic acid showed some properties to be superior to those of lubricating base oils used in industry, or at least could be used in the blends.



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Titiporn Wattanakul

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CHAPTER 1

INTRODUCTION

1.1 Statement and significance of the problems

Animal and vegetable oils were historically used as lubricants in general transportation or machinery to reduce friction and wear. However, these lubricants are not adequate for our industrialised society, either in volume or in desirable properties.

Typically, the most favorable lubricating base oil are mineral base oils from petroleum because of the high quality, good stability, and low price, comparing with animal and vegetable oils. However, the reservoirs of petroleum oil are limited and may be exhausted by the end of the next century. Recently, animal and vegetable oils have alternatively regained more interest because of its environmental benefits and the fact that it is made from renewable resources. In general, vegetable oils are non-toxic and possess excellent properties, such as high viscosity index, high flash point, low evaporative loss and high biodegradability. However, two major problems with vegetable oils as base lubricants are low resistance to thermal stability and poor low-temperature properties. This is due to the existence of unsaturated C=C bonds in vegetable oil which is also responsible for their poor oxidative stability [1].

Chemical modification of vegetable oil is an attractive way to solve these problems. Transforming alkene groups in a vegetable oil to other stable functional groups could improve the oxidative stability, whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve low-temperature performance [2]. Epoxidised vegetable oil is a promising intermediate for this purpose, since the epoxy group is readily functionalised. Due to the high reactivity of the epoxy group, oxirane ring can also act as raw materials for synthesis of a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds, and polymers like polyesters, polyurethanes and epoxy resin [3].

The production of lubricants from agro-products is one of the alternative ways of fostering the development of petrochemicals for the agricultural countries. Palm oil production is one of the important agro-industries in Thailand with major contribution to the country's development during the past 20 years. It is used in many applications, such as in the manufacture of frying/cooking oils, margarine, fuel, soap and grease [4]. Therefore, refined palm oil will be used as a starting material for production of lubricants in this work. Furthermore, naturally

occurring palm oil are mixtures of fats, particularly of unsaturated oleic acid. Hence, the production of lubricant from oleic acid was chosen as a model reaction representing unsaturated fatty acids in palm oil. This unsaturation restricts their use as a good lubricant. Epoxidation has been received special attention to improve their oxidative stability because it opened up a wide range of feasible reactions that can be carried out under moderate reaction conditions due to the high reactivity of the oxirane ring [5].

Standard industrial production for epoxidation of unsaturated compounds is based on peracid which is generated by reacting acetic or formic acid with hydrogen peroxide in the presence of strong mineral acids such as sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) [6]. The strong mineral acid leads to many side reactions, such as oxirane ring-opening to diols, hydroxyesters, estolides and other dimers formation. Furthermore, they cause equipment corrosion and must be neutralised and also removed from the end product [7]. Therefore, this research will attempt to report an alternative process using a milder reaction condition which leads to the formation of stable peracid, high product selectivity and high conversion. An optimised but small amount of sulfuric acid is, however, used to catalyse the peracid formation.

As previously mentioned, the preparation of lubricant-based stock from epoxidised vegetable oil involves two steps, ring-opening reaction via alcoholysis followed by esterification of the resulting carboxyl group through alcoholysis [7]. Moreover, several attempts reported that the product obtained by ring-opening reaction of epoxidised fatty acid ester followed by transesterification of the resulting ester group shows good performance for lower temperature lubricant applications. Due to the above reasons, this thesis is aimed to study the conversion of oleic acid, the model compound representing major unsaturated fatty acids in palm oil and also other vegetable oils. Epoxidation of oleic acid with peracetic acid can provide a 9,10-epoxystearic acid using sulfuric acid as catalyst. The synthetic lubricant will be consecutively prepared from 9,10-epoxystearic acid by an acid-catalysed ring-opening reaction followed by esterification. It is proposed that the modification by various type of alcohols would be affected on the physical and chemical properties of synthetic lubricants (i.e. viscosity, viscosity index, total acid number, pour point and thermal/oxidation stability). An interesting result will be obtained by varying the type of alcohol, namely straight-chain alcohol (i.e. *n*-butanol, *n*-hexanol, *n*-decanol), branched-chain alcohol (isobutanol), cyclic-alcohol (cyclohexanol), aromatic alcohol (i.e. benzyl alcohol). Therefore, an attempt will be made to compare the properties among the ring-opening product

and their esterification products. The conversion of oleic acid and yield of 9,10-epoxystearic acid and the yield towards its derivatives would be determined.

1.2 Goal and objectives

The specific objectives of the study are as follows:

- 1.2.1 To synthesise a 9,10-epoxystearic acid from oleic acid by epoxidation reaction with peracetic acid using sulfuric acid as catalyst.
- 1.2.2 To obtain lubricants from the ring-opening and esterification of 9,10-epoxystearic acid by the use of different type of alcohols.
- 1.2.3 To study the effect of reaction parameters on the epoxidation.
- 1.2.4 To study the physical and chemical properties of the synthetic lubricants.

1.3 Scope of the study

- 1.3.1 Synthesis of an epoxidised oleic acid, 9,10-epoxystearic acid, from a single step (generation of peracetic acid during epoxidation) and a two-step (generation of peracetic acid prior to epoxidation) synthesis using sulfuric acid as catalyst.
- 1.3.2 Characterisation of 9,10-epoxystearic acid using ^1H nuclear magnetic resonance spectroscopy (^1H NMR).
- 1.3.3 Investigation of the variables that affect the percent yield towards an epoxidised oleic acid, including :
 - 1.3.3.1 Preparation time of peracetic acid; 2, 4, 6 hours.
 - 1.3.3.2 Reaction time of epoxidation; 10, 15 and 20 hours.
 - 1.3.3.3 Ratio of hydrogen peroxide/oleic acid; 3.5:1, 4:1, 4.5:1, 6:1 and 7:1.
 - 1.3.3.4 Ratio of acetic acid/oleic acid; 2:1, 3:1, 4:1.
 - 1.3.3.5 The amount of catalysts; 0.002, 0.007, 0.013 mol.
- 1.3.4 Synthesis of the ring-opening and esterified products from 9,10-epoxystearic acid using *n*-butanol, isobutanol, *n*-hexanol, *n*-decanol, cyclohexanol, benzyl alcohol under optimised condition.
- 1.3.5 Characterisation of the ring-opening and esterified products using Gas chromatography-mass spectrometry (GC-MS)

- 1.3.6 Comparison of the percent conversion and product distribution towards the desired products obtained from different alcohol using Gas Chromatography technique.
- 1.3.7 Determination of the physical and chemical properties of the synthetic product such as viscosity @ 40 °C, viscosity @ 100 °C, viscosity index, pour point, total acid number and thermal and oxidation stability.

1.4 Expected results

- 1.4.1 A suitable synthetic condition to produce 9,10-epoxystearic acid and its ring-opening and esterified products.
- 1.4.2 A synthetic lubricant from modified oleic acid with good quality.



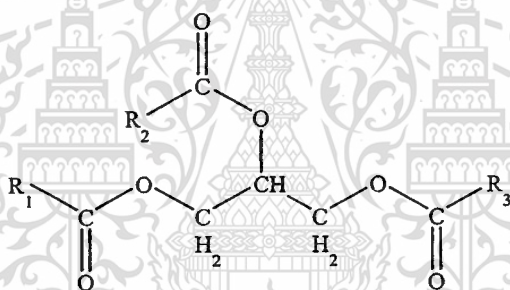
CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Vegetable oil [8,9]

Chemically, the word “fat” is coming to be used to cover vegetable oils and fats whether they are in the solid or liquid state, though in normal parlance the word “oil” is applied to a fat when it is in the liquid state.

Fat have been defined as the esters of fatty acids with the trihydric alcohol glycerol, and there must be distinguished from other simple liquids like the waxes which are esters of fatty acids with high molecular weight straight chain alcohols. The triglyceride fats which predominate in plant and animal fat have the following general formula:

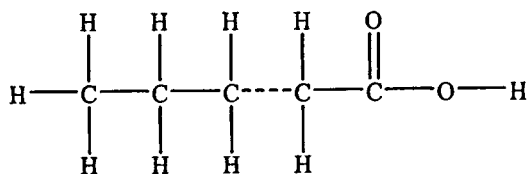


R₁, R₂ and R₃ represent the hydrocarbon chains of fatty acid. Fatty acid may also combine with glycerol to form mono- or di-glyceride when only one or two of the hydroxyl groups of the glycerol will be in fatty acid combination, but these occur naturally only in fats which have become partly hydrolysed. When more than one fatty acid radical is involved, as in tri- or diglycerides, these may be alike or different. There are many different naturally occurring fatty acids, there will therefore be a multiplicity of fats from them.

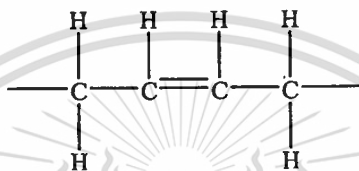
Naturally occurring vegetable fats are mixtures of fats, and their characters are taken largely from the fatty acid which predominate in them and from the arrangement of these fatty acids in the triglycerides. The fatty acids are hydrocarbon chains in which two hydrogen atoms are attached to all or the majority of carbon atoms within the chain. The carbon atom at one end of the chain has three hydrogen atoms attached to it and the one at the other end is attached to a carbonyl groups to give the general structure, as shown below:

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Fatty acids of this general formula are saturated fatty acids as they have the full number of hydrogen atoms attached to the carbon atom of the chain. In unsaturated fatty acids there are one, two or three double bonds between carbon atoms which then have only single hydrogen atoms attached to them, in the following manner:



Double bonds can occupy different position in the chain, thus giving rise to different isomer. Furthermore, there are also geometric isomers (the *cis*- or the *trans*- form) according to whether positions of a molecule joined by a double bond extended in the same or opposite direction.

2.1.1 The composition of vegetable oil

Although vegetable oil has a high proportion of the saturated palmitic acid it also contains a high quantity of unsaturated fats, principally those derived from oleic acid. About three-quarters of the glycerides are mixed saturated and unsaturated triglycerides. The oil melts over a range of temperature from 25-50 °C. The percentage composition of the mixed fatty acids in vegetable oil is shown in Table 2.1

Table 2.1 The composition of the mixed fatty acids in vegetable oil [8]

Fatty acid		Percentage
Name	Chemical structure	
<i>Saturated fatty acid</i>		
Myristic (C12)	CH ₃ (CH ₂) ₁₂ COOH	1.09
Palmitic (C16)	CH ₃ (CH ₂) ₁₄ COOH	35.09
Stearic (C18)	CH ₃ (CH ₂) ₁₆ COOH	5.42
<i>Unsaturated fatty acid</i>		
Oleic (C18:1)	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	46.13
Linoleic (C18:2)	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH	12.27
Linolenic (C18:3)	CH ₃ [CH ₂ CH=CH] ₃ (CH ₂) ₇ COOH	trace

Vegetable oil varies in color from orange-yellow to deep orange according to the color of the original fruit [8]. The color of the oil is due to a mixture of carotene and xanthophyll in the proportion of three parts of carotene to one part of xanthophyll. The color of the oil is not permanent, a bleaching effect taking place on standing for a long period, especially if the oil is exposed to light.

2.2 Lubricating Oils [10,11]

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

A lubricant is used to reduce the coefficient of friction between the rubbing surfaces in machinery, thereby reducing frictional energy losses. Most lubricating oils are derived from petroleum; however, some synthetic lubricants are also important in use. Essential properties of the lubricating oil are viscosity, viscosity-temperature relation, viscosity-pressure relation, and oiliness.

2.2.1 Basic functions [10-12]

2.2.1.1 The reduction of friction

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

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

2.2.1.2 Heat removal

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

2.2.1.3 Containment of contaminants

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

2.2.2 Lubricating base oil composition [13-16]

Materials suitable for the production of lubricating oils are comprised principally of hydrocarbon containing from 25 to 35 or even to 40 carbon atoms per molecule.

The molecule in the lubricating base oil fraction consists essentially of one long carbon atom chain to one or both ends of which a ring system or short branch may be attached. Monocycloalkanes and monoaromatics usually have several short (e.g. methyl) branches on the

ring. Most of the compounds are paraffin-naphthenes with cycloparaffinic ring attached to paraffinic chain.

Aromatic compounds usually have cycloparaffinic ring attached to them along with long paraffinic chain. Polyaromatics usually have all their ring in the single condensed nucleus which also might have short branch attached. Polycyclic saturates may have all the rings in a single condensed system or two or more ring system may be separated by alkyl chains. Aromatic compounds may also be in the form of biphenyls and their derivatives. Thus, the lubricating oils are made mainly of three general types:

- Straight and branched chain paraffinic compounds.
- Polycyclic and fused-ring saturated hydrocarbons based on cyclopentane prototype ring structures, collectively known as naphthenes.
- Aromatics, both mono and polynuclear, which are unsaturated ring structure.

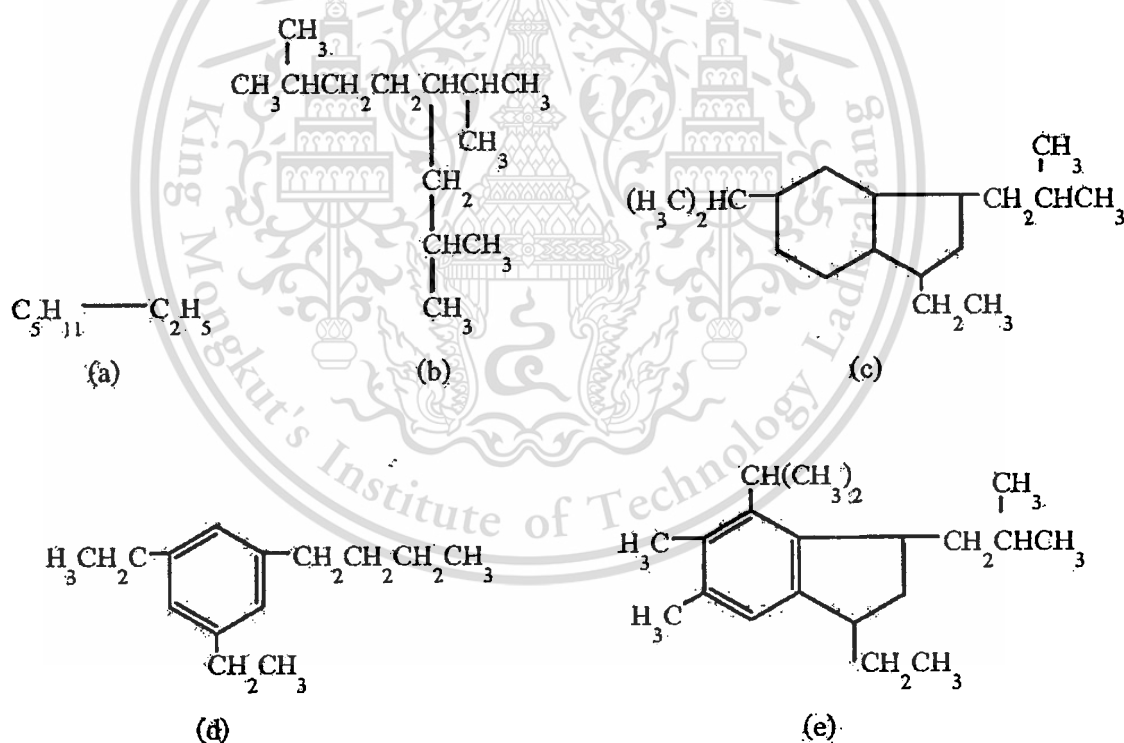


Figure 2.1 Typical structures in lube oil (a) *n*-paraffin, (b) *i*-paraffin, (c) cycloparaffin, (d) aromatic hydrocarbon, (e) mixed aliphatic and aromatic ring [16]

2.2.3 Properties and test of lubricating base oil [12,17-19]

Some of the most commonly tests for physical and chemical properties of lubricating oil are outlined in the following section, with brief explanations on significance of the test from the standard point of the refiner and consumer.

2.2.3.1 Physical properties

1) Viscosity

Viscosity is the most significant property of a lubricating oil to meet a particular application, viscosity is generally the most important for controlling the properties in manufacture and selection.

Viscosity is an index for measuring the internal resistance to the motion of the fluid by reason of the cohesion forces between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extend of the viscosity change depends upon the crude oil source and molecular weight of the constituent component.

Kinematics viscosity is the most common and measured by timing the flow rate of the fixed amount of oil through a capacity tube under gravitational force at the standard temperature (at 40 °C and 100 °C).

2) Viscosity Index

The viscosity index (VI) is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increases, all lubricating oils thin out or have lower viscosity. Likewise, oils become thicker or more viscous at the reduced temperature.

3) Pour Point

Most oils contain some dissolved wax and, as oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test. The pour point is the lowest temperature at which the oil will just flow under specified test condition and is roughly equivalent to the tendency of an oil to stop flowing from a gravity-fed system or container. The importance of the pour point is limited to applications where low temperatures are likely to influence oil flow.

4) Flash Point

The flash points test gives an indication of the presence of volatile components in the oil, and it is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a mixture which will be ignited in the presence of an open flame.

5) Color

The color of lubricating oil is measured in a standardised glass container by comparing the color of the transmitted light with that transmitted by the series of numbered glass standards. Color variation in lubricating oil is resulted from the difference in crude oils, viscosity, method and degree of treatment during refining. The test is used for manufacturing control purpose and is important since the color is readily observed by the customer.

2.2.3.2 Chemical properties [19-20]

1) Oxidation stability

The most important chemical aspect of lubricant is the degree to which atmospheric oxygen can react with lubricants under various operating conditions, since the degradation of lubricants by oxidation can lead to the development of corrosive organic acids and insoluble resinous matters, and a marked increase in viscosity of the lubricant, all of which seriously impaired the efficiency of the lubricant. Oxidative decomposition normally occurs in two stages. The first stage produces alkyl radicals which react with oxygen to give peroxides or hydroperoxides. The latter species are unstable at high temperatures and give rise to ketones, aldehydes, acid and alcohols. The limiting step is the primary oxidation reaction, while the second stage is a polymerisation .

2.3 Synthetic lubricating oils [21]

For more than 50 years synthetic fluids have been used as lubricants for a variety of specialised application. In the early 1930s, synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and the US.

2.3.1 Characteristics of synthetic lubricants

ASTM has developed a classification system for synthetic base fluids as follows:

2.3.1.1 Synthetic hydrocarbons :

- Alkylated aromatics
- Olefin oligomers
- Cycloaliphatics

2.3.1.2 Organic esters :

- Dibasic acid esters
- Polyol esters
- Poly esters

2.3.1.3 Others :

- Halogenate hydrocarbons
- Polyglycols
- Phosphate esters
- Polyphenyl ethers
- Silicate ethers
- Silicones

Many compounds have been investigated as possible base stocks for synthetic lubricants.

Gungerson and Hart (1962) identified over 25, of which seven types are major importance:

- polyalphaolefins
- alkylated aromatics
- polybutenes
- aliphatics diesters
- polyolesters
- polyalkyleneglycols
- phosphate esters

Table 2.3 Performance of Synthetic Lubricants Compared to Mineral Oil [17]

Properties	Mineral	Polyalpha-olefin	Dialkylated Benzene	Dibasic Acid Ester	Polyol Ester	Poly glycol	Phosphate Ester	Silicone Fluid
Viscosity Index	Fair	Good	Fair	Good	Good	Very good	Poor	Excellent
Low temperature	0 to -25 °F	-50 to -80°F	50 to -80°F	-40 to -60 °F	-30 to -60°F	-20 to -60 °F	0 to -50 °F	-100 °F, very low
High temperature	250-350 °F	-50 to -80°F	375-500 °F	375-550 °F	425-625 °F	400-500 °F	325-400 °F	Over 500 °F
Oxidation stability	Fair	Good	Good	Good	Excellent	Good	Fair	Good
Volatility	Fair	Excellent	Good	Excellent	Excellent	Good	Fairy good	Good
Hydrolytic stability	Excellent	Excellent	Excellent	Fair	Fair	Good	Fair	Good
Additive response	Excellent	Good	Excellent	Very good	Very good	Fair	Good	Poor
Compatibility with mineral oil	Excellent	Excellent	Excellent	Good	Fair	Poor	Poor	Poor
Compatibility with most paints & finishes	Excellent	Excellent	Excellent	Poor	Poor	Good	Poor	Good

Table 2.3 shows the relative performance characteristics of some synthetic lubricants compared with mineral oil. Other materials such as silicones, borates esters, perfluoroethers and polyphenylene ethers, are also of importance, but their applications are restricted due either to high cost or to performance limitations.

2.4 Synthetic organic esters [16, 17, 22-24]

Synthetic organic esters came into importance as lubricants during World War II. They were used in Germany in mineral oil blends to improve low temperature properties and to supplement scarce supplies of petroleum. There have been used as jet engine lubricants since the early 1950s. Esters used in lubricants have excellent physical properties compared with an SAE 10 weight grade mineral oil (Table 2.4).

Table 2.4 Physical properties of synthetic organic ester [17]

Properties	Ester	Mineral oil
Viscosity		
@ 100 °C	4.6	5.2
@ 40 °C	21.0	29.5
@ -17.8 °C	.47	a
@ -40 °C	5465	a
Viscosity index	140	102
Pour point, °C	-57	20
Flash point, °C	243	218

The ester and the mineral oil have similar viscosities at 100 °C. The ester, however, has a very low pour point because it contains no wax, so it retains its fluidity at much lower temperatures. It has much higher viscosity index, which is indicative of its excellent viscosity temperature characteristics. The ester also has very low volatility, apparent from the high flash point and low percentage distillation at 400 °C. It readily dissolves most additives and helps retain deposit precursors in solution. This solvency property renders ester base lubricant unsuitable for use with various compounds commonly found in paints and elastomers. The major type of esters and their feedstocks are reviewed in Tables 2.5 and 2.6.

Table 2.5 Major types of esters [22]

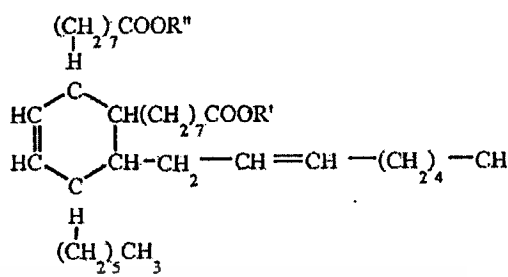
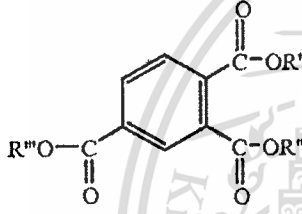
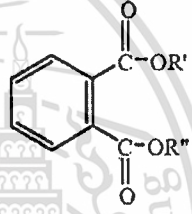
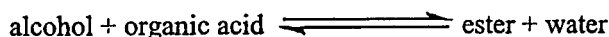
Diesters (dioates) $R'OOC(CH_2)_nCOOR''$ R', R'' = linear, branched or mixed alkyl chain $n = 4$ = adipates $n = 7$ = azelates $n = 8$ = sebacates $n = 10$ = dodecanedioates	C36 dimer acid ester  R', R'' = linear, branched or mixed alkyl chain
Trimellitate esters (1,2,4-benzene tricarboxylate)  R', R'' = linear, branched or mixed alkyl chain	Phthalate esters (1,2-benzene dicarboxylate)  R', R'' = linear, branched or mixed alkyl chain
Polyols (hindered esters) $C(CH_2OCOR)_4$ $CH_3CH_2C(CH_2OCOR)_3$ $(CH_3)_2C(CH_2OCOR)_2$ Pentaerythritol esters Trimethylolpropane esters Neopentylol esters R', R'' = linear, branched or mixed alkyl chain	

Table 2.6 Summary of ester properties [17]

	Diesters	Phthalates	Trimellitates	C ₃₆ dimer esters	Polyols	Polyoleates
Viscosity @ 40 °C	6 to 46	29 to 49	47 to 366	13 to 20	14 to 35	
Viscosity @ 100 °C	2 to 8	4 to 9	7 to 22	90 to 135	3 to 6	8 to 95
Viscosity index	90 to 70	40 to 90	60 to 120	120 to 150	120 to 130	10 to 15
Pour point (°C)	-70 to -40	-50 to -30	-55 to -25	-50 to -15	-60 to -9	130 to 180
Flash points	200 to 260	200 to 270	270 to 300	240 to 310	250 to 310	-40 to -5
Thermal stability	Good	Very Good	Very Good	Excellent	Fair	220 to 280
%Biodegradability	75 to 100	46 to 88	0 to 69	90 to 100	80 to 100	

2.4.1 Manufacture of esters

An ester is an organic, oxygen-containing material formed by the reaction of alcohol and organic acid.



This reaction is reversible, but is driven to completion by the use of excess alcohol and removal of the water as it forms. The use of azeotropic agent, e.g. toluene, to aid water removal is optional.

The acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reaction. Possible catalysts include sulfuric acid, *p*-toluene sulphonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorous oxides and stannous octanoate. After the ester has been formed, unreacted acid was neutralised using sodium carbonate or calcium hydroxide, and removed by filtration.

A significant amount of alcohol vaporised along with water must be recovered. This is accomplished by condensing the reaction 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 (NPG), trimethylol propane (TMP) or pentaerythritol (PE) with monobasic acid.

2.4.2 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 an oil measurable by conventional laboratory tests e.g. viscosity, evaporation, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricant, and many of them can only be measured satisfactorily by elaborate and expensive rigs specially developed to simulate performance.

A wide variety of raw materials can be used for the preparation of ester type base fluids and this can affect a number of lubricant properties including ; viscosity, flow properties, lubricity, thermal stability, hydrolytic stability, solvency, and biodegradability.

2.4.2.1 Viscosity

The viscosity of an ester lubricant can be altered by :

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

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

2.4.2.2 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 esters tend to be somewhat lower than their diester analogues due to the more compact configuration of the polyol molecule

The pour point of the lubricant can be decreased by:

- increasing the amount of branching
- positioning the branch-branching in the center of the molecule, giving better pour point than branches near the end
- decreasing the acid chain length
- decreasing the internal symmetry of the 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 increases. Esters made from mixtures of normal and branched acid (having the same carbon number) have viscosity indices between those of the normal and branched acid esters, but have lower pour points than esters obtained from either branched or normal acids.

2.4.2.3 Lubricity

Ester groups are polar and will therefore affect the efficiency of anti-wear additives. When a too polar base fluid is used, it 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.

Esters can be classified in terms of their polarity, or non-polarity by using the following formula (Van der Waals, 1985) :

$$\text{Non-polarity index} = \frac{\text{Total number of C atom} \times \text{Molecular weight}}{\text{Number of carboxylic groups} \times 100}$$

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. Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids/alcohols have lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/alcohols.

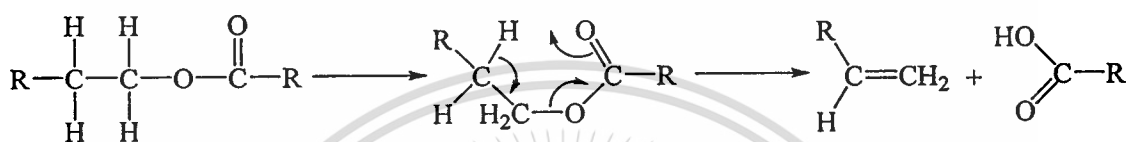
2.4.2.4 Thermal stability [22]

The ester linkage is an exceptionally stable one; bond energy determinations predict that it is more thermally stable than the C-C bond.

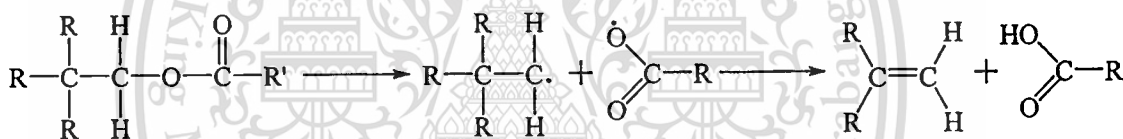
The advantage in thermal stability of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. It has been found that the absence of hydrogen atoms on the beta-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of such hydrogen atoms enables a low energy decomposition mechanism to operate via

a six-membered cyclic intermediate producing acids and 1-alkenes (Figure 2.2a). When beta-hydrogen atoms are replaced by alkyl groups the mechanism cannot operate and decomposition occurs by free radical mechanism. This type of decomposition requires more energy and can only occur at higher temperature (Figure 2.2b).

Short linear chains generally give better thermal stability than long branched chains, whilst esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increases flash points.



(a) Thermal decomposition of esters with β -hydrogens



(b) Thermal decomposition of esters without β -hydrogens

Figure 2.2 Thermal decomposition of ester (a) with β -hydrogens (b) without β -hydrogens [25].

2.4.2.5 Hydrolytic stability

The hydrolytic stability of esters depends on two main features that is processing parameters and 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 value, degree of esterification, catalyst used during esterification and the level remaining in the ester after processing. Ester must have a low acid value, a very high degree of esterification and a low ash level before the effects of molecular geometry will begin to assert themselves.

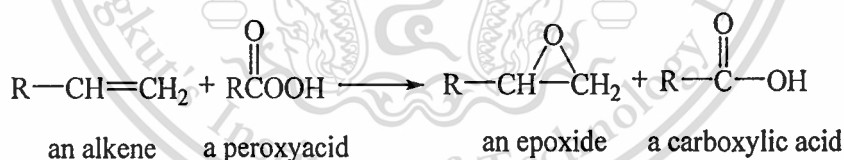
Molecular geometry can affect hydrolytic stability in several ways. By sterically hindering the acid portion of the molecule (hindrance on the alcohol portion having relatively little effect) hydrolysis can be slowed down. To this purpose, germinal di-branched acids (e.g. neoheptanoic acids) have been used. However, when using these feedstocks, there are penalties to be paid, namely very long reaction times to achieve complete esterification, and poor pour points. The hydrolytic stability of neopolyol esters can generally be regarded as superior to that of dibasic acid esters.

2.5 Chemical reaction for synthesis of lubricant from oleic acid

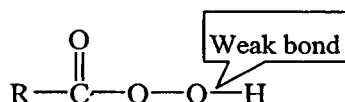
In this thesis, a novel process for the production of lubricant-based stocks from oleic acid with a lower pour point involves three steps: (i) epoxidation of oleic acid, (ii) ring-opening reactions by alcoholysis followed by (iii) esterification of the resulting product in the second step. Such reactions were shown in this section.

2.5.1 Oxidation of alkenes with peroxyacids [26]

An alkene can be oxidised to an epoxide by a peroxyacid. The overall reaction amounts to the transfer of an oxygen atom from the peroxyacid to the alkene.

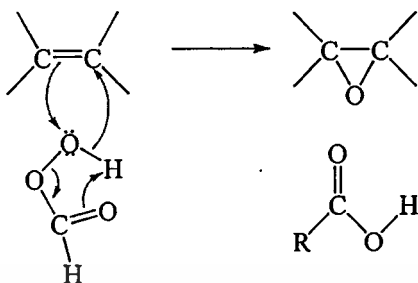


The oxygen atom of the OH group of the peroxyacid accepts a pair of electrons from the π -bond of the alkene, causing the weak O-O bond to break heterolytically.



The electrons from the O-O bond are delocalised onto the carbonyl group. The electrons left behind as the O-H bond breaks add to the carbon of the alkene that becomes electron deficient

when the π -bond breaks. Notice that **epoxidation** of an alkene is a concerted reaction: All the bond-forming and bond-breaking processes take place in a single step.



Schematic I. mechanism for epoxidation of an alkene

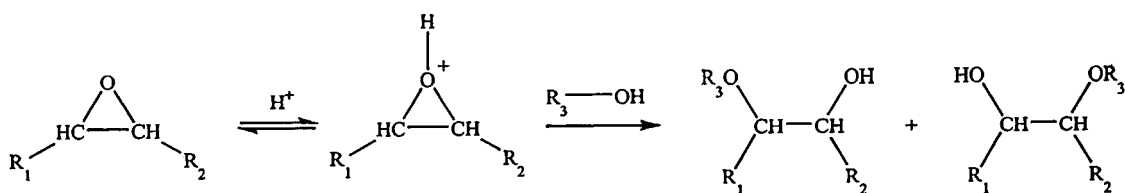
The addition of oxygen to an alkene is a stereospecific reaction. Because the reaction is concerted, the C-C bond cannot rotate, so there is no opportunity for the relative positions of the groups bonded to the sp^2 carbons of the alkene to change. Therefore, a *cis*-alkene forms a *cis*-epoxide. Similarly, a *trans*-alkene forms a *trans*-epoxide.

2.5.2 Ring-opening reactions of epoxides [26]

Ethers in which the oxygen atom is incorporated into a three-membered ring are called **epoxides** or **oxiranes**. The common name of an epoxide uses the common name of the alkene, followed by “oxide,” assuming that the oxygen atom is where the π -bond of an alkene would be.

Although an epoxide and an ether have the same leaving group, epoxides are much more reactive than ethers in nucleophilic substitution reactions because the strain in the three-membered ring is relieved when the ring opens. Epoxides, therefore, readily undergo ring-opening reactions with a wide variety of nucleophiles.

In the case of acid catalysis, protonated epoxides are reactive that they can be opened by poor nucleophiles, such as H_2O and alcohols. (HB^+ is any acid in the reaction mixture; B^- is any base.) If different substituents are attached to the two carbons of the epoxide (and the nucleophile is something other than H_2O), the product obtained from nucleophilic attack on the 2-position of the oxirane ring will be different from that obtained from nucleophilic attack on the 3-position. The major product is the one resulting from nucleophilic attack on the *more substituted* carbon.



The more substituted carbon is more likely to be attacked because, after the epoxide is protonated, it is so reactive that one of C-O the bonds begins to break before the nucleophile has a chance to attack. As the C-O bond starts to break, a partial positive charge develops on the carbon that is losing its share of the oxygen's electrons. The protonated epoxide breaks preferentially in the direction that puts the partial positive charge on the more substituted carbon, because a more substituted carbocation is more stable.

The best way to describe the reaction is to say that it occurs by a pathway that is partially $\text{S}_{\text{N}}1$ and partially $\text{S}_{\text{N}}2$. It is not a pure $\text{S}_{\text{N}}1$ reaction because a carbocation intermediate is not fully formed; it is not a pure $\text{S}_{\text{N}}2$ reaction because the leaving group begins to depart before the compound is attacked by the nucleophile.

An ether does not undergo a nucleophilic substitution reaction unless the very basic -OR leaving group is converted by protonation into a less basic ROH group. Because of the strain in the three-membered ring, epoxides are reactive enough to open without first being protonated. When a nucleophile attacks an unprotonated epoxide, the reaction is a pure $\text{S}_{\text{N}}2$ reaction. That is, the C-O bond does not begin to break until the carbon is attacked by the nucleophile. In this case, the nucleophile is more likely to attack the *less substituted* carbon because the less substituted carbon is more accessible to attack. (It is less sterically hindered.) Thus, the site of nucleophilic attack on an unsymmetrical epoxide under neutral or basic conditions (when the epoxide *is not* protonated) is different from the site of nucleophilic attack under acidic conditions (when the epoxide *is* protonated).

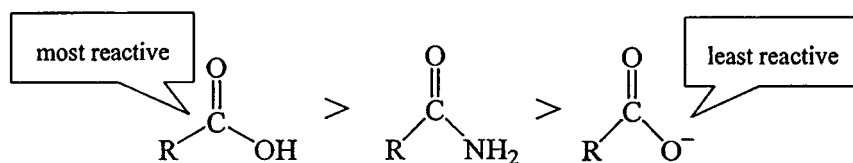
2.5.3 Esterification of carboxylic acid [26]

Carboxylic acids can undergo nucleophilic acyl substitution reactions only when they are in their acidic forms. The basic form of a carboxylic acid does not undergo nucleophilic acyl substitution reactions because the negatively charged carboxylate ion is resistant to nucleophilic attack. Thus, carboxylate ions are even less reactive toward nucleophilic acyl substitution reactions than are amides.

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relative reactivities toward nucleophilic acyl substitution



Carboxylic acids have approximately the same reactivity as esters—the HO- leaving group of a carboxylic acid has approximately the same basicity as the RO- leaving group of an ester. Therefore, like esters, carboxylic acids do not react with halide ions or with carboxylate ions.

Carboxylic acids react with alcohols to form esters. The reaction must be carried out in an acidic solution, not only to catalyze the reaction but also to keep the carboxylic acid in its acid form so that it will react with the nucleophile. Because the tetrahedral intermediate formed in this reaction has two potential leaving groups of approximately the same basicity, the reaction must be carried out with excess alcohol to drive it toward products. Emil Fischer was the first to discover that an ester could be prepared by treating a carboxylic acid with excess alcohol in the presence of an acid catalyst, so the reaction is called a **Fischer esterification**.



2.6 Literature reviews

In 2007, Xuebing Zhao et. al. reported a homogeneous kinetic model for preparation of peracetic acid from acetic acid and hydrogen peroxide under the catalysis of sulfuric acid in the liquid phase. It was found that the synthesis and hydrolysis of peracetic acid were both first-order reactions with respect to reactant concentrations and H^+ concentration. Linear relationships were discovered between the observed rate constants and H^+ concentrations at a certain temperature, with the slopes being corresponding intrinsic rate constants. The intrinsic activation energies of peracetic acid synthesis and hydrolysis were 57.8 and 60.4 kJ mol⁻¹, respectively. It has been proved that the rate-determining step in the synthesis of peracetic acid is the reaction between H_2O_2 with active carbonyl intermediary, and in the hydrolysis of peracetic acid the reaction between water and corresponding active carbonyl intermediary. The reaction between acetic acid (10.5 mol L⁻¹) and 30 % hydrogen peroxide (3.93 mol L⁻¹) catalysed by sulfuric acid (0.0626 - 0.3125 mol L⁻¹) provides the high concentration of peracetic acid about (2 - 2.3 mol L⁻¹) at 20 - 50 °C for 1 - 6 hours [27].

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In 2008, Xuebing Zhao et al. developed some mathematic models based on the kinetic equations and equilibrium constants for calculating peracetic acid concentration, equilibrium conversion rate of hydrogen peroxide, etc. The equilibrium constants determined from the forward and reverse rate constants at 20, 30, 40 and 50 °C were 2.91, 2.81, 2.72 and 2.63, respectively. The models could predict the values of equilibrium concentration of peracetic acid with average relative deviation of less than 10%. Both of the experimental and model-calculated results demonstrated that temperature and catalyst loading were the most important factors affecting the rate of peracetic acid synthesis, but high temperature led to the decrease of equilibrium concentration of peracetic acid [28].

In 2007, Srikantha Dinda et al. studied the kinetics of epoxidation of cottonseed oil by peroxyacetic acid generated in situ from hydrogen peroxide and glacial acetic acid in the presence of liquid inorganic acid catalysts. It was possible to obtain up to 78% relative conversion to oxirane with very less oxirane cleavage by in situ technique. The rate constants for sulfuric acid catalysed epoxidation of cottonseed oil were in the range of $0.39 - 5.4 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$ and the activation energy was found to be $11.7 \text{ kcal mol}^{-1}$. Some thermodynamic parameters such as enthalpy, entropy, and free energy of activation were determined to be of $11.0 \text{ kcal mol}^{-1}$, $51.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $28.1 \text{ kcal mol}^{-1}$, respectively. The order of effectiveness of catalysts was found to be sulfuric acid > phosphoric acid > nitric acid > hydrochloric acid. Acetic acid was found to be superior to formic acid for the in situ cottonseed oil epoxidation [3].

In 2008, Eugeniusz Milchert et al. reported the results of epoxidation of the rapeseed oil (RO) with peracetic and performic acid which were prepared in situ in the reaction of 30 wt.% hydrogen peroxide and appropriate carboxylic acid. The influence of temperature (30 – 75 °C), the molar ratio of $\text{H}_2\text{O}_2/\text{RO}$ (1.5:1 – 4.0:1), the molar ratio of carboxylic acid/RO (0.2:1 – 0.65:1), stirring speed (100 – 900 rpm) and the reaction time (2.5 – 7 h) were studied. The degree of oil epoxidation was determined by means of the epoxy number. The best results of epoxidation were obtained under the following conditions: a temperature of 60 °C, stirring speed – 500 rpm, the reaction time – 4 h. The molar ratio of the reagents in the presence of peracetic acid was $\text{RO}/\text{H}_2\text{O}_2/\text{acetic acid} = 1:3:0.35$, and that for performic acid: $\text{RO}/\text{H}_2\text{O}_2/\text{formic acid} = 1:3.5:0.5$. The best technological parameters are similar for both acids, but the conversion and the selectivity are higher for the process carried out in the presence of performic acid [29].

In 2001, Hong-Sik Hwang reported a production process of soybean oil-based lubricants with good oxidative stability and low pour point by epoxidation of soybean oil (SBO). Epoxidised

SBO was reacted with various alcohols in the presence of sulfuric acid as a catalyst to give a ring-opened intermediate product. In this step, the epoxy group was transformed to the functional group of $-\text{CH}(\text{OR}_1)\text{CH}(\text{OH})-$ (where R_1 = methyl, 1-butyl, 2-butyl, 1-hexyl, cyclohexyl, 2,2-dimethyl-1-propyl, or 1-decyl). The ^1H -nuclear magnetic resonance spectra of the products indicated that transesterification was accompanied by the ring-opening reaction except when the bulky 2,2-dimethyl-1-propanol was used. Acid anhydride was used to esterify the hydroxyl groups in the ring-opened product. This resulted in a fluid that is a lubricant candidate with the functional group of $-\text{CH}(\text{OR}_1)\text{CH}(\text{OCOR}_2)-$. Pour point studies of the resulting products showed that the pour points varied with the substituents, R_1 and R_2 . Products with $\text{R}_1 = \text{CH}_3(\text{CH}_2)_5-$ and $\text{R}_2 = \text{CH}_3(\text{CH}_2)_2-$, $(\text{CH}_3)_2\text{CH}-$, or $\text{CH}_3(\text{CH}_2)_4-$ showed the lowest pour points (-39 , -39 , and -45 °C, respectively) when 1% of pour point depressant was added. For the oxidative stability test, two products, in which $\text{R}_1, \text{R}_2 = \text{CH}_3(\text{CH}_2)_5-$, $(\text{CH}_3)_2\text{CH}-$ and $\text{R}_1, \text{R}_2 = \text{CH}_3(\text{CH}_2)_5-$, $\text{CH}_3(\text{CH}_2)_4-$, were chosen for a modified Penn State micro-oxidation test. In the oxidative stability test, the products gave 69 – 71% of oxidative evaporation and 10 – 17% of tetrahydrofuran-insoluble deposits in 3 h at 175 °C. The amounts of deposits were much lower than those of soybean oil (96 %) and epoxidised SBO (83%) and even less than those of most petroleum-based lubricant basestocks (3 – 93 %) [30].

In 2005, Hong-Sik Hwang reported that synthetic lubricant basestocks with oxidative stabilities and pour points comparable with commercial synthetic lubricant basestocks have been prepared by reacting epoxidised soybean oil with Guerbet alcohols. Four different Guerbet alcohols, C12-, C14-, C16-, and C18-Guerbet alcohols were used. Reaction of epoxidised soybean oil with a Guerbet alcohol in the presence of a catalytic amount of sulfuric acid provided open-ringed products. ^1H -NMR has shown that transesterification follows after ring-opening reaction under the given reaction conditions. Two types of ring-opened products, 0% and 100% transesterified products, could be obtained under controlled reaction conditions. Pour points of the ring-opened products ranged from -18 to -36 °C without pour point depressant (PPD) and from -21 to -42 °C with 1% of PPD. Acetylation of hydroxy groups in the ring-opened products further lowered pour points that ranged from -27 to -42 °C without PPD and from -30 to -48 °C with 1% of PPD. Oxidative stability was examined using a modified Penn State microoxidation test and compared with those of synthetic lubricant basestocks and mineral oil. Oxidative evaporations of two selected products in the microoxidation test were similar to mineral oil and less than synthetic lubricant-based oils, polyalphaolefin (PAO₄) and diisododecyl adipate.

Deposits of these products were similar to synthetic lubricant-based oils and less than mineral oil [2].

In 2005, Campanella et. al. reported the main process variables (agitation, pH, temperature, volumetric ratio and concentration levels) on the degradation of the oxirane ring of epoxidised vegetable oil (VO) by hydrolysis and hydrogen peroxide in two-phase (polar-organic) systems, when a homogeneous acid catalyst is used. Acid hydrolysis of epoxidised VO is a very slow reaction that proceeds at the liquid-liquid interphase, but only after an extended 'induction period' of several hours, during which enough active interfacial area is developed. The process is transport controlled, as the influence of temperature was found to be almost negligible ($E_a = 349.2 \pm 10.15 \text{ cal mol}^{-1}$). On the contrary, the degradation of the oxirane ring with aqueous H_2O_2 in acid media is fast and proceeds under kinetic regime ($E_a = 16.3 \pm 0.72 \text{ kcal mol}^{-1}$), without any observable induction times. If the concentration of H_2O_2 is kept within moderate values the reaction order with respect to this reactant is two, the expected value [31].

In 2005, Brajendra K. et. al. reported a series of structural modifications of vegetable oils using anhydrides of different chain lengths. The ring-opening reaction was carried out using perchloric acid as oxidant leading to the formation of dihydroxy derivative of soybean oil: DiOH-SBO. Such products was esterified by acetic anhydride giving Ace-SBO (or butyric, isobutyric, and hexanoic anhydride for preparation of the diester derivatives But-SBO, Isobut-SBO, and Hex-SBO, respectively). The reaction was monitored and products were confirmed by NMR, FTIR, gel permeation chromatography, and thermogravimetric analysis (TGA). Experimental conditions were optimised for research quantity and for laboratory scale-up (up to 4 lb = 1.8 kg). The thermo-oxidation stability of these new lubricant base fluids was tested using pressure differential scanning calorimetry and TGA. The chemically modified base fluids exhibit superior oxidation stability in comparison with unmodified vegetable oils. These base fluids in combination with suitable additives exhibit equivalent oxidation stability compared with mineral oil-based formulations [32].

In 2006, Piyush S. Lathi et. al. developed a novel process for the production of biodegradable lubricant-based stocks from epoxidised vegetable oil with a lower pour point via cationic ion-exchange resins as catalysts. This involves two steps, first, ring-opening reactions by alcoholysis followed by esterification of the resultant hydroxy group in the first step. The ring-opening reaction of epoxidised soybean oil with different alcohols such as *n*-butanol, *i*-amyl alcohol and 2-ethylhexanol was carried out in presence of Amberlyst 15 (Dry) as a catalyst;

identity of products was confirmed by IR and NMR. Pour points of the products were observed in the range of -5 to -15 °C. The hydroxy group of ring-opening product of *n*-butanol was further reacted with acetic anhydride in presence of catalyst Amberlyst 15 (Dry), which was previously used to carry out ring-opening reaction by alcoholysis and identity of the resulting product was confirmed by IR. Pour point of the resulting product was observed to be -5 °C [7].

In 1998, Esa Uosukainen reported that biodegradable trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] esters of rapeseed oil fatty acids were synthesised by transesterification with rapeseed oil methyl ester both by enzymatic and chemical means, both in bench and pilot scales. Nearly complete conversions were obtained with both techniques. A reduced pressure of about 2 to 5 kPa, to remove the methanol formed during transesterification, was critical for a high product yield. The quantity of added water was also critical in the biocatalysis. *Candida rugosa* lipase was used as biocatalyst and an alkaline catalyst in chemical transesterifications. In biocatalysis the maximum total conversion to trimethylolpropane esters of up to 98% was obtained at 42°C, 5.3 kPa, and 15% added water. The maximum conversion of about 70% to the tri-ester was obtained at the slightly higher temperature of 47°C. The reaction time was longer in the biocatalysis, but considerably higher temperatures were required in chemical synthesis. In the chemical synthesis tri-ester yields increased when the temperature was first held at 85 to 110 °C for 2.5 h and subsequently increased to up to 120 °C for 8 h. The trimethylolpropane esters obtained were tested as biodegradable hydraulic fluids and compared to commercially available hydraulic oils. The hydraulic fluids based on trimethylolpropane esters of rapeseed oil had good cold stability, friction and wear characteristics, and resistance against oxidation at elevated temperatures [33].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

- 1) Benzyl alcohol (Analytical grade) from Riedel
- 2) Butanol (Analytical grade) from Acros organic
- 3) Cyclohexanol (Analytical grade) from BDH
- 4) Decanol (Analytical grade) from Acros organic
- 5) Deuterated chloroform (Analytical grade) from Aldrich
- 6) Dichloromethane (Analytical grade) from Merck
- 7) Diethyl ether (Analytical grade) from BDH
- 8) Distilled water
- 9) Ethyl acetate (Analytical grade) from Carlo Erba
- 10) Gracial acetic acid (Analytical grade) from J.T.Baker
- 11) Hexanol (Analytical grade) from Fluka
- 12) Hydrogen peroxide (Analytical grade) from Fisher
- 13) Isobutanol (Analytical grade) from Acros organic
- 14) MCPBA (Analytical grade) from Fluka
- 15) Oleic acid (Analytical grade) from Aldrich
- 16) Sodium hydrogen carbonate (Analytical grade) from Carlo Erba
- 17) Sodium metabisulfite (Analytical grade) from Mallinckrodt
- 18) Sodium sulphate anhydrous (Analytical grade) from Carlo Erba
- 19) Sulfuric acid (Analytical grade) from J.T.Baker

3.2 Apparatus

- 1) Beaker
- 2) Buchner flask
- 3) Clamp
- 4) Condensor
- 5) Cooling trap
- 6) Dropper

- 7) Filter paper 0.45 μm
- 8) Gas chromatograph with flame ionisation detector (FID) (CP-3800 : Varian)
- 9) Heating bath
- 10) Hot plate
- 11) Metal rings
- 12) Nuclear Magnetic Resonance Spectrometer: Advance DPX300, Bruker
- 13) Pipette
- 14) Round bottom flask
- 15) Separatory funnel
- 16) Supporting stand
- 17) Thermogravimetric Analyser : Pyris 1 TGA, Perkin Elmer, Scientific Instruments
Service Centre ; KMITL
- 18) Three-necked round bottom flask 250 ml
- 19) Vacuum oven: Isotemp 282A, Fisher scientific
- 20) Vial 5 mL
- 21) Wash bottle

3.3 Process of study

A process of study on the conversion of oleic acid to synthetic lubricants comprises the following stages:

3.3.1 Single-step synthesis of epoxidised oleic acid

- 3.3.1.1 Synthesis of 9,10-epoxystearic acid by epoxidation reaction of oleic acid with peracetic acid which generated during epoxidation.

3.3.2 Two-step synthesis of epoxidised oleic acid

- 3.3.2.1 Preparation of peracetic acid by reaction between glacial acetic acid and hydrogen peroxide using sulfuric acid as catalyst.
- 3.3.2.2 Synthesis of 9,10-epoxystearic acid by epoxidation reaction of oleic acid with peracetic acid (prepared from 3.3.2.1)

3.3.3 Characterisation of 9,10-epoxystearic acid

3.3.3.1 Investigation of the change in functional group in order to calculate the conversion of oleic acid, and yield of 9,10-epoxystearic acid and by-products using ^1H nuclear magnetic resonance spectra.

3.3.4 Synthesis of synthetic lubricants

3.3.4.1 Preparation of synthetic lubricants by acid-catalysed ring-opening of 9,10-epoxystearic acid followed by esterification with different type of alcohols.

3.3.5 Characterisation of synthetic lubricants

3.3.5.1 Investigation and calculation of the conversion of 9,10-epoxystearic acid and product distribution of synthetic lubricants using Gas Chromatography .

3.3.5.2 Determination of the physical and chemical properties of the synthetic products such as viscosity @ 40 °C, viscosity @ 100 °C, viscosity index, pour point, total acid number and thermal and oxidation stability.

3.4 Synthesis and characterisation of an epoxidised oleic acid

3.4.1 Single-step synthesis of epoxidised oleic acid

A certain volume of acetic acid, sulfuric acid, and oleic acid were transferred into a 250 mL clean round-bottom flasks equipped with a mechanical stirrer, and then placed in a water bath. To start the epoxidation, hydrogen peroxide was gradually charged into the mixture. The system was kept at 30 °C and the mixture was continuously stirred for the desired time duration. The following parameters were varied during the epoxidation of oleic acid: the mole of acetic acid (0.1 – 0.4 mol), the mole of hydrogen peroxide (0.35 – 0.6 mol), the mole of oleic acid (0.1 mol), the amount of sulfuric acid (0.007 mol) and the reaction time (15 hours). The reaction mixture were then extracted with diethyl ether in order to separate oil product from water phase, and washed with water successively to remove free acids. After that, the lower aqueous phase was siphoned off and the retained product was dried to remove diethyl ether using vacuum oven at 40 °C. The resulting product was weighed and characterised by ^1H NMR technique.

3.4.2 Two-step synthesis of epoxidised oleic acid

A certain volume of acetic acid, sulfuric acid, and hydrogen peroxide were transferred into a 250 mL of clean round-bottom flasks equipped with a mechanical stirrer, and then placed in a water bath. The system was kept at 50 °C (or 30 °C) and the mixture was continuously stirred for 2 – 6 hours. Then the mixture was cooled down to 30 °C and 0.1 mol of oleic acid was gradually added. After the charging of oleic acid was completed, the reaction continued by stirring it for the desired time duration. The following parameters were varied during the epoxidation of oleic acid: the mole of acetic acid (0.1 – 0.4 mol), the mole of hydrogen peroxide (0.35 – 0.7 mol), the mole of oleic acid (0.1 mol), the amount of sulfuric acid (0.007 mol) and the reaction time (15 hours). Then, the product was separated and analysed by ^1H NMR technique.

3.4.3 Complete epoxidation of oleic acid by MCPBA [34]

Aliquots of 1 g of oleic acid were dissolved in 25 ml of CH_2Cl_2 and 1.1 to 1.2 equiv. MCPBA was added in small portions. The solution was stirred either for 2 to 3 h at 20 °C or 24 h at -10 °C. The CH_2Cl_2 layer was washed twice using a 25 ml water with 0.5 mol $\text{Na}_2\text{S}_2\text{O}_5$ /mol MCPBA and 2 mol NaHCO_3 /mol MCPBA, respectively, and two times more with 25 ml of water, then dried.

3.4.4 Characterisation of epoxidised oleic acid

The conversion of oleic acid and yield of epoxidised oleic acid were determined using the ^1H NMR technique. The sample was dissolved in deuterated chloroform (CDCl_3). The measurement was performed on a Bruker (AVANCE DPX300 NMR spectrometer) with 300 MHz ^1H resonance frequency. The integral spectra were obtained in separated scans from 0 to 16 parts per million (ppm) (Fig. 3.1). The conversion and yield were calculated as the peak percent value.

It is clear that reaction yield can be calculated from ^1H NMR by evaluating the appearing and disappearing signals. Reaction conversion, expressed as conversion of double bonds, can be calculated by evaluating the new arising of the epoxide signal at 2.90 ppm ($-\text{CHOCH}-$,b), dihydroxy signal at 3.40 ppm ($-\text{CHOH}$,c) and hydroxy-acetoxy signal at 4.80 ppm ($\text{HO}-\text{CH}-\text{CHOCOCH}_3$,d). Equation (1) and (2) can be used to calculate reaction conversion and yield, respectively:

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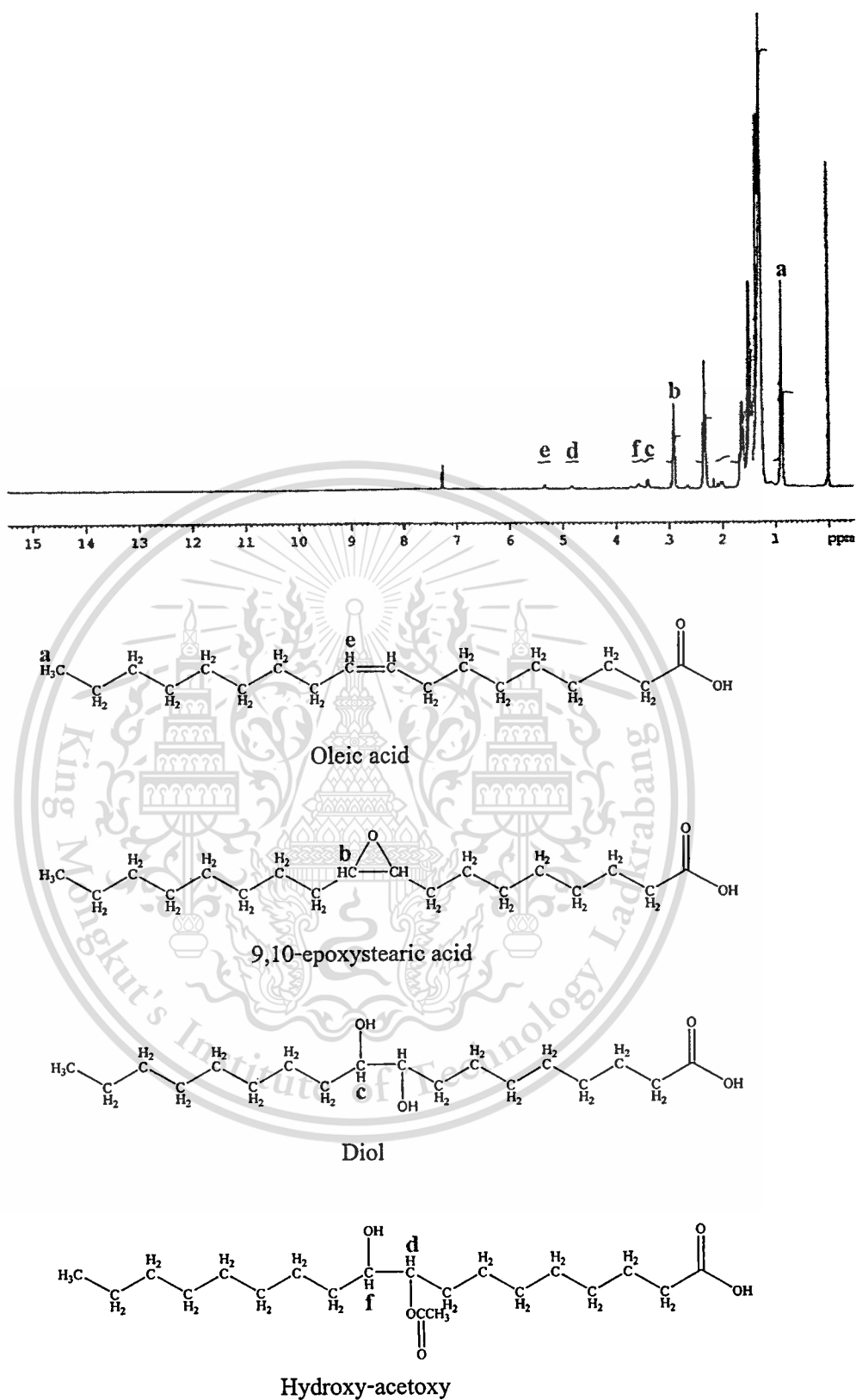


Figure 3.1 ^1H NMR spectrum of the epoxidised product from oleic acid.

$$\% \text{ Conversion} = \% \text{Yield epoxidised product} + \% \text{Yield of by-product}$$

$$\% \text{Yield of epoxidised product} = \frac{\frac{A_{2.90}}{N_{2.90}}}{\frac{A_{2.90}}{N_{2.90}} + \frac{A_{3.40}}{N_{3.40}} + \frac{A_{4.80}}{N_{4.80}} + \frac{A_{5.30}}{N_{5.30}}} \times 100$$

$$\% \text{Yield of Diol} = \frac{\frac{A_{3.40}}{N_{3.40}}}{\frac{A_{2.90}}{N_{2.90}} + \frac{A_{3.40}}{N_{3.40}} + \frac{A_{4.80}}{N_{4.80}} + \frac{A_{5.30}}{N_{5.30}}} \times 100$$

$$\% \text{Yield of Hydroxy - acetoxy} = \frac{\frac{A_{4.80}}{N_{4.80}}}{\frac{A_{2.90}}{N_{2.90}} + \frac{A_{3.40}}{N_{3.40}} + \frac{A_{4.80}}{N_{4.80}} + \frac{A_{5.30}}{N_{5.30}}} \times 100$$

$$\% \text{ Selectivity of epoxidised product} = \frac{[\% \text{ Yield of epoxidised product}] \times 100}{\% \text{ Conversion}}$$

$$\% \text{ Selectivity of by-product} = \frac{[\% \text{ Yield of diol} + \% \text{Yield of Hydroxy - acetoxy}] \times 100}{\% \text{ Conversion}}$$

in which $A_{2.90}$, $A_{3.40}$ and $A_{4.80}$ represent the peak areas of the resonance signals at 2.90, 3.40 and 4.80 ppm, and $N_{2.90}$, $N_{3.40}$ and $N_{4.80}$ are the amount of protons for which the peak stands. The amount of proton represents the response factors of each hydrogen atom in a sample analysed by ^1H NMR. Thus, by comparing the integrals of each peak observed in a ^1H NMR spectrum, one can determine a mole of a functional group.

3.5 Synthesis of lubricant

3.5.1 Ring-opening and esterification of 9,10-epoxystearic acid

A mixture of epoxidised oleic acid (200 g, 0.47 mole of epoxy groups) and an alcohol (i.e. *n*-butanol, isobutanol, *n*-hexanol, *n*-decanol, cyclohexanol, and benzyl alcohol) (1.88 mole) was heated at 80 °C with stirring. Sulfuric acid (40 drop) was added dropwise, and the mixture was stirred at 120 °C for 20 h. The reaction mixture was cooled down, and saturated aqueous sodium bicarbonate (100 mL) was added. The mixture was extracted with ethyl acetate (200 mL), dried over anhydrous sodium sulfate, filtered, and evaporated using a rotary evaporator. Any volatile materials including the remaining solvent were evaporated under vacuum (41.37 – 68.95 Pa) at 80 °C overnight to give the ring-opened and esterified product.

3.5.2 Determination of the physical and chemical properties of oleic acid and products

3.5.2.1 Determination of the physical properties of oleic acid and products

The physical properties of oleic acid and products were tested by PTT Public Company (Phrakhanong Office and Oil Terminal) and Focus laboratories Ltd. These properties include :

1. Viscosity @ 40 °C by ASTM D 445
2. Viscosity @ 100 °C by ASTM D 445
3. Viscosity Index by ASTM D 2270
4. Pour point by ASTM D 97
5. Total acid number by ASTM D 974

3.5.2.2 Determination of the chemical properties of oleic acid and products

1. Gas chromatography (GC) to determine the composition and conversion.

The conversion and composition of synthetic lubricant were determined using the Gas chromatography technique, samples were analysed with an Varian 3800 gas chromatograph using a MXT-1 column measuring 60m × 0.25mm × 0.25 µm film thickness (Restek). The carrier gas was nitrogen flowing at 5 mL/min. The oven was programmed from an initial temperature of 100 °C with a 2 min hold then increased to 300 at 20°/min with a 60 min hold for a total run time of 72 min. Injection volumes were 1 µL with the inlet set to splitless

mode. Detection of eluents was made by FID detector. The conversion and yield were calculated from the peak area.

From the chromatogram, the peak of samples were identified using mass spectrometer detector. In the normalisation method, the areas of all eluted peak were computed after correcting these areas for differences in the detector response to different compound types. After correcting areas, the concentration of the analyte was found from the ratio of its area to the total area of all peaks.

The percent yield of each component in sample was calculated as follows:

$$\% \text{ product distribution in each product} = \frac{\text{Corrected area of product} \times 100}{\text{Total corrected area}}$$

Where Corrected area is Area/RF , RF is the response factor of the analyte sample which calculated from the C number minus O number.

2. Thermogravimetric Analyser to determine the thermal and oxidative stability.

The thermal and oxidative stability of products and oleic acid were investigated using TGA (Pyris 1 TGA, Perkin Elmer Scientific Instruments Service Centre, KMITL). Approximately 10 mg of the sample was placed into a platinum pan hanging from a microbalance with a 10 °C/min constant heating rate from 50 °C to 700 °C. Nitrogen was used as the purge gas at a 20 mL/min flow rate for the thermal stability test. For the oxidative stability test, oxygen was used as the purge gas at a 20 mL/min flow rate.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Synthetic of 9,10-epoxystearic acid

Epoxide of oleic acid (9,10-epoxystearic acid) was prepared by epoxidation using H_2O_2 under various reaction conditions catalysed by acetic acid. The products were all analysed using ^1H NMR spectra. The differences on NMR spectra between oleic acid and products are compared and given in Figure. 4.1.

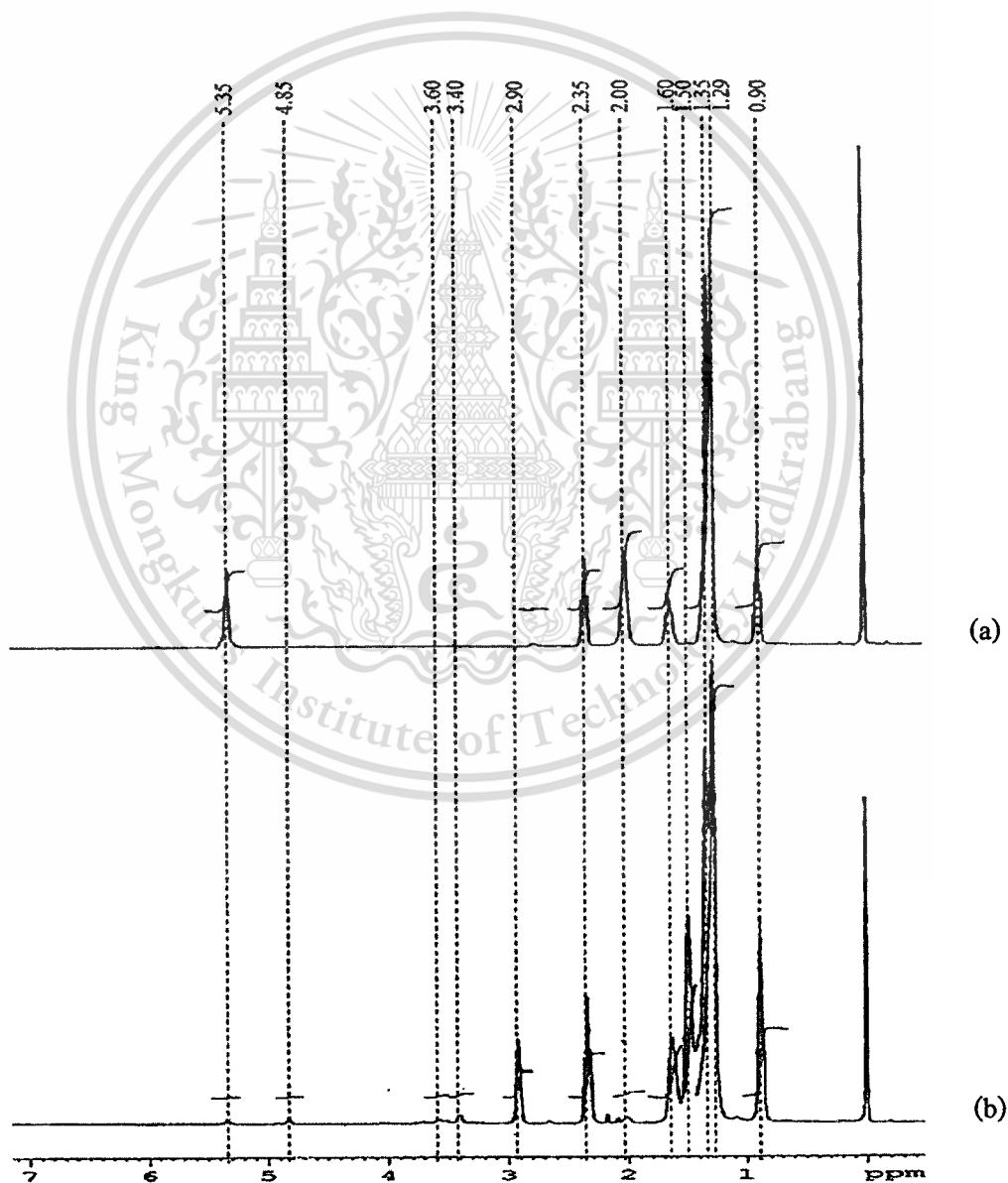
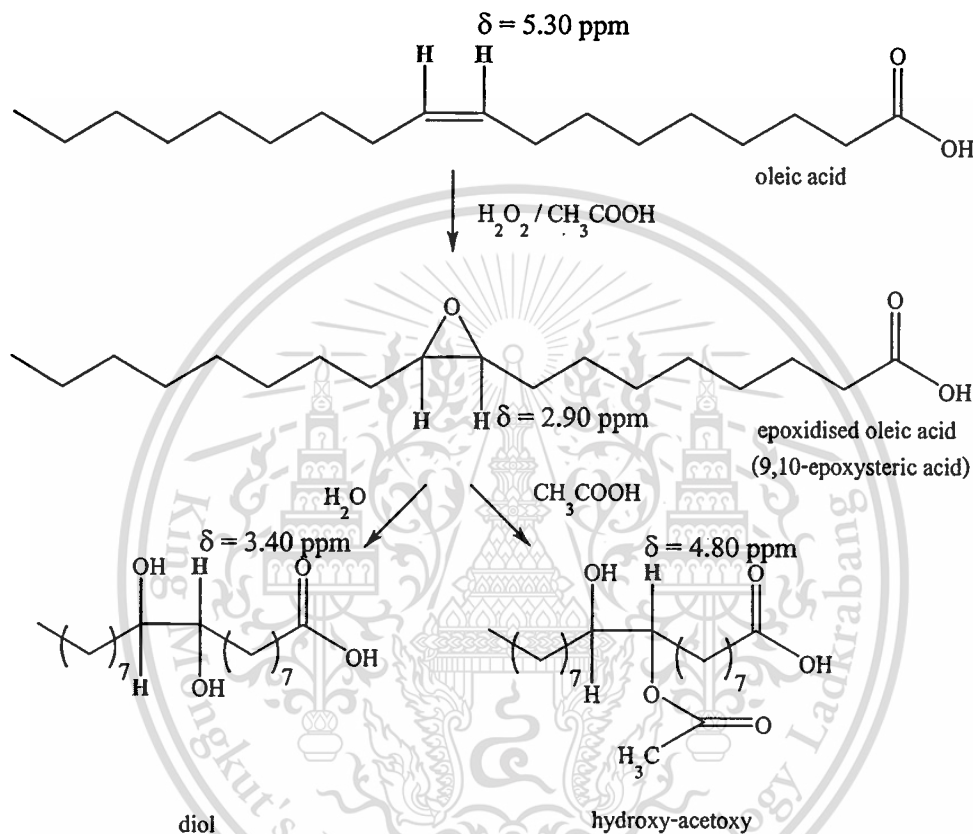


Figure 4.1 ^1H NMR spectra of oleic acid (a) and epoxidised oleic acid (b).

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It is clearly seen from Figure 4.1 that the signal of unsaturation of oleic acid at 5.30 ppm ($-\text{CH}=\text{CH}-$) is decreased. On the other hand, the signals at 2.90, 3.40 and 4.80 ppm are pronounced (Figure 4.1b). It is known that the signals at 2.90, 3.40 and 4.80 ppm represent an epoxidised product ($-\text{CHOCH}-$), a diol ($-\text{CHOH}$) and a hydroxy-acetoxy ($\text{HO}-\text{CH}-\text{CHOCOCH}_3$), respectively, as illustrated in Scheme I shown below.



Scheme I

The formation of epoxidised product from oleic acid was proposed by epoxidation with peracetic acid generated from acetic acid and hydrogen peroxide while the by-products, diol and hydroxy-acetoxy compounds, were derived by ring-opening of epoxidised product with water and acetic acid, respectively [3, 35-38].

4.1.1 Effect of hydrogen peroxide

The effect of H_2O_2 -to-oleic acid mole ratio on the conversion to epoxidised product was studied in the ratios ranged from 3.5 to 7 over two-step synthesis. Figure 4.2 shows that the conversion of oleic acid slightly increased as the concentration of H_2O_2 in the system increased.

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Interestingly, a dramatic increase in yield of epoxidised product was obtained by using 0.35 – 0.6 mol of hydrogen peroxide but was decreased at relatively higher hydrogen peroxide content (0.7 mol) and *vice versa* for the yield of by products.

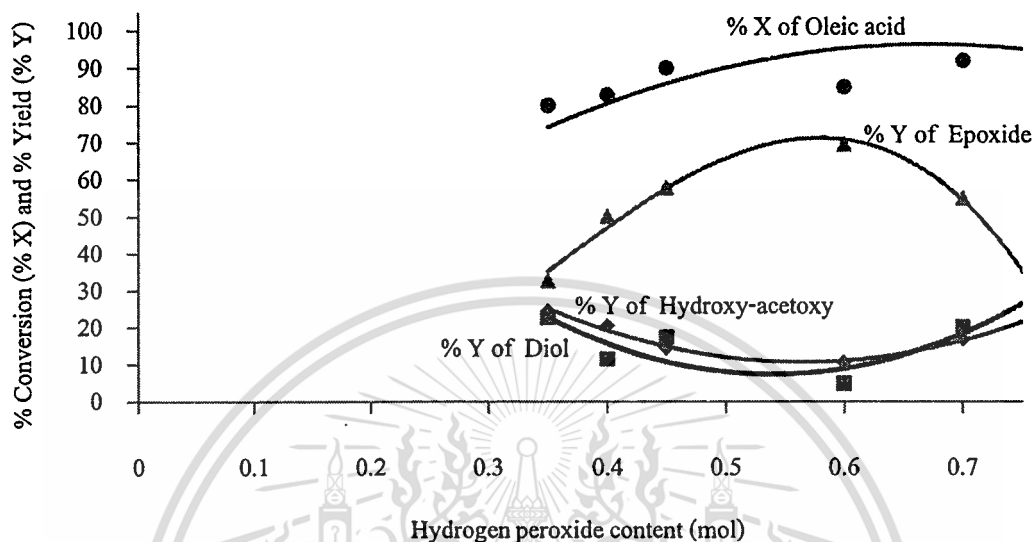


Figure 4.2 Effect of hydrogen peroxide content over two-step synthesis of 9,10-epoxystearic acid (Acetic acid = 0.3 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.4 mL, Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 15 hours)

A decrease in yield of by-product obtained by using 0.35 – 0.6 mol of hydrogen peroxide is presumably explained by the decrease in the acid concentration. When hydrogen peroxide is added (0.35 – 0.6 mol) in the catalytic system without equal volume adjustment by solvent, volume of the catalytic system increase and acid concentration decrease. It can reduce the protonated oxirane ring leading to a reduction of by-product. This confirms that both acetic acid and sulfuric acid plays important role in epoxidation reaction. The effect of acetic acid and sulfuric acid will be discussed in next part (4.1.2 and 4.1.5).

With an increase in hydrogen peroxide from 0.35 mol to 0.6 mol, peracetic acid generated from the acetic acid and hydrogen peroxide not only reacts inside the organic phase, but also acts as an interphase layer between aqueous phase and organic phase. This can inhibit the water transferring to organic phase leading to the reduction of diol. This suggestion is consistent with several reports that an excess hydrogen peroxide relative to the ethylenic unsaturation can minimise the formation of diol by-product through ring-opening reactions [35,39]. Moreover, it is

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also suggested that some part of acetic acid generated after epoxidation can readily return to the aqueous phase to minimise hydroxy-acetoxy compounds and to reinitiate the peracetic acid.

Although by-products are largely produced at low hydrogen peroxide concentration (< 0.45 mol), the direct hydration of oleic acid to diol shall not be the case. This suggestion is confirmed by the reaction of oleic acid under the system containing water, sulfuric acid and hydrogen peroxide (but without acetic acid) at the same reaction temperature and time that no diol (hydration product, a signal at 3.40 ppm) can be observed by NMR, as shown in Figure 4.3.

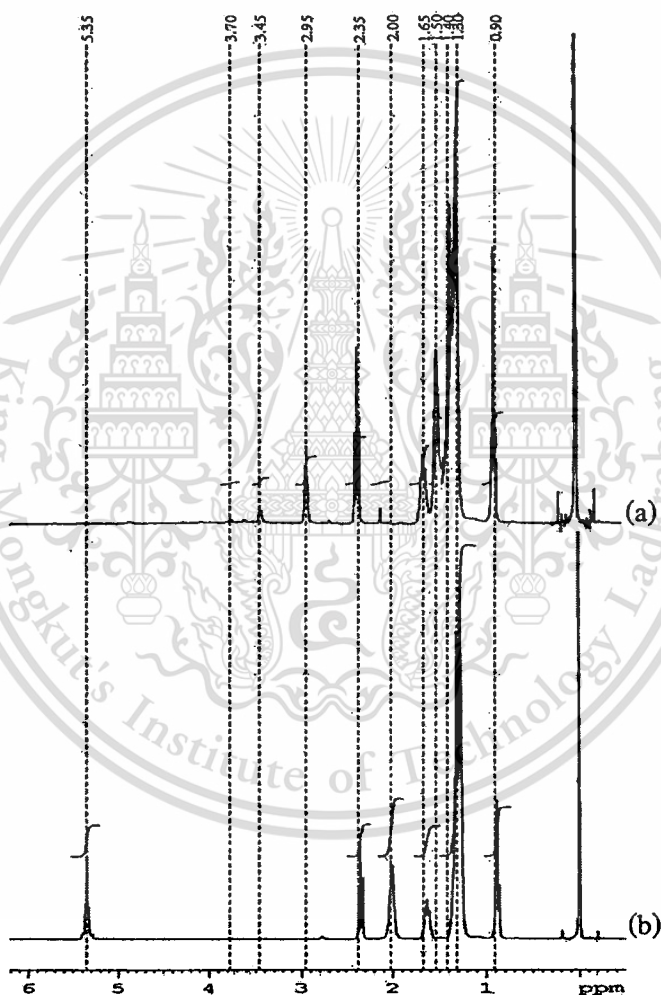


Figure 4.3 ^1H -NMR spectrum of epoxidised product with acetic acid (a) and without acetic acid (b) at the same reaction temperature and time. (Hydrogen peroxide = 0.45 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50°C , Time = 4 hours, Step 2: Temperature = 30°C , Time = 15 hours)

Moreover, the trace yield of epoxidised product observed in the same reaction condition confirms that acetic acid was found to be an important oxygen carrier which obtained oxygen from hydrogen peroxide to form peracetic acid that, by then, can epoxidise unsaturated hydrocarbons to form oxirane ring [40].

The reaction of oleic acid and acetic acid under the system containing water, and sulfuric acid (but without hydrogen peroxide) at the same reaction temperature and time is also carried out to confirm the direct acetylation of oleic acid to hydroxy-acetoxy. The NMR spectrum (Figure 4.4) shows that no hydroxy-acetoxy (acetylation product, a signal at 4.80 ppm) can be observed.

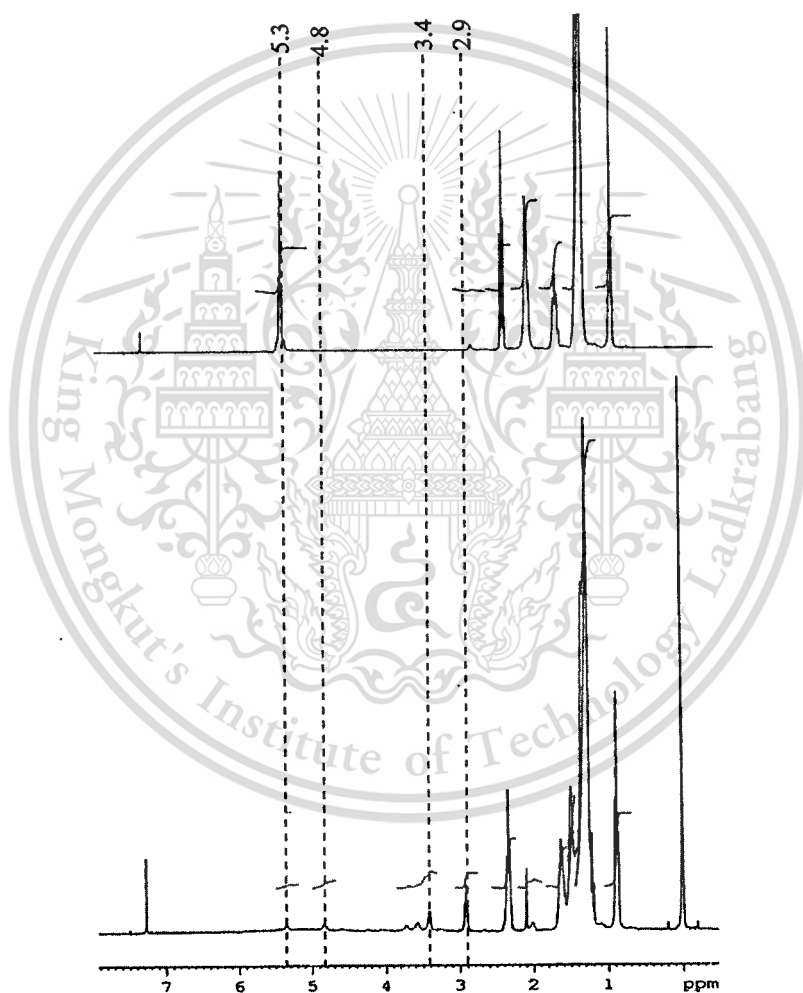


Figure 4.4 ^1H -NMR spectrum of epoxidised product with acetic acid and hydrogen peroxide (a) and without hydrogen peroxide (b) at the same reaction temperature and time. (Hydrogen peroxide = 0.35 mol, Acetic acid = 0.3 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50°C , Time = 4 hours, Step 2: Temperature = 30°C , Time = 15 hours)

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From the above results, it is confirmed that both diol and hydroxy-acetoxy cannot be generated by the direct hydration and direct acetylation of oleic acid, respectively. Certainly, diol and hydroxy-acetoxy compounds were derived by ring-opening of epoxidised product with water and acetic acid, respectively.

However, a decrease in yield of epoxidised product is obtained when using 0.7 mol of hydrogen peroxide (Figure 4.2). This is presumably explained that the use of 0.7 mol of 30% hydrogen peroxide can also increase the water content. The opportunity for such water to be in contact with the epoxidised product would be increased, resulting in the lower yield of epoxidised product and *vice versa* for the yield of by-products. From this result, it is interesting to note that the yield of desired product depends largely on the mass transfer across the interface between the aqueous phase and the organic phase.

From the above results, it can be concluded that peracetic acid generated in the aqueous phase can transfer to the organic phase and then further react to form epoxidised oleic acid (EOA). Unfortunately, water presented in 30% hydrogen peroxide and produced from the reaction of hydrogen peroxide together with acetic acid presented in the system and produced after epoxidation of peracetic acid can consecutively perform the ring-opening leading to the high yield of by-products.

Consistently over the single-step synthesis shown in Figure 4.5, the yield of epoxidised product increases while the yield of by-products decreases when the increase in hydrogen peroxide content is from 0.35 - 0.6 mol. However, a dramatic decrease in conversion of oleic acid is obtained when using 0.6 mol of hydrogen peroxide. This implies that the reaction between oleic acid and peracetic acid may be diminished due to a decrease in concentration of peracetic which was generated *in situ* and/or a decrease in delivering into the organic phase. This shall not affect the conversion of oleic acid over two-step synthesis. This is because an excess concentration of peracetic acid which was previously generated during 4 hours preparation prior to epoxidation can be obtained in the system. It indicates that the rate of peracetic acid formation plays important role on the conversion of oleic acid. This is consistent with the previous report [36, 39].

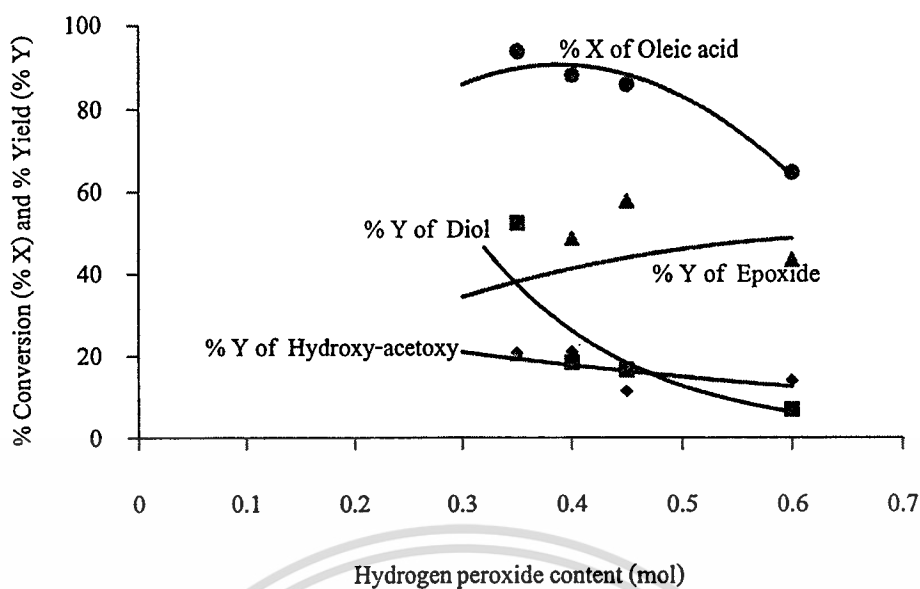


Figure 4.5 Effect of hydrogen peroxide content over single-step synthesis of 9,10-epoxystearic acid (*Acetic acid* = 0.3 mol, *Oleic acid* = 0.1 mol, H_2SO_4 = 0.007 mol, *Step 1*: *Temperature* = 30 °C, *Time* = 15 hours)

From the above result, the high conversion of oleic acid and high yield of epoxidised product can be obtained when using 0.6 and 0.45 mol of hydrogen peroxide over the two-step and single-step synthesis, respectively. Further experiments were therefore carried out with these hydrogen peroxide contents to study the effects of acetic acid.

4.1.2 Effect of acetic acid

Acetic acid acts as the oxygen carrier and gets regenerated once the epoxidation reaction takes place [36, 39]. Hence, acetic acid also acts as a catalyst in the epoxidation reaction. However, acetic acid can also hydrolyse the oxirane ring formed during the epoxidation [3, 37]. The level of acetic acid should be such that both effects are balanced. Therefore, the effect of acetic acid on the epoxidation of oleic acid was investigated at various acetic acid contents (0.2-0.4 mol).

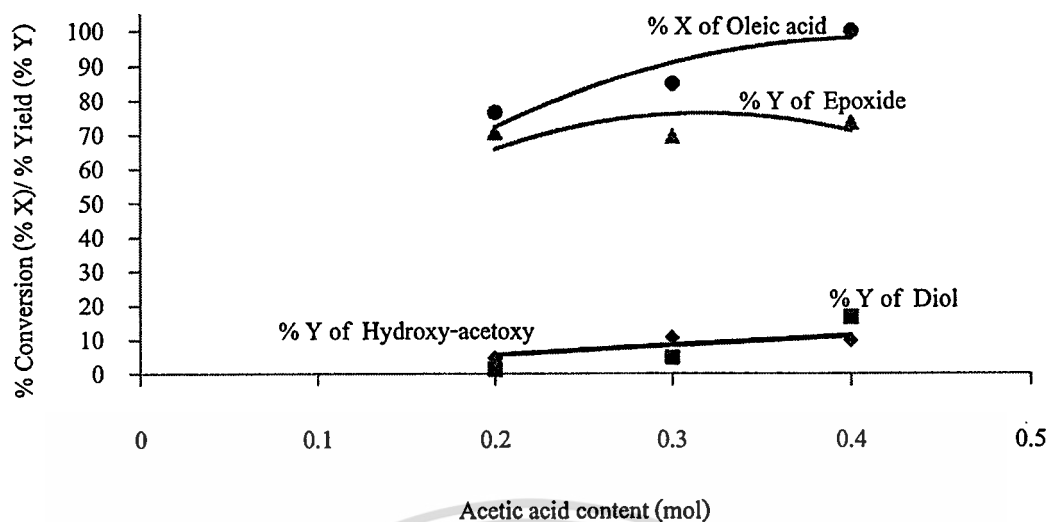


Figure 4.6 Effect of acetic acid content over two-step synthesis of 9,10-epoxystearic acid
(Hydrogen peroxide = 0.6 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 15 hours)

From Figure 4.6, it is clearly seen that as acetic acid content increases, the conversion of oleic acid increases over two-step synthesis. However, the increased acetic acid content has a detrimental effect on the epoxidised product, as the acid promotes the hydrolysis of the epoxide, hence decreasing its final yield. As can be seen from Figure 4.6, a 0.2 mol of acetic acid gives a moderately high conversion of oleic acid and a negligible rate of ring-opening.

Although an increase in conversion of oleic acid is initially obtained when increases acetic acid content in the case of single-step synthesis (Figure 4.7), a dramatic decrease in conversion of oleic acid is obtained when using acetic acid at 0.4 mol. Again, this implies that reaction between oleic acid and peracetic acid may be diminished, as earlier discussed in the effect of hydrogen peroxide. In addition, only a slightly change in yield of epoxidised product can be observed when using acetic acid over 0.1 mol.

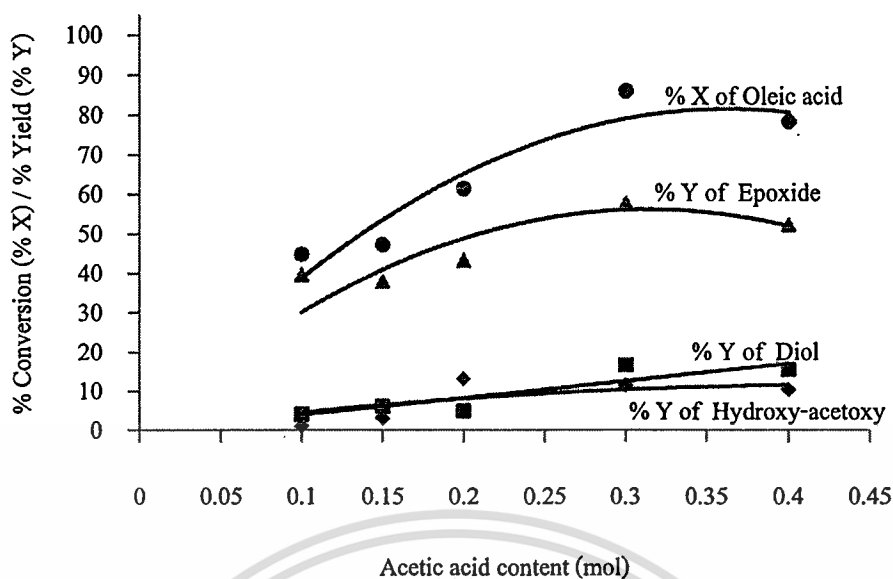


Figure 4.7 Effect of acetic acid content over single-step synthesis of 9,10-epoxystearic acid
(Hydrogen peroxide = 0.45 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1:
Temperature = 30 °C, Time = 15 hours)

From the above result, a relative higher conversion of oleic acid and yield of epoxidised product can be obtained over two-step synthesis, as compared to single-step synthesis. This is presumably due to the relative higher peracetic acid concentration generated at higher reaction temperature (50 °C). It is interesting to investigate the effect of peracetic preparation temperature.

4.1.3 Effect of reaction temperature and time over peracetic preparation

In the case of two-step synthesis, the higher relative selectivity of epoxidised product (88.87%) is pronounced (Figure 4.8), although the lower relative conversion of oleic acid (64.21%) can be obtained when the preparation of peracetic acid was done at 30 °C, as compared to the preparation at 50 °C. It is interesting to note that two-step (B) synthesis can provide the higher selectivity of epoxidised product, as compared to single-step synthesis with a slightly difference in conversion of oleic acid obtained. This implies that the prior generation of peracetic acid can stabilise the selectivity of epoxidised product and diminish the selectivity of by-products, as earlier discussed. Therefore, only two-step synthesis should be investigated over the other parameters.

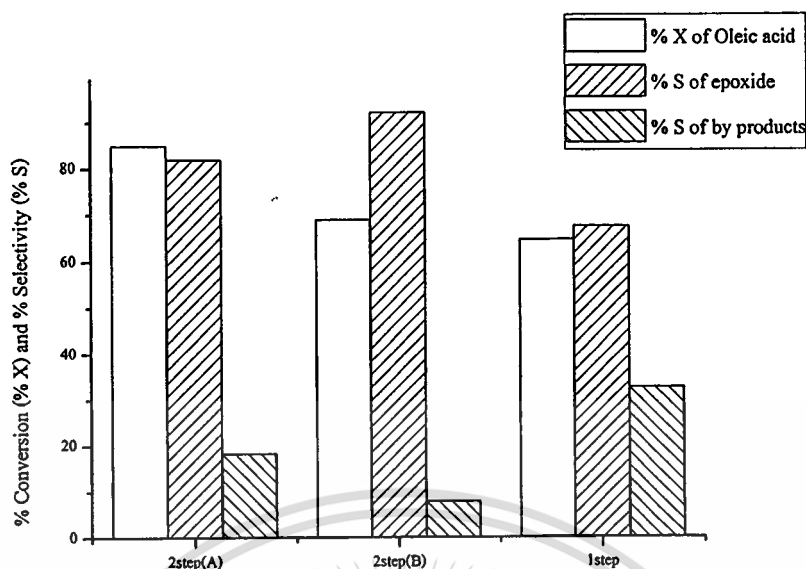


Figure 4.8 Data comparison between % conversion and % selectivity obtaining from single step, two-step (A) and two-step (B) synthesis of 9,10-epoxystearic acid (*Hydrogen peroxide = 0.6 mol, Acetic acid = 0.3 mol, Oleic acid = 0.1 mol, $H_2SO_4 = 0.007$ mol,* Single step : Temperature = 30 °C, Time = 15 hours
Two-step (A) Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 15 hours
Two-step (B) Step 1: Temperature = 30 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 15 hours

As expected, the conversion of oleic acid increases when the preparation time of peracetic acid increases (Figure 4.9) due to an increase in concentration of peracetic acid. However, a marked drop of the yield of epoxidised product is obtained. This is presumably because the water generated from the reaction of hydrogen peroxide and acetic acid can also be pronounced in the reaction system. Such water and acetic acid can consecutively carry out the ring-opening leading to the high yield of by-products, as earlier discussed.

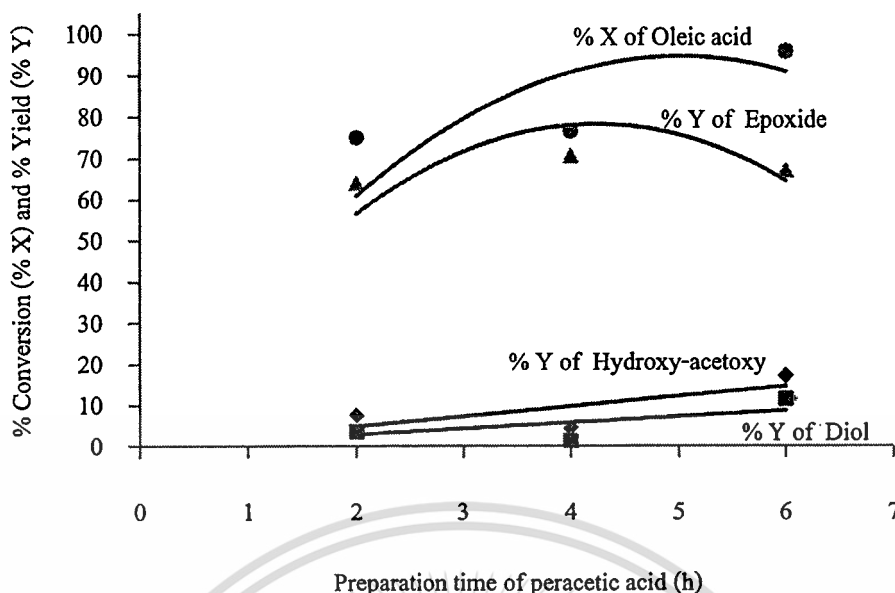


Figure 4.9 Effect of the preparation time of peracetic acid two-step synthesis of 9,10-epoxystearic acid (*Acetic acid* = 0.2 mol, *Hydrogen peroxide* = 0.6 mol, *Oleic acid* = 0.1 mol, H_2SO_4 = 0.007 mol, *Step 1: Temperature* = 50 °C, *Time* = 2, 4, 6 hours, *Step 2: Temperature* = 30 °C, *Time* = 15 hours)

4.1.4 Effect of reaction time

From Figure 4.10, the conversion of oleic acid increases with reaction time. However, a decrease in epoxidised product is also observed. It is indicated that an increase in reaction time can also increase the ring-opening reaction leading to the decrease in yield of epoxidised product. It is consistent with the Campanella's report [39] that hydrolysis of epoxidised product is a slow reaction that proceeds at the liquid-liquid interphase, but only after an extended reaction time, when enough active interfacial area is developed. Hence, the 15 hours of reaction time was chosen to investigate the effect of H_2SO_4 content.

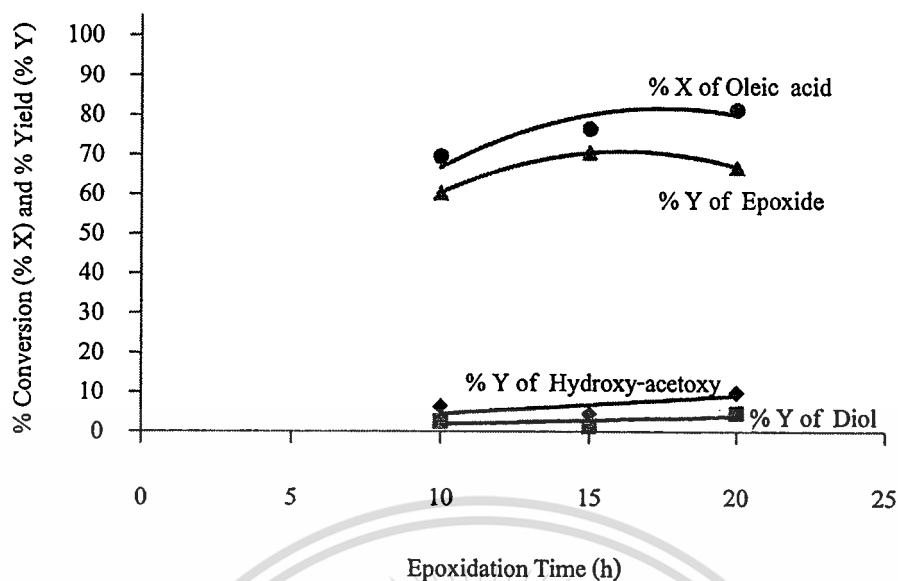


Figure 4.10 Effect of reaction time over two-step synthesis of 9,10-epoxystearic acid
(Hydrogen peroxide = 0.6 mol, Acetic acid = 0.2 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 10, 15, 20 hours)

4.1.5 Effect of sulfuric acid

To investigate the effect of H_2SO_4 content on the epoxidation reaction, the amount of acid was varied from 0.002 to 0.013 mol. Generally, with an increase in acid content, conversion of oleic acid increases (Figure 4.11). It is also observed that the yield of epoxidised product reaches the maximum when using 0.007 mol of H_2SO_4 . It is evident that the relative higher sulfuric acid can promote the ring-opening reaction leading to the increase in the yield of by-products. This is consistent with the previous discussion that the by-products, diol and hydroxy-acetoxy compounds, were derived by ring-opening of epoxidised product with water and acetic acid, particularly under acid catalysed condition.

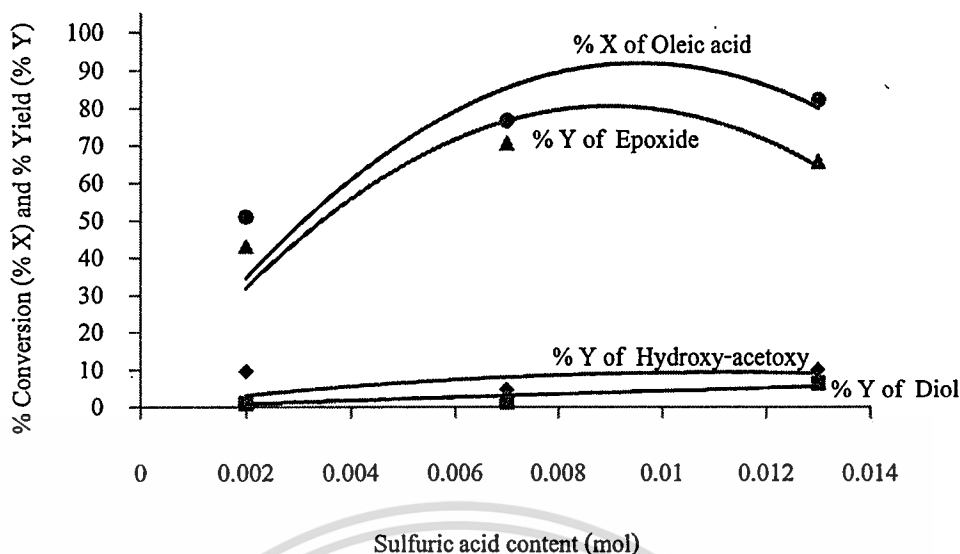
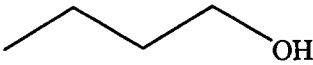
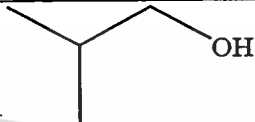
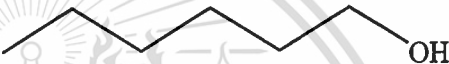
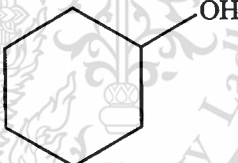
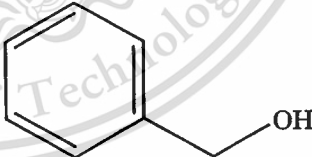


Figure 4.11 Effect of sulfuric acid over two-step synthesis of 9,10-epoxystearic acid
*(Hydrogen peroxide = 0.6 mol, Acetic acid = 0.2 mol, Oleic acid = 0.1 mol,
 Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C,
 Time = 15 hours)*

4.2 Synthesis of synthetic lubricants

As previously mentioned, the preparation of lubricant-based stock from unsaturated oleic acid involves two steps: (i) epoxidation of oleic acid via H_2O_2 (section 4.1) and (ii) ring-opening reaction via alcoholysis and esterification of the carboxyl group through alcohol. For the investigation of the effect of alkyl group on the physical and thermal properties, different alcohols were used in the reaction (Table 4.1).

Table 4.1 Type of alcohols used to investigate the effect of branch chain group which influenced the physical and thermal properties of synthetic lubricants.

Alcohol	Chemical Structure
<i>n</i> -Butanol	
Isobutanol	
<i>n</i> -Hexanol	
<i>n</i> -Decanol	
Cyclohexanol	
Benzyl alcohol	

Reaction of epoxidised oleic acid (EOA) with various alcohols, namely *n*-butanol, isobutanol, *n*-hexanol, cyclohexanol, benzyl alcohol, and *n*-decanol (Table 4.1) were performed in the presence of a catalytic amount of sulfuric acid. The main purpose for choosing the above alcohols is that *n*-butanol is a short straight chain alcohol, isobutanol is a short branch chain alcohol, *n*-hexanol and *n*-decanol are a medium and a longer straight chain alcohol, respectively, while cyclohexanol and benzyl alcohol are a bulkier cyclic and aromatic alcohol.

4.2.1 Effect of alcohol

The resulting products from the reaction of various alcohols with EOA were analysed by ^1H -NMR (Figure 4.12) and GC (Figure 4.13).

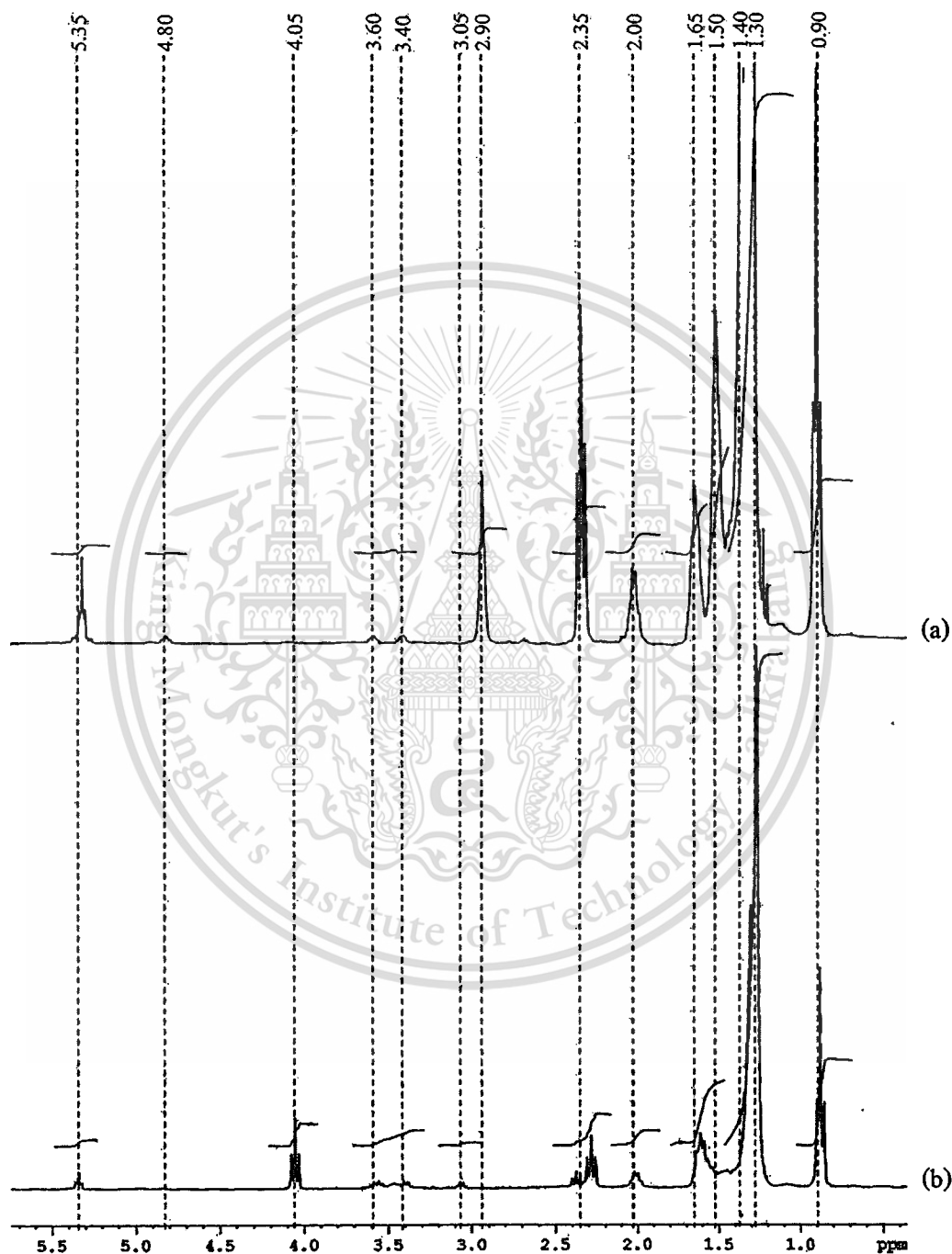


Figure 4.12 ^1H -NMR spectrum of the resulting product from the epoxidation of oleic acid (a) and the resulting product from the reaction of epoxidised oleic acid and *n*-decanol (b).

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From Figure 4.12b, there is no signal at 2.90 ppm which represents the epoxidised oleic acid. It is confirmed that epoxidised oleic acid can completely react with *n*-decanol. However, ^1H -NMR spectra cannot be used to identify the difference between products in the mixture from the reaction with various alcohols. Using of GC, otherwise, can separate the mixture which then be analysed by MS. An example of GC chromatogram is shown in Figure 4.13.

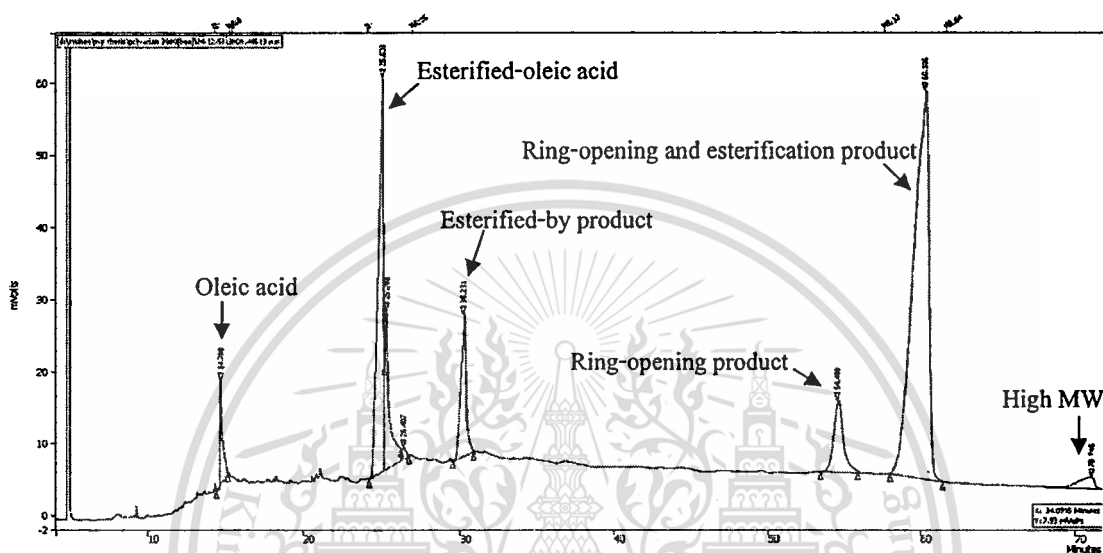
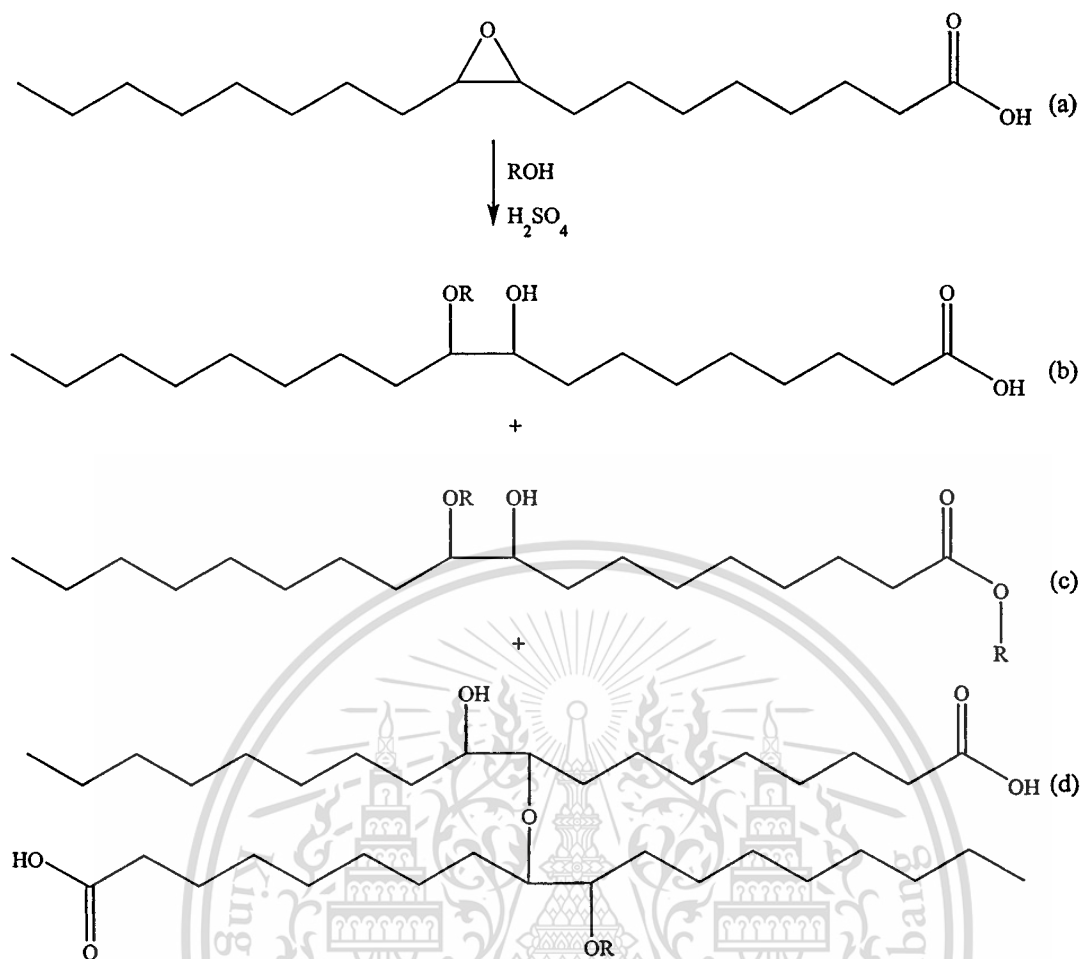


Figure 4.13 GC chromatogram of the resulting product mixture from the reaction of epoxidised oleic acid and *n*-decanol.

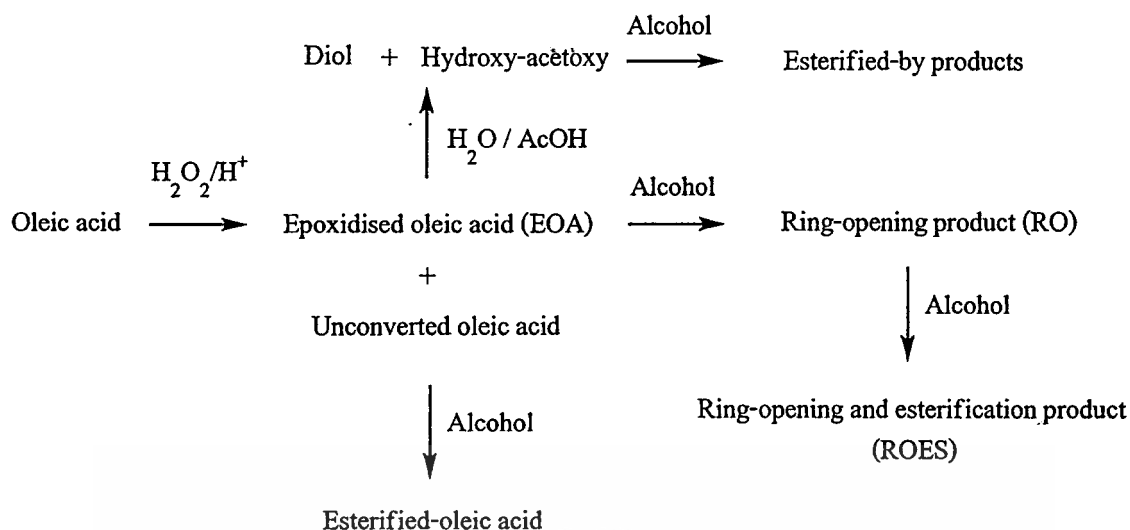
Consistently, no yield of epoxidised oleic acid (EOA) can be observed in the reaction using *n*-decanol as nucleophile. This confirmed that EOA can be completely converted. As expected, the reaction of EOA and alcohols gave the majorities of ring-opening reaction (RO) and ring-opening with esterification reaction (ROES) which led to products shown as structure b and c in Scheme II, respectively



Scheme II

Moreover, a trace amount of high molecular weight product (with MW higher than that of ROES) can be observed. This may be derived from intermolecular epoxy-epoxy reaction which gives a variety of products including oligomers (Scheme II, structure d).

Note that the nuclear magnetic resonance spectra gave the resulting product from the epoxidation of oleic acid yielding 70.64 % of epoxidised oleic acid, 1.40 % of diol (the nucleophilic attack by water on the oxirane ring of EOA), 4.58 % of hydroxy-acetoxy (the nucleophilic attack by acetic acid on the oxirane ring of EOA), and 23.38 % of oleic acid (unconverted reactant) (see section 4.1). Under the reaction conditions used, not only the epoxidised oleic acid can be converted to RO and ROES but also the unconverted oleic acid, diol and hydroxy-acetoxy can be transformed to esterified products (Scheme III).



Scheme III

Therefore, the resulting product mixtures from the reaction of various alcohols with EOA were analysed by GC-MS as summarised in Table 4.2. These lubricating products will be designated as L-alcohol such as L-butanol, L-isobutanol.

Table 4.2 Product distribution of alcohol-modified EOA

% Product distribution (% D) / Conversion (% X)	Alcohol-modified EOA					
	L- Butanol	L- isobutanol	L- hexanol	L- decanol	L-cyclo Hexanol	L-benzyl alcohol
% D of Oleic acid	1.23	1.19	1.43	2.12	3.42	3.67
% D of Esterified- oleic acid	24.93	26.21	26.57	23.95	23.41	24.37
% D of Esterified- by products	8.37	10.23	9.22	9.17	10.11	10.54
% D of RO ^a	5.97	11.57	6.45	8.56	15.89	21.84
% D of ROES ^b	57.89	48.29	54.16	54.78	46.28	38.34
% D of High MW	1.6	2.52	2.17	1.42	0.9	1.24
Total % D	100.00	100.00	100.00	100.00	100.00	100.00
% X of EOA	100.00	100.00	100.00	100.00	100.00	100.00
% X of Ring-opening	90.88	81.45	89.73	86.78	74.81	64.44
% X of non-EOA	96.44	96.84	96.16	93.98	90.74	90.49

^a Product generated by ring-opening reaction of EOA and alcohol

^b Product generated by both ring-opening and esterification reaction of EOA and alcohol

Reactant composition : epoxidised oleic acid = 70.62, diol = 1.15, hydroxy-acetoxy = 4.75, oleic acid = 23.38

Reaction conditions : temperature = 120 °C, time = 20 h, EOA = 1 mol, alcohol = 4 mol

% X of EOA can be calculated from the remaining of epoxidised oleic acid (EOA)

% X of Ring-opening can be calculated from the conversion of RO to ROES and High MW

% X of non-EOA can be calculated from the conversion of oleic acid, diol and hydroxy-acetoxy to esterified-oleic acid and esterified-by products

% X of EOA is calculated as follows:

$$\% \text{ X of EOA} = \frac{(\text{initial yield of EOA} - \text{final yield of EOA}) \times 100}{\text{Initial yield of EOA}}$$

For example; (Reaction of EOA with *n*-decanol)

$$\begin{aligned} \% \text{ X of EOA} &= \frac{(\text{initial yield of EOA} - 0) \times 100}{\text{Initial yield of EOA}} \\ &= 100 \% \end{aligned}$$

From Table 4.2, a 100 % conversion of EOA (%X of EOA) can be observed over all reactions with alcohols. This implies that a complete conversion of EOA to ring-opening products (RO) can be performed. This is due to the fact that epoxy group can readily functionalised [26].

% X of Ring-opening is calculated as follows:

$$\% \text{ X of Ring-opening} = \frac{(\% \text{ D of ROES} + \% \text{ D of high MW}) \times 100}{(\% \text{ D of RO} + \% \text{ D of ROES} + \% \text{ D of high MW})}$$

For example; (Reaction of EOA with *n*-decanol)

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$$\begin{aligned}
 \%X \text{ of Ring-opening} &= \frac{(54.78 + 1.42) \times 100}{(8.56 + 54.78 + 1.42)} \\
 &= 86.78 \%
 \end{aligned}$$

As expected, the ring-opening product (RO) can be consecutively converted to form the esterified product (ROES) and a trace product distribution of high MW products. It is explained that the rate of intermolecular epoxy-epoxy reaction is lower due to its molecular motion, as compared to rate of esterification. However, the conversion of ring-opening product (%X of Ring-opening) depends largely on the type of alcohols. A branched short chain alcohol (isobutanol) gives lower product distribution of esterified product, as compared to the straight short chain alcohol (*n*-butanol). This is due to the fact that the presence of branching groups creates a lot of steric hindrance. Reactive centers near bulky groups usually fail to react except under forcing conditions.

Regarding to the effect of chain length of straight alcohols, it was observed that as the chain length of straight alcohols increased (*n*-butanol, *n*-hexanol, and *n*-decanol), it provides a slightly lower product distribution of ROES and % X of Ring-opening. Accordingly, a longer chain alcohol can readily react with the carboxylic acid to form ROES, as compared to a branched alcohol. This indicates that steric hindrance is more important when the substituents are in a plane perpendicular to C-OH. This shall not be the case of cyclohexanol and benzyl alcohol. A dramatic decrease in product distribution of ROES can be observed. This is clearly because of the effect of the bulkier group of cyclic and aromatic ring. This result is consistent with the previous reports [41-43] that longer or bulkier alcohols provide a lower product distribution of product generated both ring-opening and esterification reaction.

Moreover, the observed lower product distribution of both ring-opening and esterification of epoxidised oleic acid by benzyl alcohol can be explained by the protonation effect [44]. Generally, the reaction mechanism for the formation of esters from carboxylic acids and alcohols in the presence of concentrated sulfuric acid acting as the catalyst can be derived by the following step: (i) the carboxylic acid takes a proton from the concentrated sulfuric acid and delocalises to form the positive charge on carbon atom and (ii) lone pairs on the oxygen atom of alcohol molecule attaches positive carbon to form ester and liberate water molecule [45]. However, the

benzyl alcohol can also readily take proton leading to the weaker nucleophile. Thus, the reaction of lone pair of alcohol and positive carbon to form ester is diminished.

% X of non-EOA is calculated as follows:

$$\%X \text{ of non-EOA} = \frac{(\% D \text{ of esterified-oleic acid} + \% D \text{ of esterified-by products}) \times 100}{(\% D \text{ of oleic acid} + \% D \text{ of esterified-oleic acid} + \% D \text{ of esterified-by products})}$$

For example; (Reaction of EOA with *n*-decanol)

$$\begin{aligned} \%X \text{ of non-EOA} &= \frac{(23.95 + 9.17) \times 100}{(2.12 + 23.95 + 9.17)} \\ &= 93.98 \% \end{aligned}$$

From Table 4.2, the esterified-oleic acid and esterified-by products can be obtained. These products were derived by the esterification of alcohols with the unconverted oleic acid (Esterified-oleic acid) and with diol or hydroxy-acetoxy by-products (Esterified-by products) which are contaminants from the epoxidation of oleic acid (Scheme III). The conversion of unconverted oleic acid, diol and hydroxy-acetoxy by-products (%X of non-EOA) is nearly a 100 %. This is because a high reaction rate can be obtained at high reaction temperature (> 100 °C). Moreover, removal of water from the reaction mixture can facilitate the shift toward the equilibrium leading to the high conversion.

Consistently, Izabelly *et.al.* [46] report that the high ester yield can be achieved over the oleic acid esterification, particularly at high reaction temperature. Accordingly, the oleic acid can be improved by the chemical modification with a suitable alcohol which is influenced with physical and thermal properties.

4.2.2 The physical properties of alcohol-modified EOA

It is noted that, by analysing the physical and thermal properties of the resulting alcohol-modified EOA, the effects of the molecular structure (such as the branching, length of the carbon chain, and bulky cyclic and aromatic ring) and various product distribution in the reaction

systems would be considered. It is difficult to study the effect of alcohol structure on the properties of alcohol-modified EOA with difference product distribution. However, since the product distribution of L-butanol, L-hexanol and L-decanol are close, the structure-properties trend can be made. Moreover, with short chain alcohol such as isobutanol and *n*-butanol, the properties of alcohol-modified EOA will not be much different with significant change in product distribution.

Table 4.3 The physical properties of alcohol-modified EOA.

Alcohol-modified EOA lubricating oil	Physical properties				
	Vis40 (cSt)	Vis100 (cSt)	VI	Pour point (°C)	TAN (mgKOH/g)
Oleic acid	19.1	7.6	424	-6	-
L-butanol	35.5	6.7	147	-18	1.03
L-isobutanol	32.1	5.5	113	-15	1.75
L-hexanol	37.8	7.5	172	-39	1.24
L-decanol	40.4	4.8	-	-18	1.34
L-cyclohexanol	119.1	14.6	125	-36	2.82
L-benzyl alcohol	53.8	8.8	142	-39	3.56

One of the most important lubricants properties derived from petroleum and modified bio-oil is viscosity. Interestingly, modification of the oleic acid through chemical processing to improve its viscosity is possible for achieving the ultimate goal (Table 4.3). The nucleophilic reagents of alcohol are known to add to an oxirane ring, resulting in ring-opening product (RO) (part 2.5.2). These ring-opening reactions in EOA could result in the additional chain at the oxirane carbons (earlier sites of unsaturation in oleic acid). Additionally, the presence of hydrogen-bonded OH groups results in the increased viscosity of the modified EOA.

It is expected that branching of alcohol would play a marked role in altering the viscosity of the modified EOA. Such branching of alcohol reduces the interactions between carbon chains by hindering the approach of neighboring molecules. However, when comparing the resulting product of alcohol-EOA derived from the *n*-butanol (L-butanol) and isobutanol (L-isobutanol) that contained the same number of carbon atoms, little variation in the viscosity of the systems was observed, as shown in Table 4.3. This is presumably because of their shorter hydrocarbon

chains (C4 alcohols). This agrees with Knothes's study and Yao's study [47,48] that the viscosity of the branched isopropyl oleate was close to its straight chain counterpart, propyl oleate. The branch on the alcohol moieties does not affect viscosity very much.

Regarding to the viscosity of the resulting product of alcohol-EOA reaction with the same straight chain structure but with different chain length (L-butanol, L-hexanol, and L-decanol) (Table 4.3). It is observed that a tendency toward a viscosity increase with increasing length of the hydrocarbon segment. Moreover, the effect became more evident at lower temperatures (Vis40), where the molecular movement was even more restricted. The increase of viscosity of the longer chain length alcohol-modified EOA is most certainly due to the gradual increase of the extents of inter and intra chain interaction and entanglements between the chains. It is expected that the resulting product of longer chain alcohol-EOA reaction would provide a higher viscosity when the product distribution of ring-opening and consecutively esterification is increased (ROES). However, that is not the case due to the limitation of reaction of long chain alcohol and EOA.

Although the lower product distribution generated by both ring-opening and esterification (ROES) when using cyclohexanol and benzyl alcohol is obtained, as compared to the straight and branch chain alcohol a dramatic increase in viscosity can be obtained over the reaction between cyclic (L-cyclohexanol) and aromatic ring (L-benzyl alcohol) with EOA. It is evidenced that the viscosity of chemically-modified lubricating oil depends largely on the molecular structure of alcohol.

A dramatic increase in viscosity of L-cyclohexanol and L-benzyl alcohol is presumably explained that cyclic and aromatic ring can pronounce the stronger interaction between the chains, as compared to straight longer chain alcohol. In the case of using benzyl alcohol as nucleophile, the aromatic rings of the resulting product are capable of π - π , π /CH and π /OH interactions. Such interaction of modified bio-oil is similar to that of phenylalanine, tyrosine and tryptophan interaction which is found in enzyme catalytic activity [49]. In the case of using cyclohexanol as nucleophile, it is presumable suggested that improper H-bonded between axial C-H bonds in cyclohexane derivatives and O-H contacts, can allow the chains to come close leading to the increase in viscosity. The improper hydrogen-bonded cyclohexane was studied by Nikolaos Zervos and *et. al.* [50]. Moreover, the melting point and boiling point of cyclohexanol (mp = 26 °C, bp = 161 °C) is higher than 1-hexanol (mp = -47 °C, bp = 157 °C) [51-52]. This implies that the stronger interaction of cyclohexane derivatives can be obtained, as compared to the long chain

hexanol derivatives. From the above results, it can be concluded that this approach of chemical modification significantly improves the viscosity of oleic acid, particularly using cyclic and aromatic alcohol.

There is an important fact in determining of how well an oil will behave as a potential lubricant is to evaluate the pour point. The low temperature flow property of bio-oils is extremely poor and this limits their use at low operating temperatures especially as automotive and industrial fluids. Accordingly, the prepared compounds described above were screened for low-temperature behavior through determination of pour point.

Modified EOA exhibited a pour point of -15 to -39 °C (Table 4.3), which is an improvement over that of oleic acid. The chemically modified EOA would interfere with the formation of macrocrystalline structures during low-temperature applications and would provide enhanced fluidity to oleic acid. From Table 4.3, it was found that both L-butanol and L-isobutanol provide a slightly decrease in pour point, as compared to oleic acid. While a dramatic decrease in pour point can be obtained when use a medium chain (L-hexanol), cyclic (L-cyclohexanol) and aromatic (L-benzyl alcohol) alcohols as nucleophile. This is consistent with the Lathi and *et. al.* [7] that a six-carbon chain-length ester has been observed to deliver the most desired pour point properties for the modified bio-oil.

As expected, as the chain length (in the case of *n*-hexanol) and bulkier group (in the case of cyclohexanol and benzyl alcohol) of the ester increased, a corresponding improvement in pour point is observed, which may be due to the greater ability of the longer-chain and bulkier group esters to more effectively disrupt macrocrystalline formation at reduced temperatures. Interestingly, a negative effect on the low-temperature performance of the resultant products was observed when a longer chain alcohol, *n*-decanol, was used (L-decanol). This is presumably due to the body motion of the modified EOA molecules decreases with increasing chain length. This leads to the crystalline aggregate. Consistently, Hwang *et. al.* [30] report that, with the changing in the alcohol group of epoxidised soybean oil from methyl to longer alkyl chains up to the hexyl group, pour points were depressed further. In addition, they also reported that, when the decyl group was incorporated in the product, the pour points increased remarkably. Pour point studies of the resulting products showed that the pour points varied with the substituents alcohol. Products with the substitution of C4 alcohol (both *n*-butanol and isobutanol) and long chain C10 alcohol showed the highest pour points (-18, -15, and -18°C, respectively). While, a better of

low temperature flow property can be obtained when use *n*-hexanol, cyclohexanol, and benzyl alcohol as nucleophile.

It is known that the chemically modified fatty acids show a poor corrosion protection due to the presence of unconverted carboxylic functionality [53]. From the Table 4.3, it shows that the total acid number of chemically modified EOA is higher than that the lube base oil (0.01-0.05 mgKOH/g, see Table 4.5). This corresponds the unconverted oleic acid and the remaining ring-opening products, as discussed earlier.

4.2.3 The thermal properties of alcohol-modified EOA

This thesis presents a systematic approach to improve not only the low temperature fluidity of modified EOA, but also the thermal and oxidation behavior. It is known that unsaturated fatty acids, like oleic acid have poor thermal and oxidative stability primarily due to the presence of bis-allylic protons [54,55]. The stability of modified EOA was studied using thermogravimetric analysis (TGA), determined as their onset temperatures. The onset temperature is the temperature at which a rapid increase in the rate of decomposition and oxidation is observed and obtained by extrapolating the tangent drawn on the steepest slope of reaction exotherm to the baseline. A high onset temperature would suggest a high stability of the modified oil. The degradation under thermal conditions has mostly been studied in the inert nitrogen and has been concerned with structure determination and degradation mechanisms, while the presence of air can accelerate the oxidation reaction.

Figure 4.14 shows the thermogram of alcohol-modified EOA obtained from TGA in both N₂ and air. The onset temperature will be calculated and shown in Table 4.4.

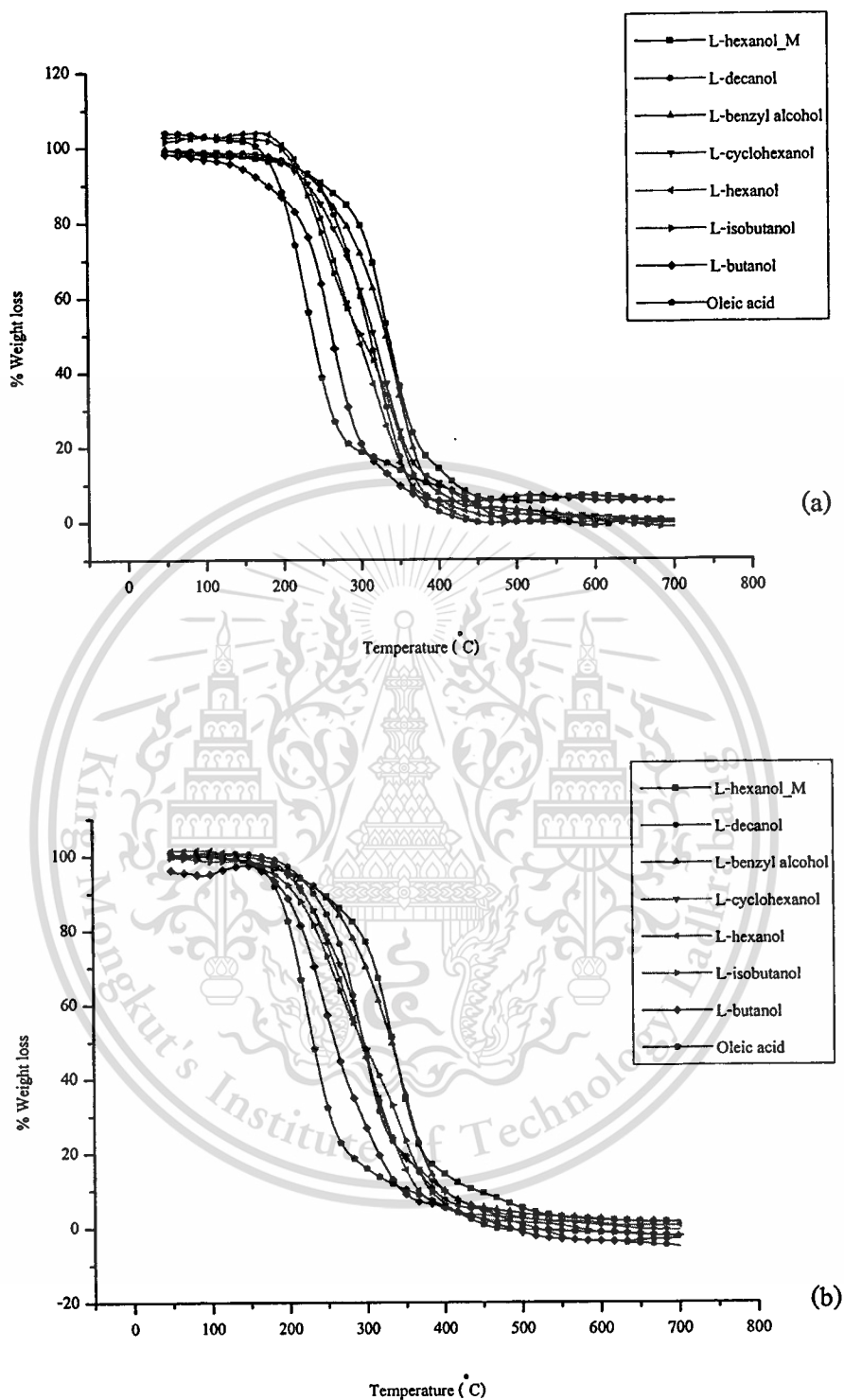


Figure 4.14 TGA of alcohol-modified EOA in N_2 (a) and TGA of alcohol-modified EOA in air (b)

Table 4.4 The thermal properties of alcohol-modified EOA.

Alcohol-modified EOA	Onset temperature (°C)	
	In N ₂	In air
Oleic	190	185
L-butanol	220	200
L-isobutanol	205	200
L-hexanol	220	210
L-decanol	250	245
L-cyclohexanol	260	240
L-benzyl alcohol	270	260
L-hexanol_MCPBA	295	287

From Table 4.4, it is found that the onset temperatures of oleic acid and modified EOA in the inert nitrogen are consistent with those in the presence of air. As expected, the L-hexanol MCPBA synthesised from the 100 % EOA (section 3.4.3) provides the higher stability. This confirmed that the chemically modified EOA can improve the stability of unsaturated fatty acid. However, the chemically modified EOA synthesised by hydrogen peroxide provides the lower stability because such resulting product contains the several composition, as discussed above.

The alcohol-modified EOA samples show higher oxidation stability than the oleic acid. This shows that oxidation stability considerably improved due to the removal of unsaturation. No significant change was observed with an increasing chain length of the C4 alcohol both *n*-butanol (L-butanol) and isobutanol (L-isobutanol). Additionally, the oxidation onset temperature increases with the chain length of the alcohol group. L-decanol has the highest value (250 °C) of onset temperature, while L-butanol has the lowest (220 °C).

Conversely, Sharma *et.al.* [32] reported that the oxidation onset temperature decreases with the chain length of the branching group. Experimentally, ring-opening product from the reaction of soybean oil with acetic anhydride (Ace-SBO) has the highest value (174°C) of onset temperature, while ring-opening product from the reaction of soybean oil with hexanoic anhydride (Hex-SBO) has the lowest (161°C). This shall not be the case with alcohol-modified EOA. This is due to the fact that the chemically modified fatty acid possesses the lower molecular

weight, as compared to chemically modified vegetable oil (~ 1:3 times). The substitution of longer chain on primarily hydroxyl group of glycerol can significantly affect the sterically hinder leading to the rapidly degradation and chain transfer. While, the longer chain substitution on EOA can contribute the inter and intra chain interaction and entanglements between the chains leading to the reduction of chain motion. Steric hindrance may be a possible reason, which provides the poor stability of chemically modified vegetable oil.

Moreover, the cyclohexanol modified EOA (L-cyclohexanol) and benzyl alcohol-modified EOA (L-benzyl alcohol) provides a better stability, as compared to long chain alcohol-modified EOA. This is presumably due to the increase in interaction between chains, as discussed above.

Table 4.5 The physical and chemical properties of lube base oil and alcohol-modified EOA.

Properties	Viscosity @ 40 °C, cSt	Viscosity @ 100 °C, cSt	Viscosity index	Pour point, °C	Total acid number, mg KOH/g
60 SN	8.5-12	report	95	-9	0.05
150 SN	30.31	5.23	103	-12	0.01
500 SN	93.75	10.77	98	-9	0.01
150 SB	report	31-34	95	-9	0.05
L-butanol	35.5	6.7	147	-18	1.03
L-iso butanol	32.1	5.5	113	-15	1.75
L-hexanol	37.8	7.5	172	-39	1.24
L-decanol	40.4	4.8	-	-38	1.34
L-cyclohexanol	119.1	14.6	125	-36	2.82
L-benzyl alcohol	53.8	8.8	142	-39	3.56

From Table 4.5, it can be concluded that the chemically modified EOA is suitable to be used as a lube base oil substitute because the viscosities both at 40 and 100 °C which are in the range, as compared to the lube base oil 150 SN. However, the high total acid number of the chemically modified EOA is obtained due to the remaining of carboxylic group. Therefore, these

synthetic products would be more suitable if further modified to increase the conversion of oleic acid and product distribution of esterified product.



Chapter 5

Conclusions and Suggestions

5.1 Conclusions

Epoxide of oleic acid (9,10-epoxystearic acid) can be prepared by epoxidation using hydrogen peroxide and acetic acid under various reaction conditions catalysed by sulfuric acid. The products were all analysed using ^1H NMR spectra. The formation of epoxidised product from oleic acid was proposed by epoxidation with peracetic acid generated from acetic acid and hydrogen peroxide while the by-products, diol and hydroxy-acetoxy compounds, were derived by ring-opening of epoxidised product with water and acetic acid, respectively.

Two-step synthetic process (generation of peracetic acid prior to epoxidation) provided the higher yield of epoxidised product, as compared to single-step synthesis (generation of peracetic acid during epoxidation). The suitable epoxidation condition was investigated by the variation of hydrogen peroxide, acetic acid and sulfuric acid content, reaction time, and reaction temperature. It was found that an excess amount of hydrogen peroxide was necessary in the reaction to achieve high reaction conversion and high yield. However, the water presented in the feed (30% hydrogen peroxide) and from the reaction of hydrogen peroxide and acetic acid in the presence of high sulfuric acid content produced the by-products. The conversion of oleic acid increases when the preparation time of peracetic acid increases (for the two-step synthesis) due to an increase in concentration of peracetic acid. However, a marked drop of the yield of epoxidised product is obtained due to the formation of by-products. In addition, the conversion of oleic acid increases with reaction time. However, a decrease in epoxidised product is also observed due to the formation of ring-opening reaction of water and acetic acid. Additionally, conversion of oleic acid increases with an increase in acid content and the epoxidised product reaches the maximum when using 0.007 mol of sulfuric acid. A 76 % conversion of oleic acid and 70 % yield of epoxidised product can be obtained by using 0.6 mol of hydrogen peroxide, 0.2 mol of acetic acid, 0.1 mol of oleic acid and 0.007 mol of H_2SO_4 . The optimised reaction temperature for

peracetic acid preparation and for epoxidation were 50 °C and 30 °C whereas the optimised reaction time for peracetic acid preparation and for epoxidation were 4 and 15 hours, respectively.

A 100 % conversion of oxirane ring of 9,10-epoxystearic acid can be observed over all reactions with alcohols used in this work. This is due to the fact that epoxy group can readily be activated. However, a conversion of carboxylic group of 9,10-epoxystearic acid forming esterified-product can partially be achieved. The derivatives generated by chemically modified epoxidised oleic acid showed improvement on some physical properties and thermal/oxidation stability. The properties which depend largely on the bulkiness and chain-length of alcohols were as follows: viscosity@40 °C, 32.1 – 119.1 cSt; viscosity@100 °C, 4.8 – 14.6 cSt; viscosity index (VI), 113 – 172; pour point, -18 – -39 °C, total acid number (TAN), 1.03 – 3.56 mgKOH/g; onset temperature under N₂, 205 – 295 °C; onset temperature under O₂, 200 – 287 °C.

From the above results, these derivatives from oleic acid could be used as a lube base oil substitute because the viscosities both at 40 and 100 °C are in the usable range, as compared to the lube base oil 150 SN. However, the high total acid number of the chemically modified epoxidised oleic acid is obtained due to the remaining of carboxylic group. Therefore, these synthetic products could be further modified by increasing the conversion of oleic acid and product distribution of esterified product.

5.2 Suggestions

The high total acid number of the chemically modified epoxidised oleic acid is obtained due to the remaining of carboxylic group. Therefore, the investigation of the reaction condition to provide high product distribution of esterified product should be studied in order to decrease total acid number.

Generally, vegetable oils possess a high content of unsaturated fatty acids, which are rich in oleic (20 – 45%) and linoleic (10 – 60%). Therefore, vegetable oil will be of interest to be used as a starting material for production of lubricants in a future work. Epoxidation followed by ring opening and esterification should be optimised to improve their properties.

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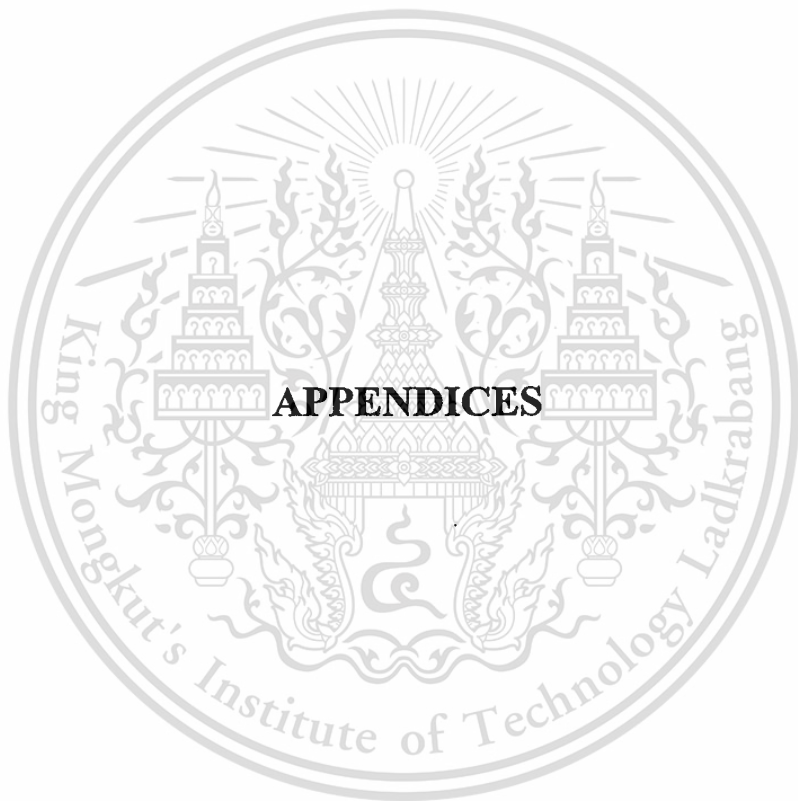
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APPENDIX A

NMR DATA OF PRODUCTS

Table A1 ^1H -NMR data of product from epoxidation in two-step synthesis using Acetic acid = 0.3 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 15 hours.

H_2O_2 (mol)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy- acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
0.35	2.134	1.489	0.798	1.303	80.02	32.72	22.83	24.47
0.4	2.778	0.646	0.570	0.948	82.87	50.40	11.72	20.68
0.45	7.885	2.390	1.000	1.364	90.00	57.81	17.52	14.66
0.6	4.624	0.321	0.355	1.000	84.97	69.48	4.82	10.67
0.7	6.540	2.403	1.000	0.952	92.00	54.98	20.20	16.81

Table A2 ^1H -NMR data of product from epoxidation in single-step synthesis using Acetic acid = 0.3 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 30 °C, Time = 15 hours.

H_2O_2 (mol)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy- acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
0.35	1.677	4.273	0.846	0.505	93.80	20.58	52.45	20.77
0.4	4.111	1.557	0.887	1.000	88.15	48.70	18.44	21.01
0.45	10.078	2.916	1.000	2.436	86.02	57.82	16.73	11.47
0.6	1.937	0.311	0.313	1.573	64.63	43.56	6.99	14.08

Table A3 ^1H -NMR data of product from epoxidation in two-step synthesis using Hydrogen peroxide = 0.6 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50 °C, Time = 4 hours, Step 2: Temperature = 30 °C, Time = 15 hours

Acetic acid (mol)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy-acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
0.2	3.022	0.060	0.098	1.000	76.62	70.64	1.40	4.58
0.3	4.624	0.321	0.355	1.000	84.97	69.48	4.82	10.67
0.4	14.942	3.382	1.000	0.000	100	73.52	16.64	9.84

Table A4 ^1H -NMR data of product from epoxidation in single-step synthesis using Hydrogen peroxide = 0.45 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 30 °C, Time = 15 hours.

Acetic acid (mol)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy-acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
0.1	0.718	0.075	0.009	1.000	44.78	39.65	4.14	0.99
0.15	0.718	0.118	0.029	1.000	47.20	37.91	6.23	3.06
0.2	1.472	0.168	0.225	1.314	61.40	43.24	4.94	13.22
0.3	10.078	2.915	1.000	2.436	86.02	57.82	16.72	11.48
0.4	2.416	0.721	0.241	1.000	78.35	52.31	15.61	10.44

Table A5 ^1H -NMR data of product from epoxidation in single-step and two-step synthesis using Acetic acid = 0.3 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, H_2O_2 = 0.6 mol.

	Integration				%X of oleic acid	%S of epoxidized product	%S of by-product
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm			
2step(A)	4.624	0.321	0.355	1.00	84.87	81.77	18.23
2step(B)	2.035	0.019	0.078	1.000	68.85	92.08	7.92
1step	1.937	0.311	0.313	1.573	64.63	67.40	32.60

Table A6 ^1H -NMR data of product from epoxidation in two-step using Acetic acid = 0.2 mol, Hydrogen peroxide = 0.6 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50 °C, Time = 2, 4, 6 hours, Step 2: Temperature = 30 °C, Time = 15 hours

Time (h)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy-acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
2	2.674	0.149	0.158	1.043	75.06	63.94	3.56	7.56
4	3.022	0.060	0.098	1.000	76.62	70.64	1.40	4.58
6	213.52	36.63	27.40	13.29	95.82	67.09	11.51	17.22

Table A7 ^1H -NMR data of product from epoxidation in two-step synthesis using Hydrogen peroxide = 0.6 mol, Acetic acid = 0.2 mol, Oleic acid = 0.1 mol, H_2SO_4 = 0.007 mol, Step 1: Temperature = 50°C , Time = 4 hours, Step 2: Temperature = 30°C , Time = 10, 15, 20 hours.

Time(h)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy-acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
10	2.086	0.093	0.112	1.052	69.55	60.38	2.69	6.48
15	3.022	0.060	0.098	1.000	76.62	70.64	1.40	4.58
20	4.494	0.317	0.333	1.242	81.52	66.88	4.72	9.91

Table A8 ^1H -NMR data of product from epoxidation in two-step synthesis using Hydrogen peroxide = 0.6 mol, Acetic acid = 0.2 mol, Oleic acid = 0.1 mol, Step 1: Temperature = 50°C , Time = 4 hours, Step 2: Temperature = 30°C , Time = 15 hours.

Sulfuric acid (mol)	Integration				%X of oleic acid	%Y of epoxidized product	%Y of Diol	%Y of Hydroxy-acetoxy
	2.9 ppm	3.4 ppm	4.8 ppm	5.3 ppm				
0.002	1.149	0.028	0.129	1.229	51.04	43.13	1.05	9.68
0.007	3.022	0.060	0.098	1.000	76.62	70.64	1.40	4.58
0.013	3.986	0.388	0.303	1.079	82.19	65.79	6.40	10.00

APPENDIX B

GAS ANALYSIS OF PRODUCTS

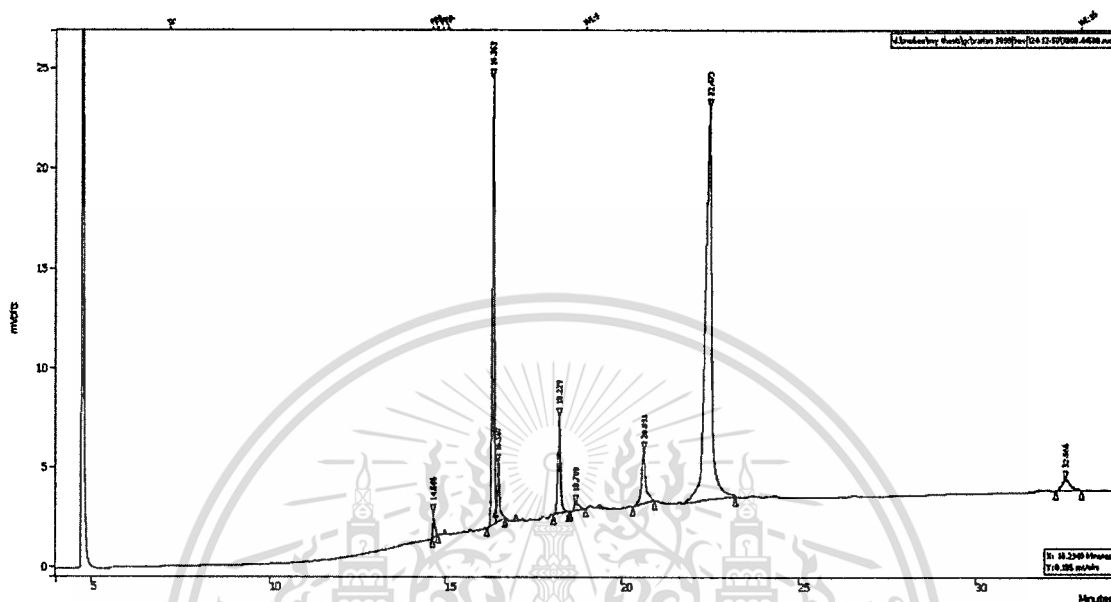


Figure B1 GC chromatogram of the resulting product from the reaction of epoxidised oleic acid and *n*-butanol.

Table B1 GC analysis of the resulting product from the reaction of epoxidised oleic acid and *n*-butanol.

	Oleic	Esterified- oleic acid	Esterified- by product	RO	ROES	High MW	Total
Time	14.686	16.353	18.223	20.593	22.473	32.566	-
Area	3695	84116	28253	20142	238744	9913	-
RF	16	18	18	18	22	33	-
Corrected area	231	4673	1570	1119	10852	300	18745
% D	1.23	24.93	8.37	5.97	57.89	1.60	100

$$\% \text{ D in each product} = \frac{\text{Corrected area} \times 100}{\text{Total corrected area}}$$

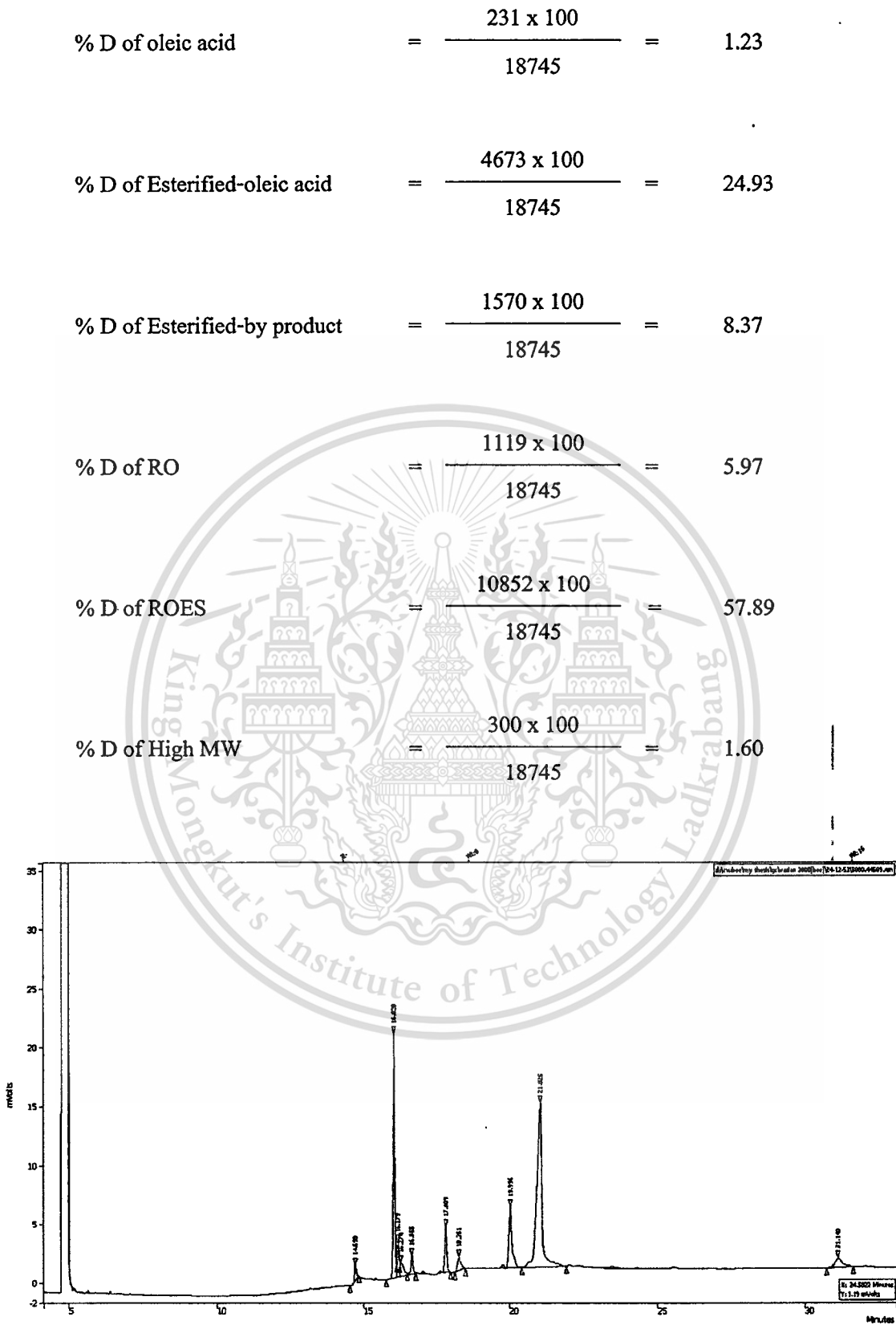


Table B2 GC analysis of the resulting product from the reaction of epoxidised oleic acid and isobutanol.

L-isobutanol	Oleic	Esterified- oleic acid	Esterified- by product	RO	ROES	High MW	total
Time	14.698	16.028	17.809	19.996	21.025	31.14	-
Area	3061	75646	29516	33395	170376	13312	-
RF	16	18	18	18	22	33	-
Corrected area	191	4203	1640	1855	7744	403	16037
% D	1.19	26.21	10.23	11.57	48.29	2.52	100

$$\% \text{ D in each product} = \frac{\text{Corrected area} \times 100}{\text{Total corrected area}}$$

$$\% \text{ D of oleic acid} = \frac{191 \times 100}{16037} = 1.19$$

$$\% \text{ D of Esterified-oleic acid} = \frac{4203 \times 100}{16037} = 26.21$$

$$\% \text{ D of Esterified-by product} = \frac{1640 \times 100}{16037} = 10.23$$

$$\% \text{ D of RO} = \frac{1855 \times 100}{16037} = 11.57$$

$$\% \text{ D of ROES} = \frac{7744 \times 100}{16037} = 48.29$$

$$\% \text{ D of High MW} = \frac{403 \times 100}{16037} = 2.52$$

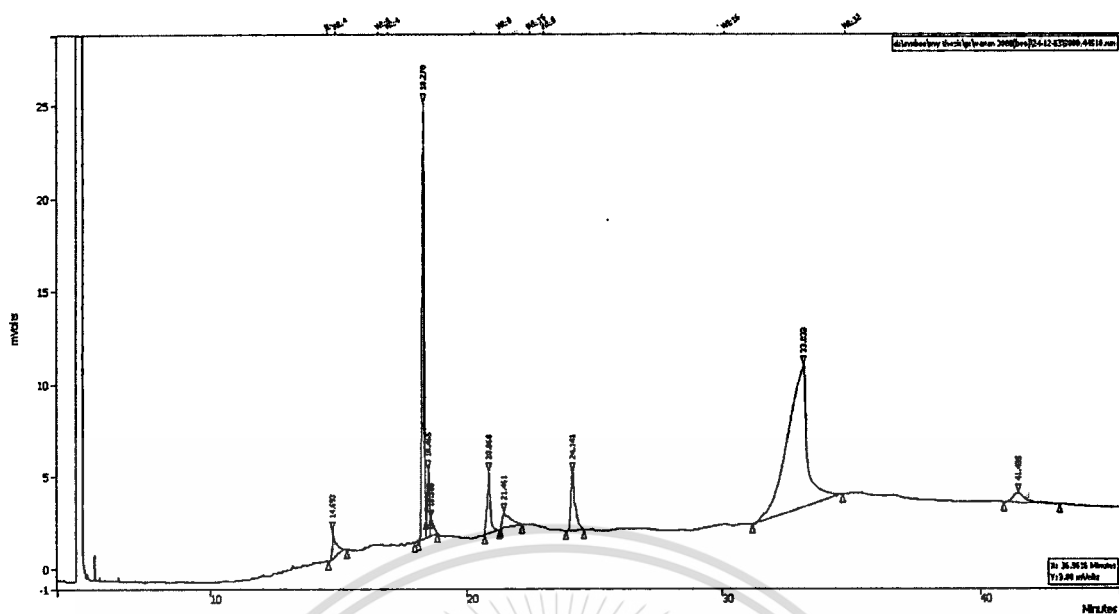


Figure B3 GC chromatogram of the resulting product from the reaction of epoxidised oleic acid and *n*-hexanol.

Table B3 GC analysis of the resulting product from the reaction of epoxidised oleic acid and *n*-hexanol.

L-hexanol	Oleic	Esterified- oleic acid	Esterified- by product	RO	ROES	High MW	total
Time	14.693	18.27	20.868	24.141	33.033	41.435	-
Area	5483	127756	44355	31034	338628	18244	-
RF	16	20	20	20	26	35	-
Corrected area	343	6388	2218	1552	13024	521	24045
% D	1.43	26.57	9.22	6.45	54.16	2.17	100

% D in each product

=

Corrected area x 100

Total corrected area

% D of oleic acid

=

343 x 100

24045

=

1.43

$$\% \text{ D of Esterified-oleic acid} = \frac{6388 \times 100}{24045} = 26.57$$

$$\% \text{ D of Esterified-by product} = \frac{2218 \times 100}{24045} = 9.22$$

$$\% \text{ D of RO} = \frac{1552 \times 100}{24045} = 6.45$$

$$\% \text{ D of ROES} = \frac{13024 \times 100}{24045} = 54.16$$

$$\% \text{ D of High MW} = \frac{521 \times 100}{24045} = 2.17$$

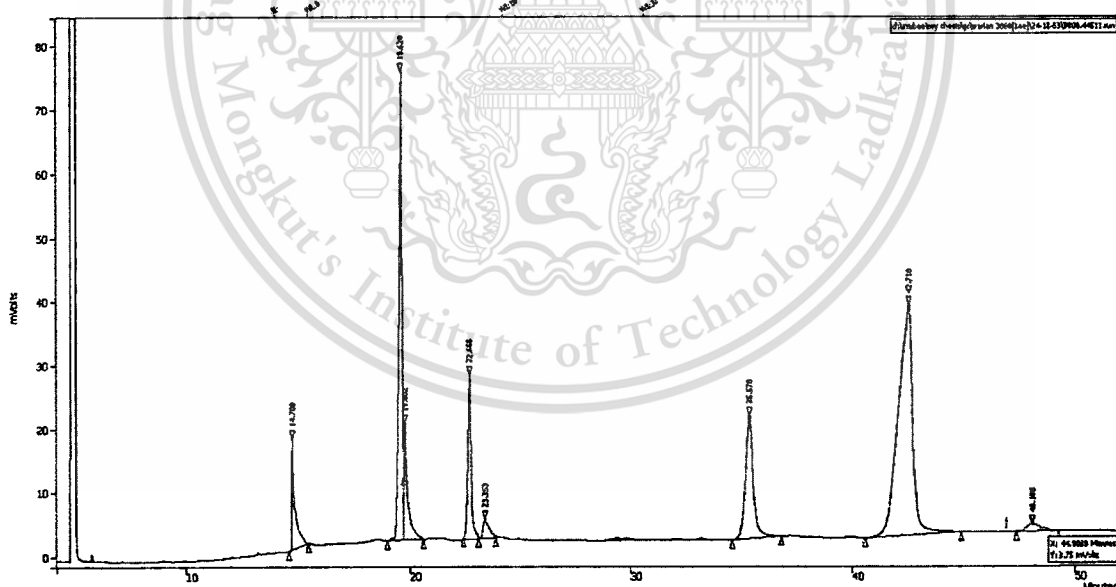


Figure B4 GC chromatogram of the resulting product from the reaction of epoxidised oleic acid and cyclohexanol.

Table B4 GC analysis of the resulting product from the reaction of epoxidised oleic acid and cyclohexanol.

L-cyclohexanol	Oleic	Esterified-oleic acid	Esterified-by product	RO	ROES	High MW	total
Time	14.7	19.62	22.666	35.57	42.724	48.1	-
Area	78534	706419	304996	479712	1862423	45341	-
RF	16	20	20	20	26	35	-
Corrected area	5154	35321	15250	23986	69841	1360	150911
% D	3.42	23.41	10.11	15.89	46.28	0.90	100

$$\% \text{ D in each product} = \frac{\text{Corrected area} \times 100}{\text{Total corrected area}}$$

$$\% \text{ D of oleic acid} = \frac{5154 \times 100}{150911} = 3.42$$

$$\% \text{ D of Esterified-oleic acid} = \frac{35321 \times 100}{150911} = 23.41$$

$$\% \text{ D of Esterified-by product} = \frac{15250 \times 100}{150911} = 10.11$$

$$\% \text{ D of RO} = \frac{23986 \times 100}{150911} = 15.89$$

$$\% \text{ D of ROES} = \frac{69841 \times 100}{150911} = 46.28$$

$$\% \text{ D of High MW} = \frac{1360 \times 100}{150911} = 0.90$$

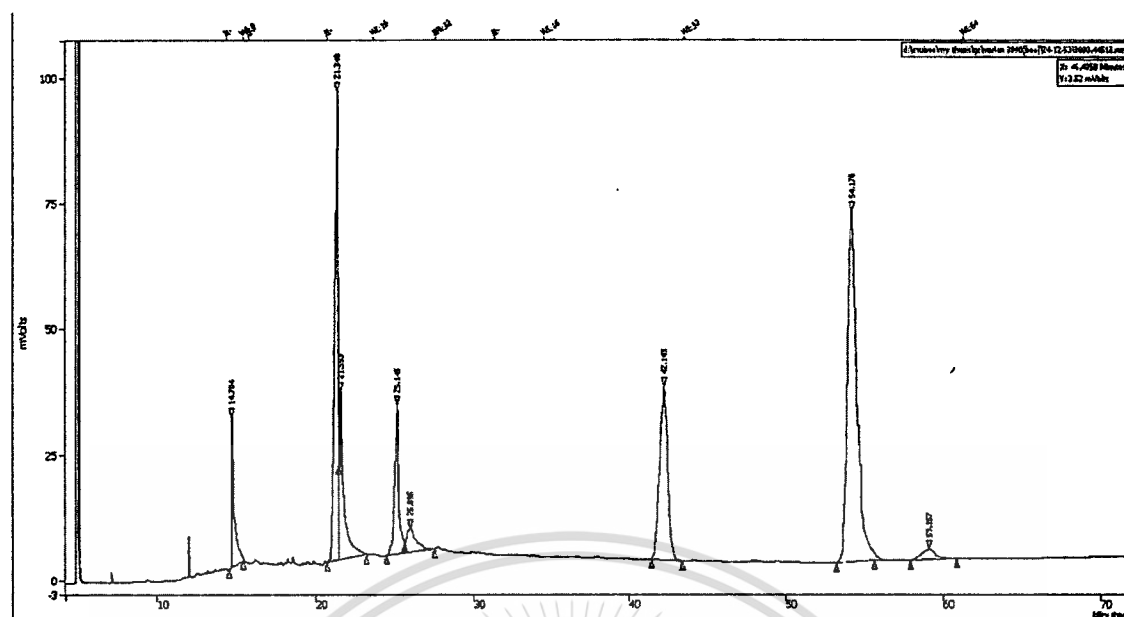


Figure B5 GC chromatogram of the resulting product from the reaction of epoxidised oleic acid and benzyl alcohol

Table B5 GC analysis of the resulting product from the reaction of epoxidised oleic acid and benzyl alcohol.

L-benzyl alcohol	Oleic	Esterified-oleic acid	Esterified-by product	RO	ROES	High MW	total
Time	14.704	21.348	25.145	42.143	54.176	59.156	-
Area	158526	1381983	597476	1238725	2898507	121006	-
RF	16	21	21	21	28	36	-
Corrected area	9908	65809	28451	58987	103518	3361	270034
% D	3.67	24.37	10.54	21.84	38.34	1.24	100

$$\% \text{ D in each product} = \frac{\text{Corrected area} \times 100}{\text{Total corrected area}}$$

$$\% \text{ D of oleic acid} = \frac{9908 \times 100}{270034} = 3.67$$

$$\% \text{ D of Esterified-oleic acid} = \frac{65809 \times 100}{270034} = 24.37$$

$$\% \text{ D of Esterified-by product} = \frac{28451 \times 100}{270034} = 10.54$$

$$\% \text{ D of RO} = \frac{58987 \times 100}{270034} = 21.84$$

$$\% \text{ D of ROES} = \frac{103518 \times 100}{270034} = 38.34$$

$$\% \text{ D of High MW} = \frac{3361 \times 100}{270034} = 1.24$$

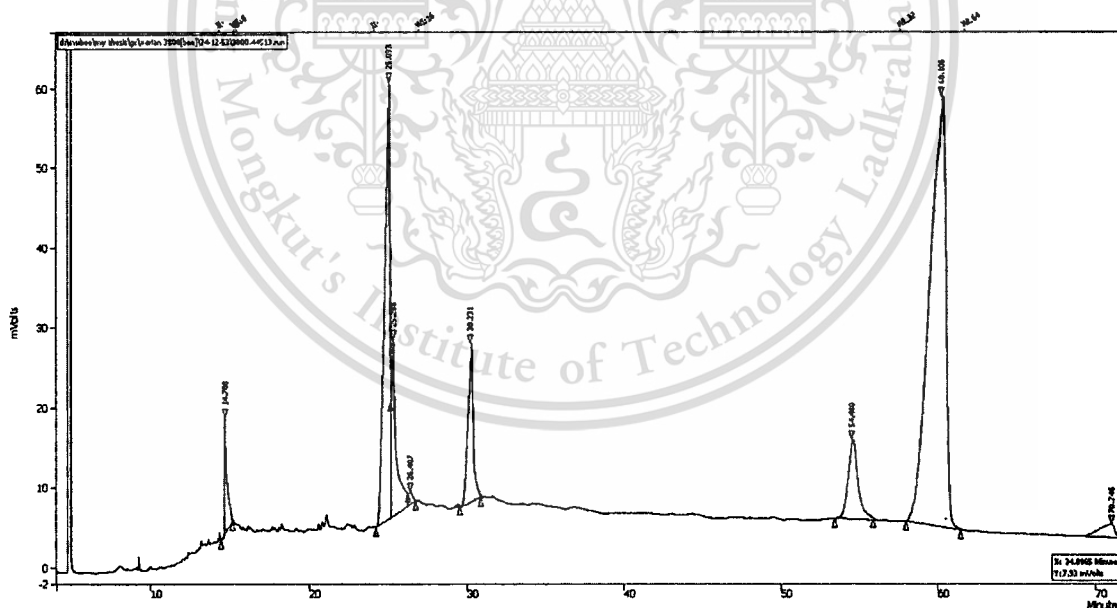


Figure B6 GC chromatogram of the resulting product from the reaction of epoxidised oleic acid and *n*-decanol.

Table B6 GC analysis of the resulting product from the reaction of epoxidised oleic acid and *n*-decanol.

L-decanol	Oleic	Esterified- oleic acid	Esterified- by product	RO	ROES	High MW	total
Time	14.708	25.019	30.231	54.49	60.106	60.106	-
Area	72349	1226678	469584	438209	3974702	118296	-
RF	16	24	24	24	34	39	-
Corrected area	4522	51112	19566	18259	116903	3033	213394
% D	2.12	23.95	9.17	8.56	54.78	1.42	100

% D in each product

$$= \frac{\text{Corrected area} \times 100}{\text{Total corrected area}}$$

$$\% \text{ D of oleic acid} = \frac{4522 \times 100}{213394} = 2.12$$

$$\% \text{ D of Esterified-oleic acid} = \frac{51112 \times 100}{213394} = 23.95$$

$$\% \text{ D of Esterified-by product} = \frac{19566 \times 100}{213394} = 9.17$$

$$\% \text{ D of RO} = \frac{18259 \times 100}{213394} = 8.56$$

$$\% \text{ D of ROES} = \frac{116903 \times 100}{213394} = 54.78$$

$$\% \text{ D of High MW} = \frac{3033 \times 100}{213394} = 1.42$$

APPENDIX C

MASS SPECTRA

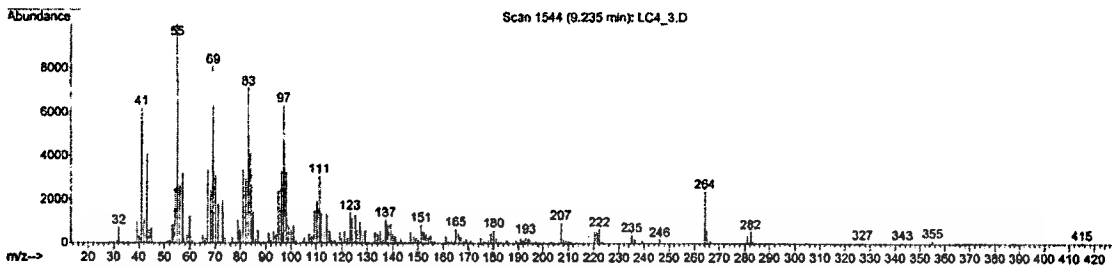


Figure C1 Mass spectrum of oleic acid (L-butanol)

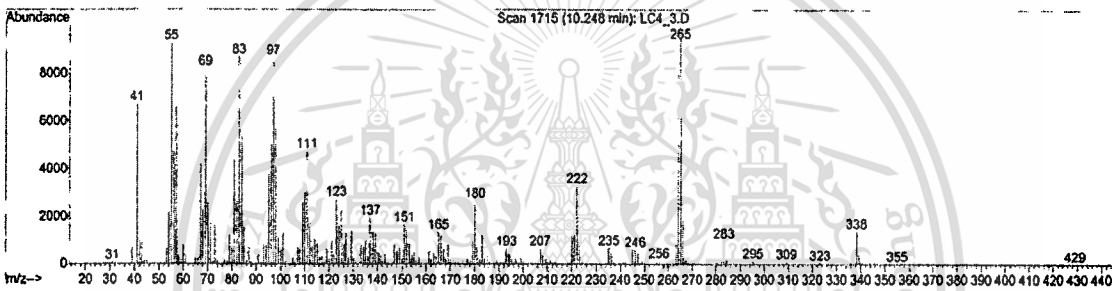


Figure C2 Mass spectrum of esterified oleic acid (L-butanol)

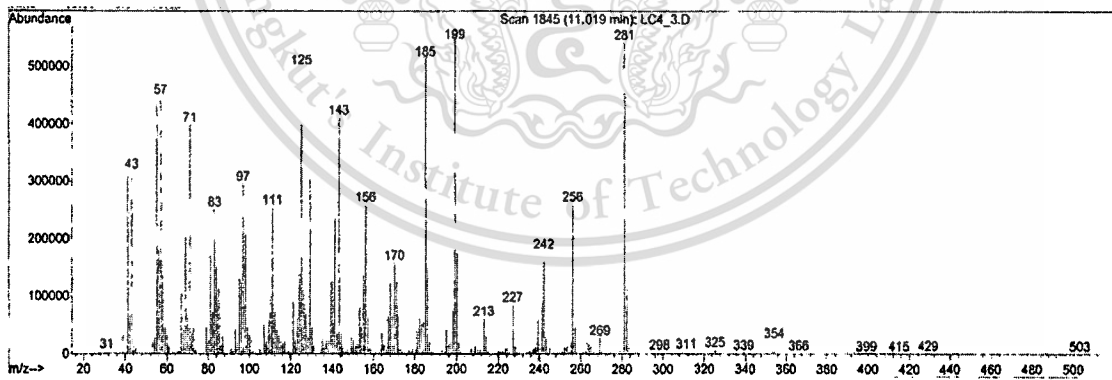


Figure C3 Mass spectrum of esterified by-product (L-butanol)

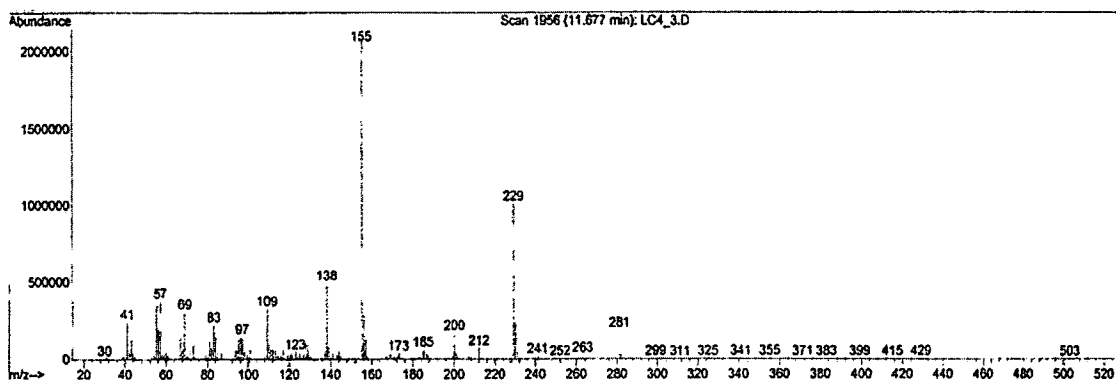


Figure C4 Mass spectrum of ring-opening product (L-butanol)

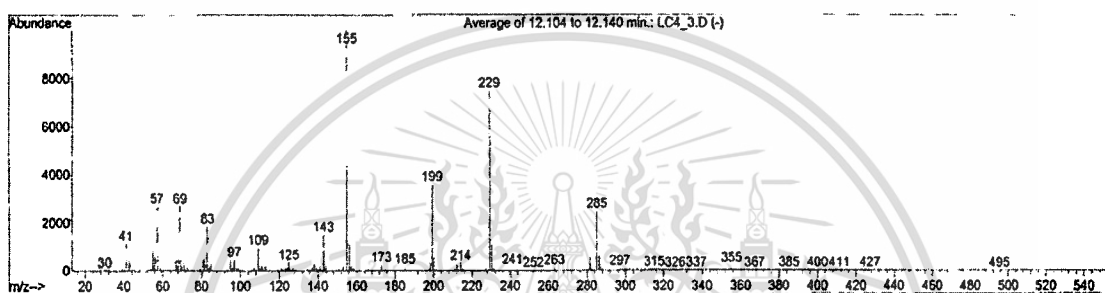


Figure C5 Mass spectrum of ring-opening and esterified product (L-butanol)

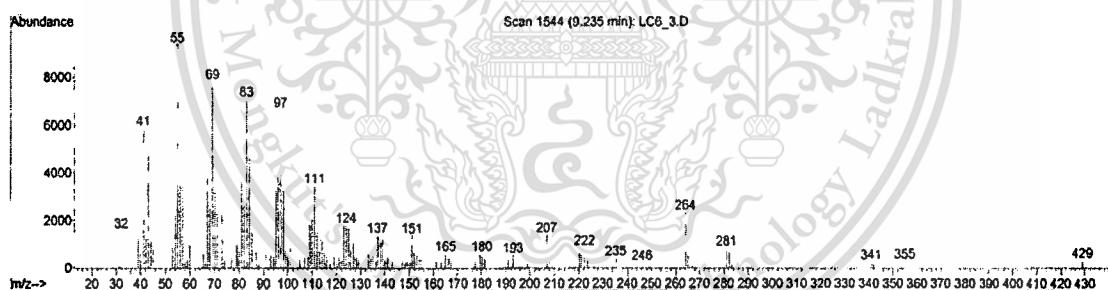


Figure C6 Mass spectrum of oleic acid (L-hexanol)

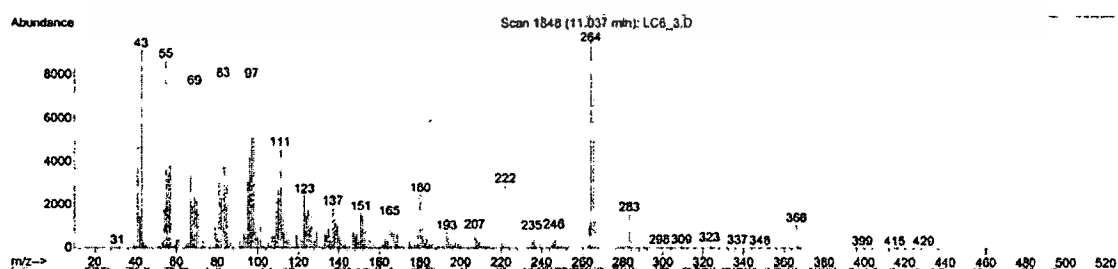


Figure C7 Mass spectrum of esterified oleic acid (L-hexanol)

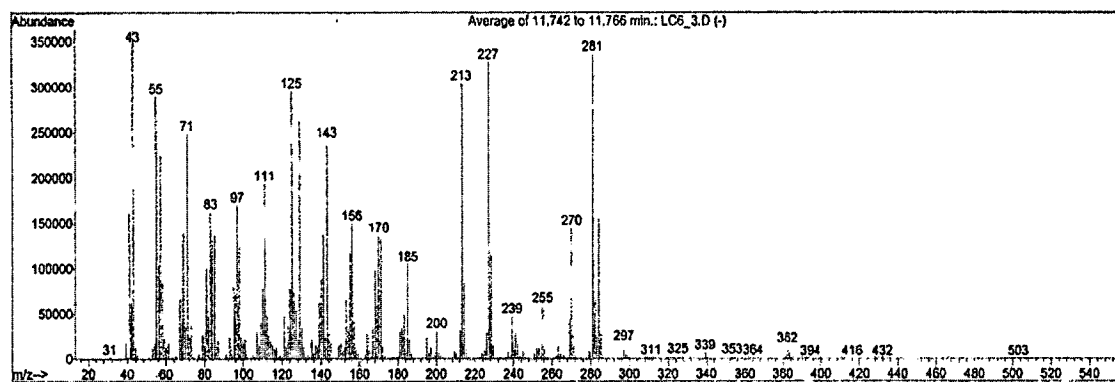


Figure C8 Mass spectrum of esterified by-product (L-hexanol)

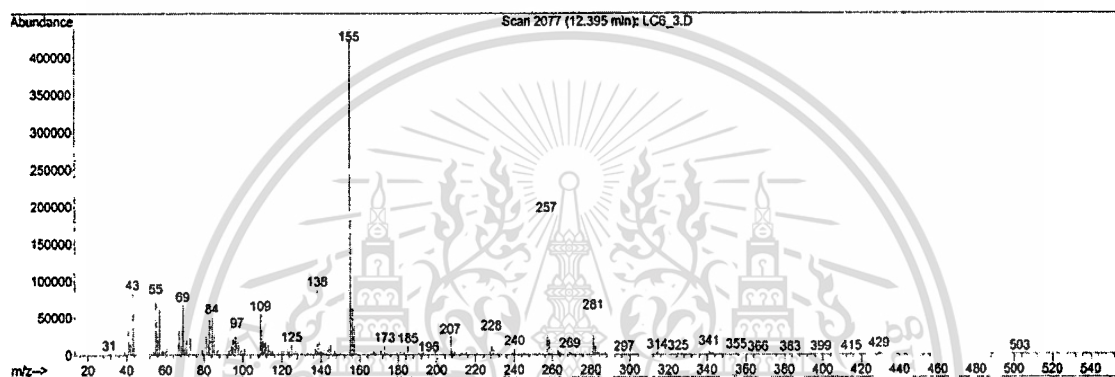


Figure C9 Mass spectrum of ring-opening product (L-hexanol)

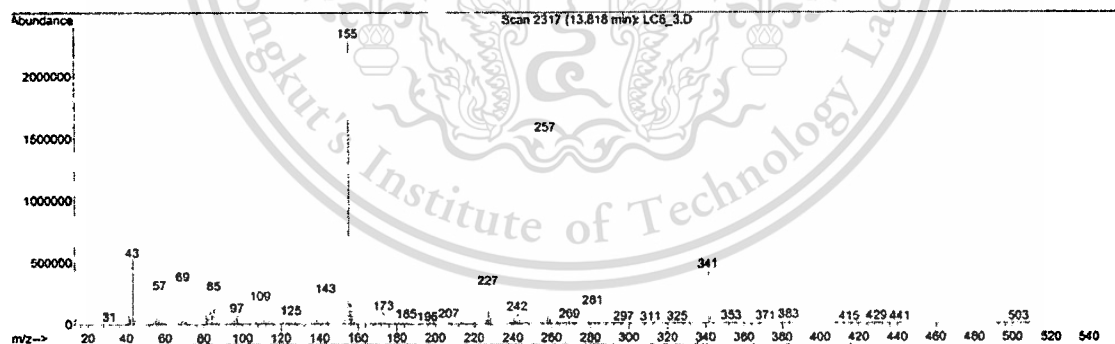


Figure C10 Mass spectrum of ring-opening and esterified product (L-hexanol)

APPENDIX D

TGA THERMOGRAM

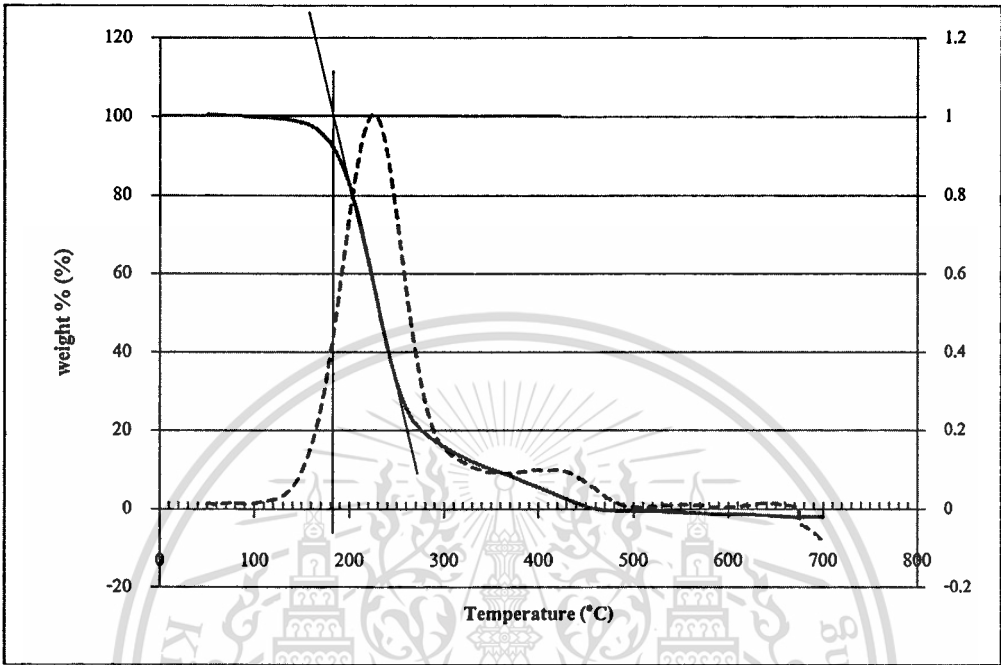


Figure D1 Thermogram of oleic acid in air

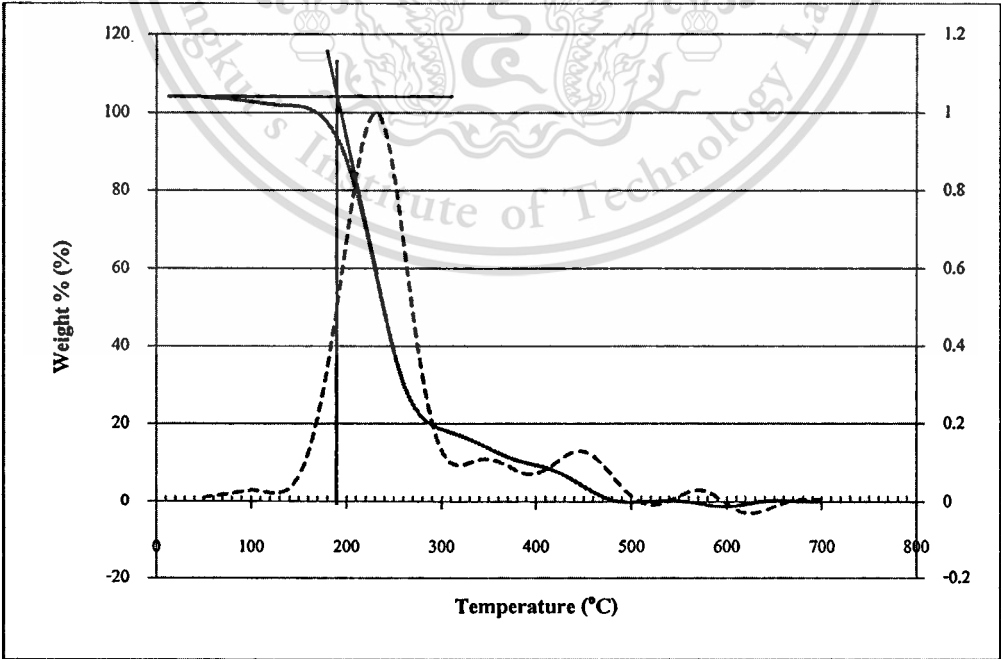


Figure D2 Thermogram of oleic acid in N₂

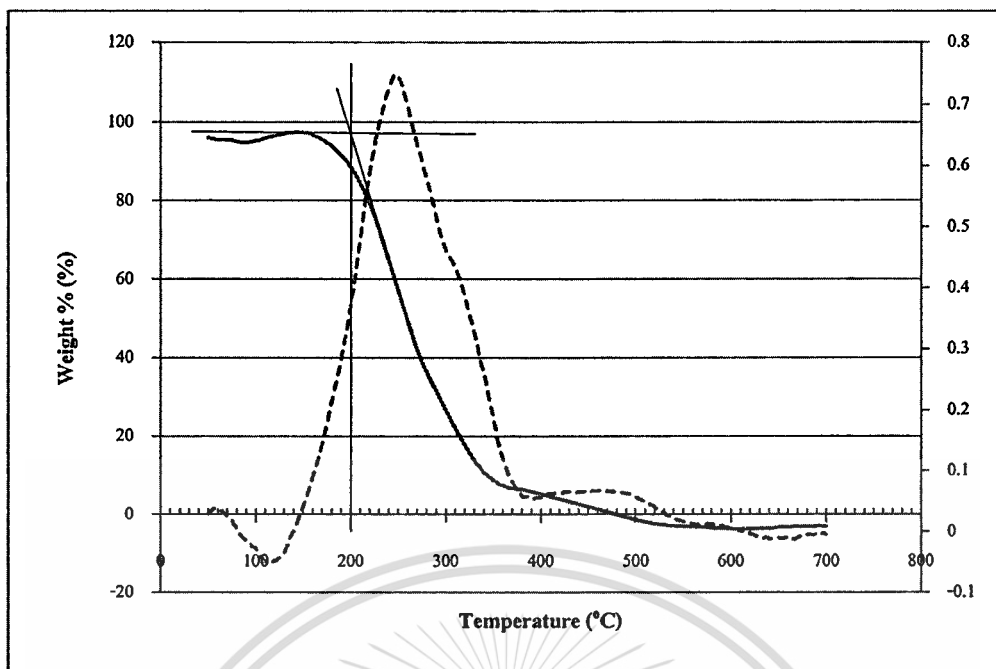


Figure D3 Thermogram of L-butanol in air

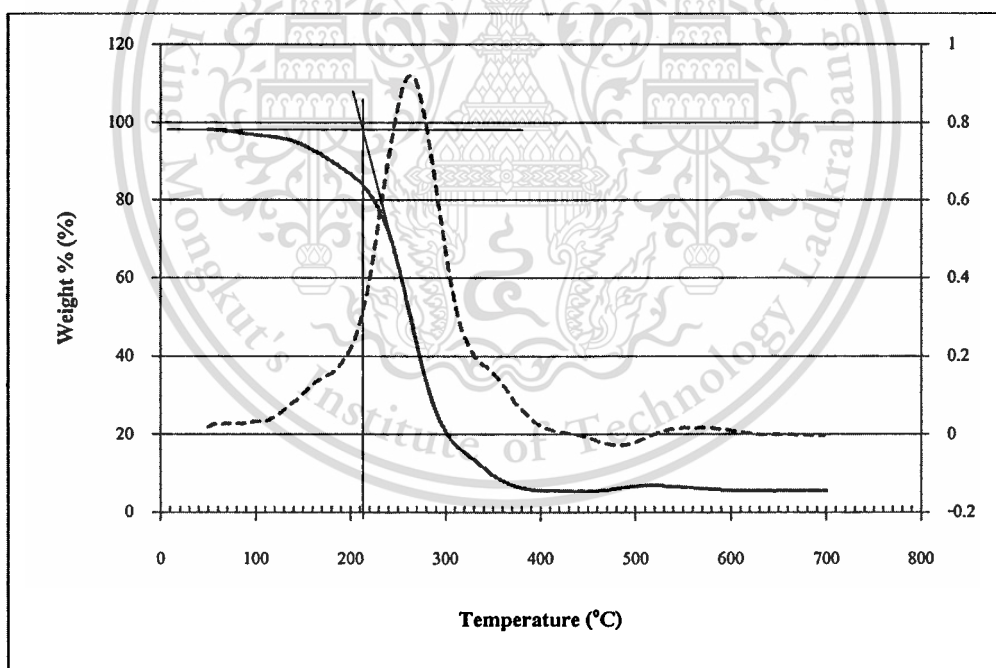


Figure D4 Thermogram of L-butanol in N_2

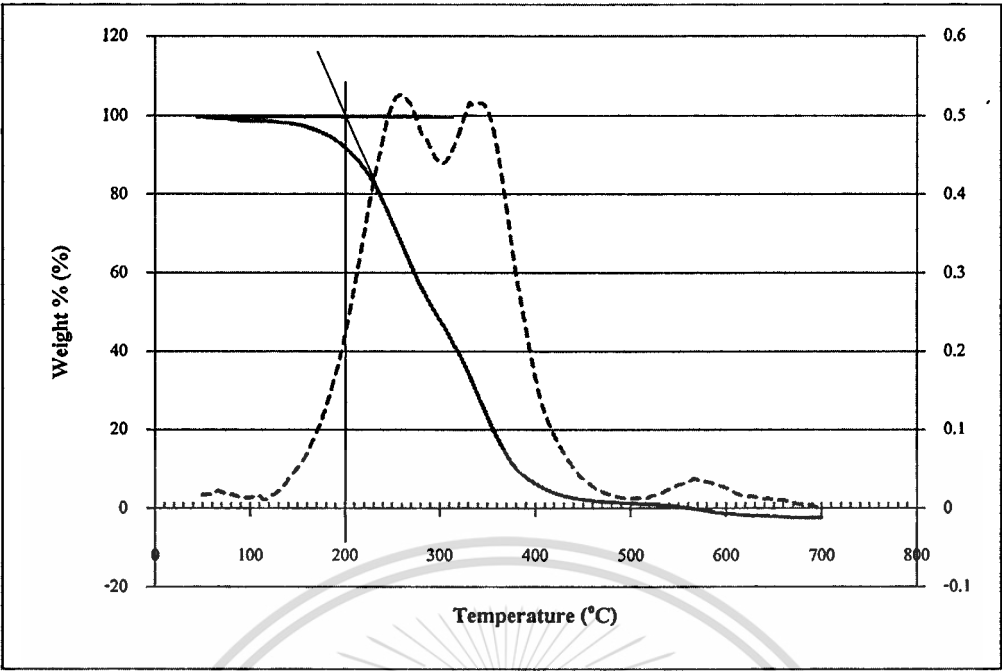


Figure D5 Thermogram of L-isobutanol in air

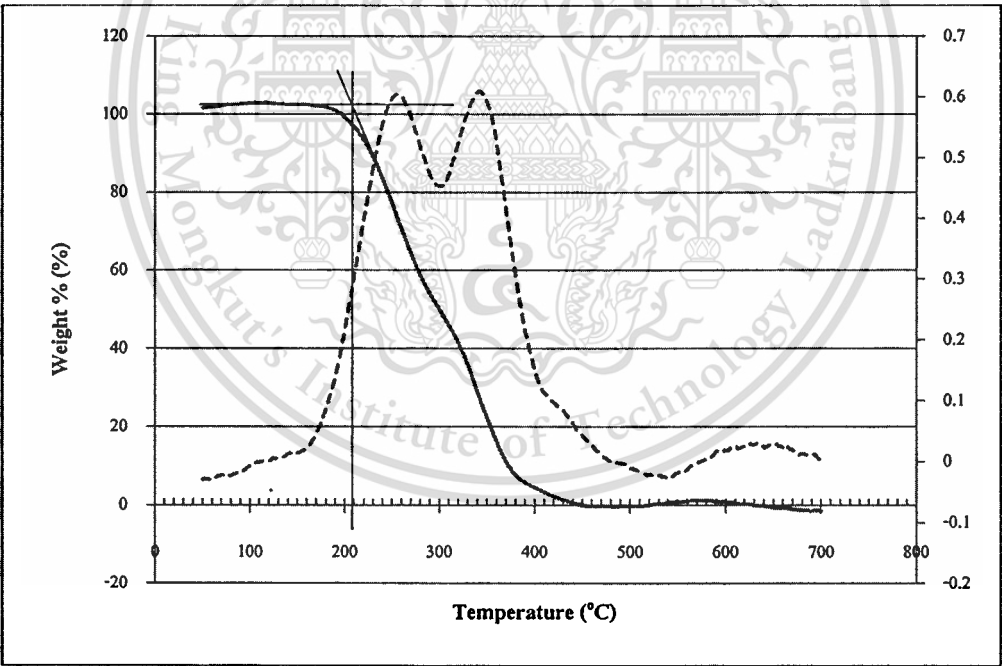


Figure D6 Thermogram of L-isobutanol in N₂

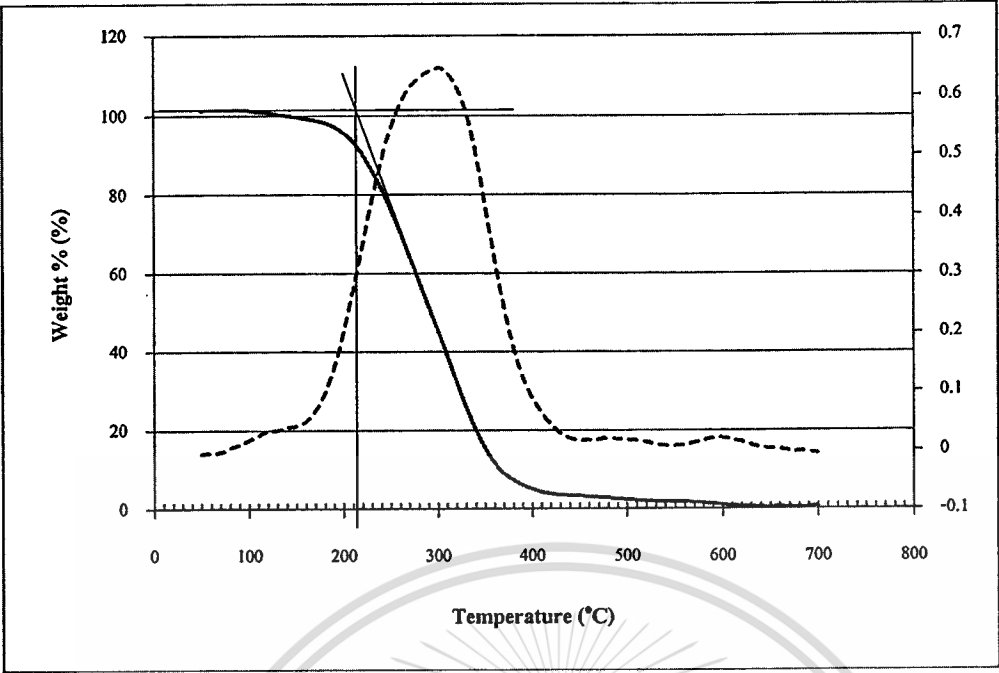


Figure D7 Thermogram of L-hexanol in air

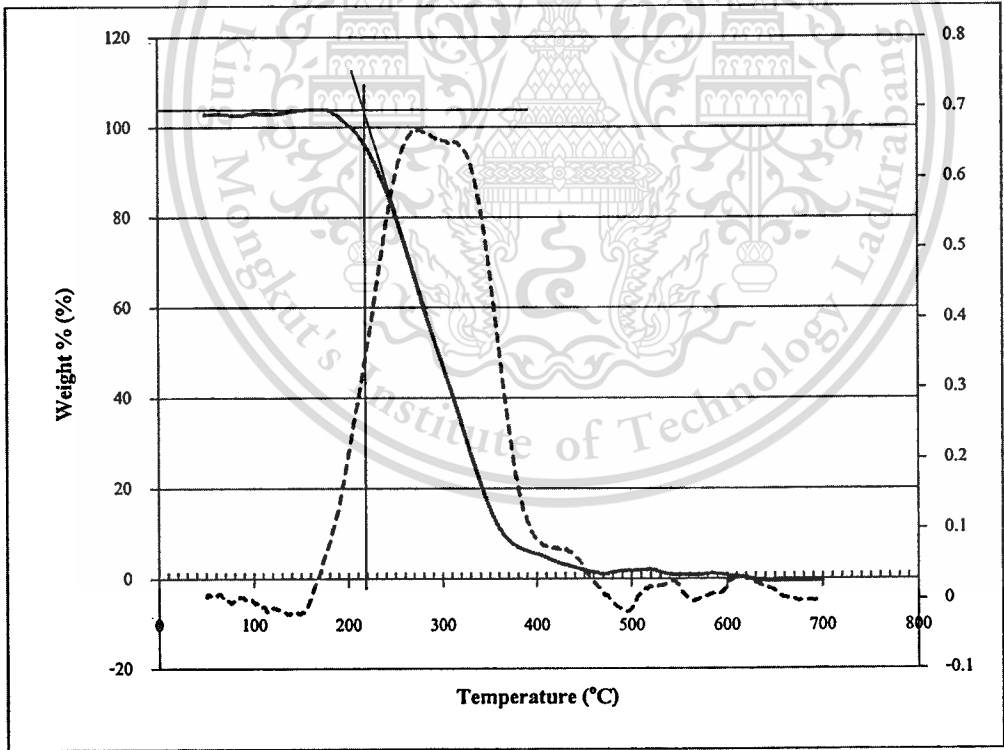


Figure D8 Thermogram of L-hexanol in N₂

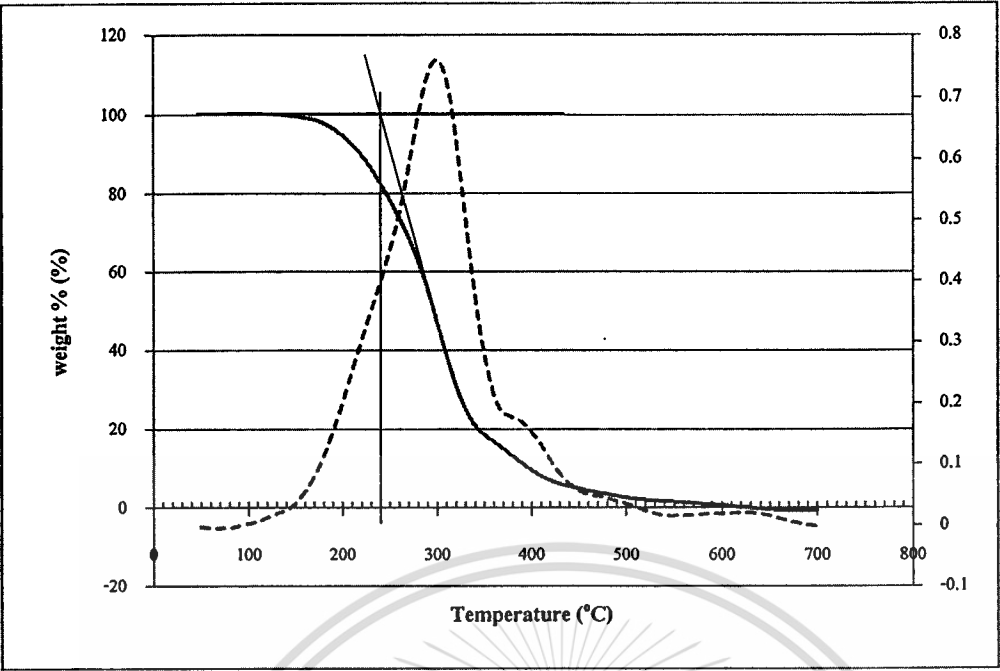


Figure D9 Thermogram of L-cyclohexanol in air

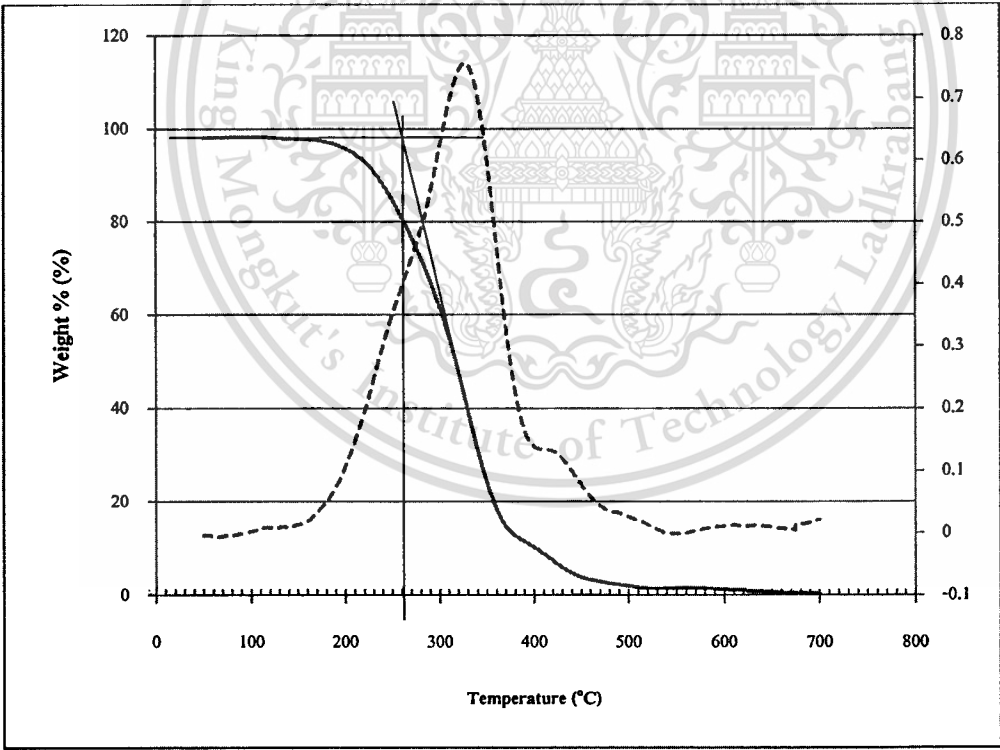


Figure D10 Thermogram of L-cyclohexanol in N₂

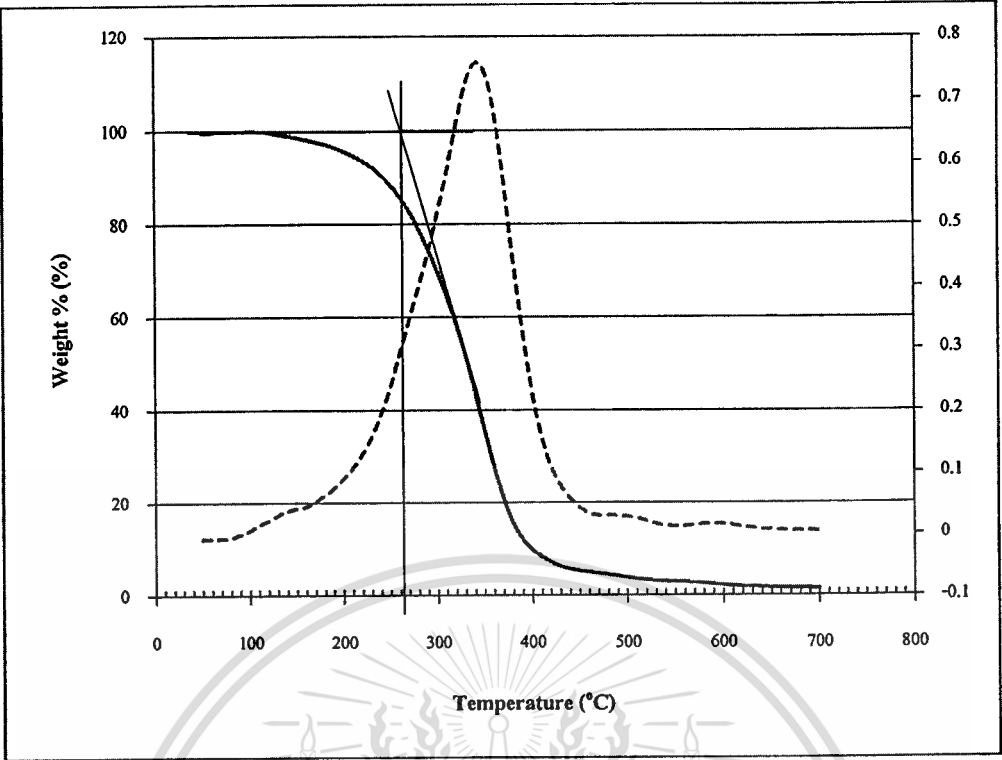


Figure D11 Thermogram of L-benzyl alcohol in air

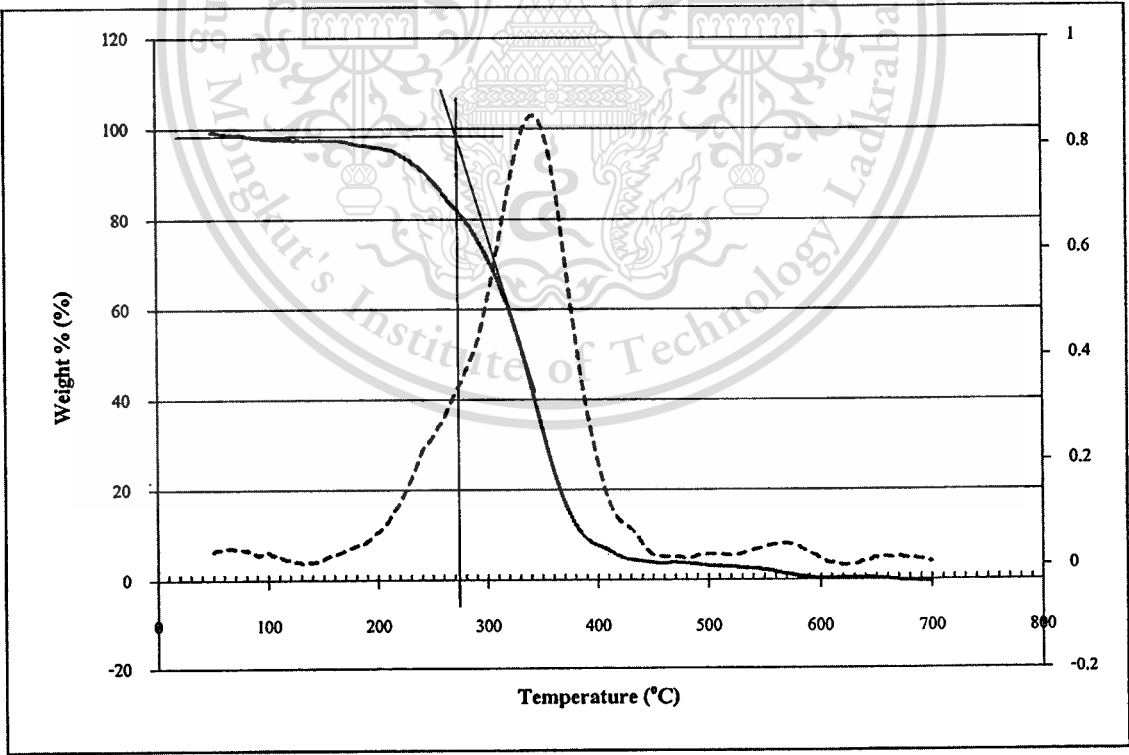


Figure D12 Thermogram of L-benzyl alcohol in N₂

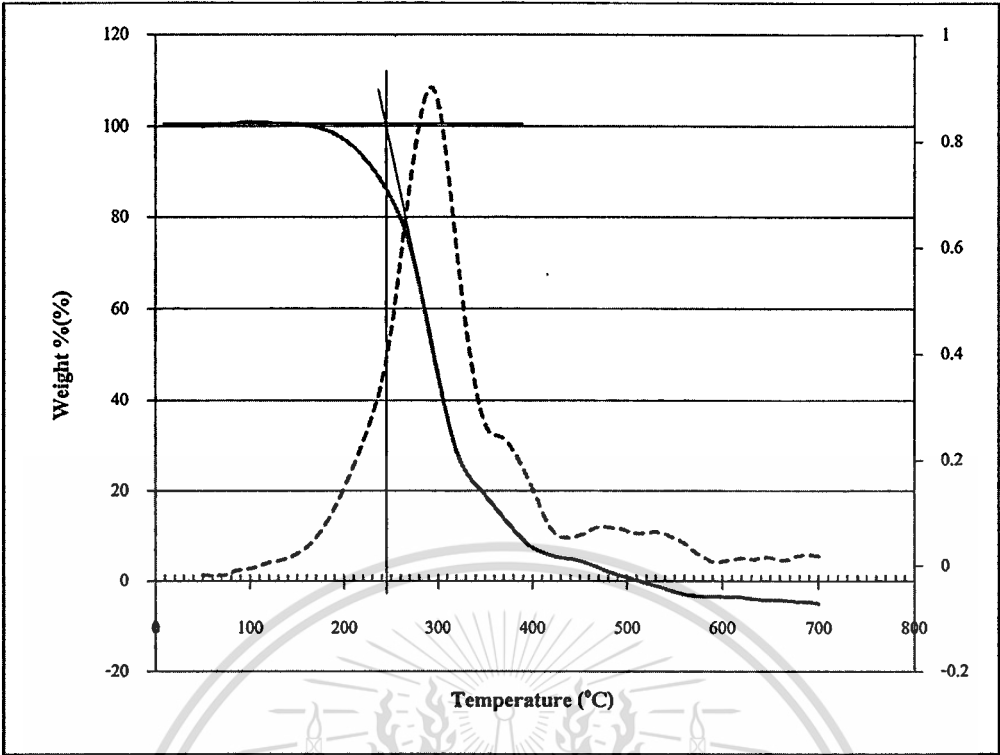


Figure D13 Thermogram of L-decanol in air

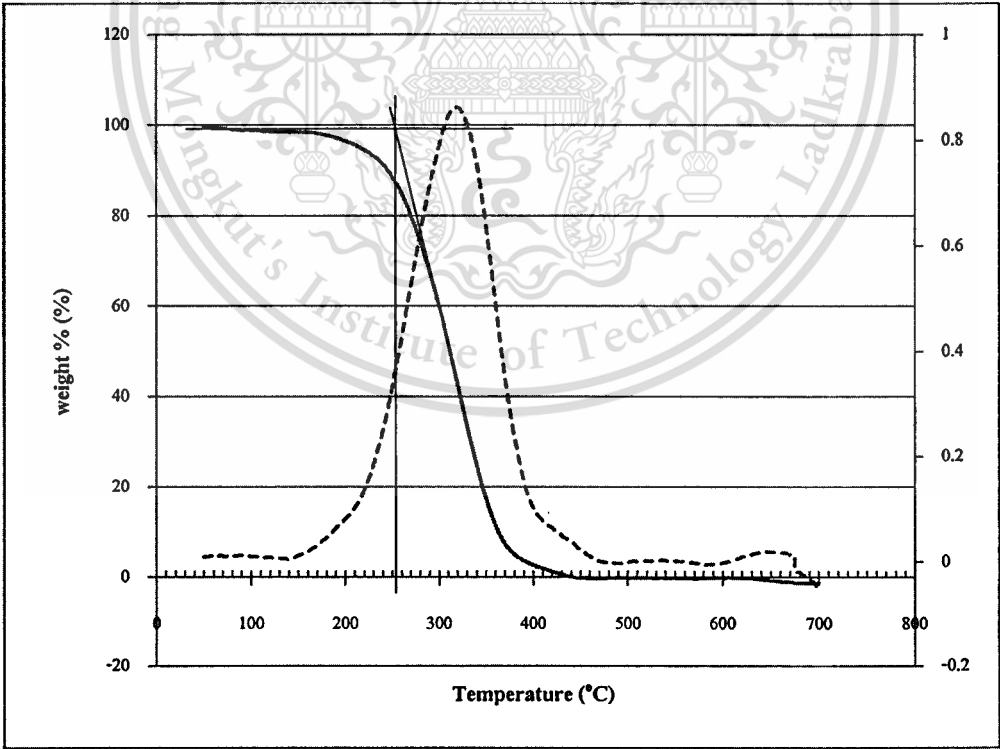


Figure D14 Thermogram of L-decanol in N₂

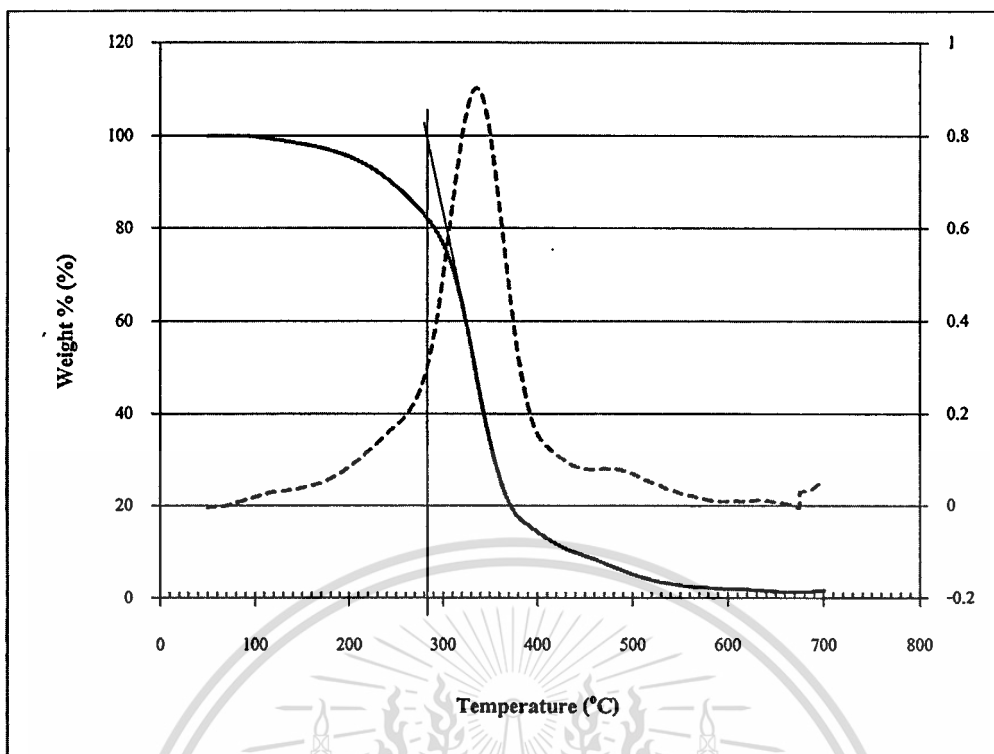


Figure D15 Thermogram of L-hexanol_MCPBA in air

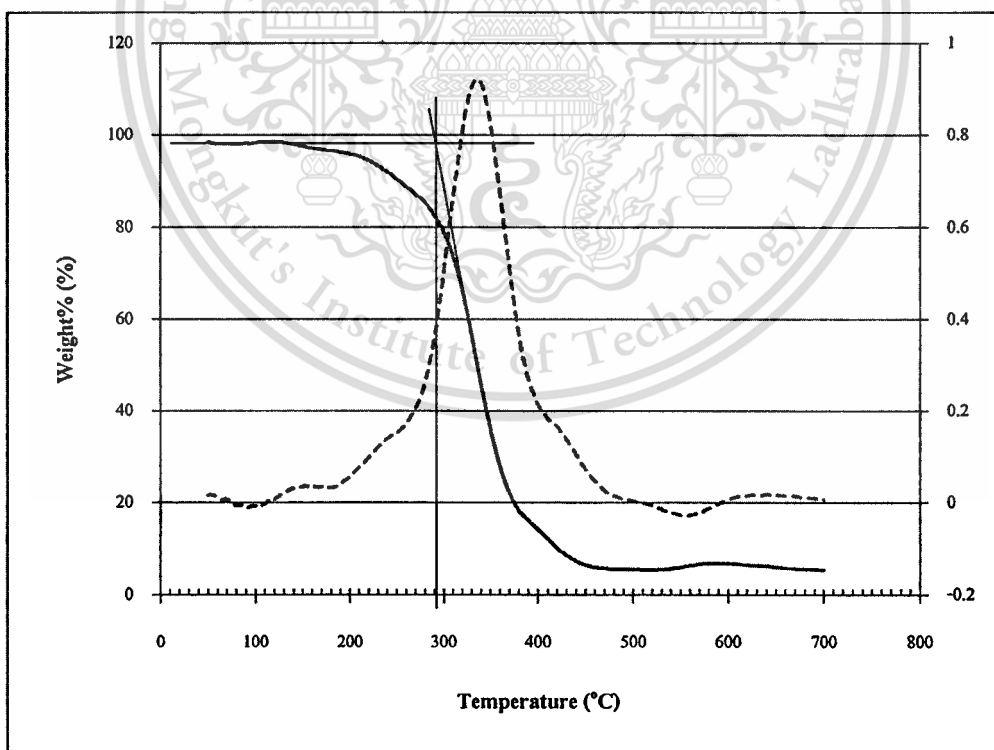


Figure D16 Thermogram of L-hexanol_MCPBA in N₂

APPENDIX E

RELATED ASTM STANDARD TEST METHODS

Standard test method for pour point of Petroleum Products

1. Scope

- 1.1. This test method covers and is intended for use on any petroleum product. A procedure suitable for black specimens, cylinder stock, and nondistillate fuel oil is described in 8.8. The cloud point procedure formerly part of this test method now appears as Test Method D2500.
- 1.2. Currently there is no ASTM test method for automated Test Method D97 pour point measurements.
- 1.3. Several ASTM test methods offering alternative procedures for determining pour points using automatic apparatus are available. None of them share the same designation number as Test Method D97. When an automatic instrument is used, the ASTM test method designation number specific to the technique shall be reported with the results. A procedure for testing the pour point of crude oils is described in Test Method D5853.
- 1.4. The values state in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.5. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced documents

2.1. ASTM standard.

D117 Guide for sampling, test methods, and specifications for electrical insulating oils of petroleum origin

D396 Specification for fuel oils

D2500 Test method for cloud point of petroleum products

This n D5833 Test method for pour point of crude oils, not allowed for commercial use.

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D6300 Practice for determination of precision and bias data for use in test methods for petroleum products and lubricants

E1 Specification for ASTM liquid-in-glass thermometers

2.2 Energy institute standard:

Specification for IP standard thermometers.

3. Terminology

3.1. Definitions:

- 3.1.1. Black oil, *n* – lubricant containing asphaltic materials. Black oils are used in heavy-duty equipment applications, such as mining and quarrying, where extra adhesiveness is desired.
- 3.1.2. Cylinder stock, *n* – lubricant for independently lubricated engine cylinders, such as those of steam engines and air compressors. Cylinder stock are also used for lubrication of valves and other elements in the cylinder area.
- 3.1.3. Pour point, *n* – in petroleum products, the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test.
- 3.1.4. Residual fuel, *n* – a liquid fuel containing bottoms remaining from crude distillation or thermal cracking; some-times referred to as heavy fuel oil.
 - 3.1.4.1. Discussion – Residual fuels comprise Grades 4, 5 and 6 fuel oils, as defined in specification D396.

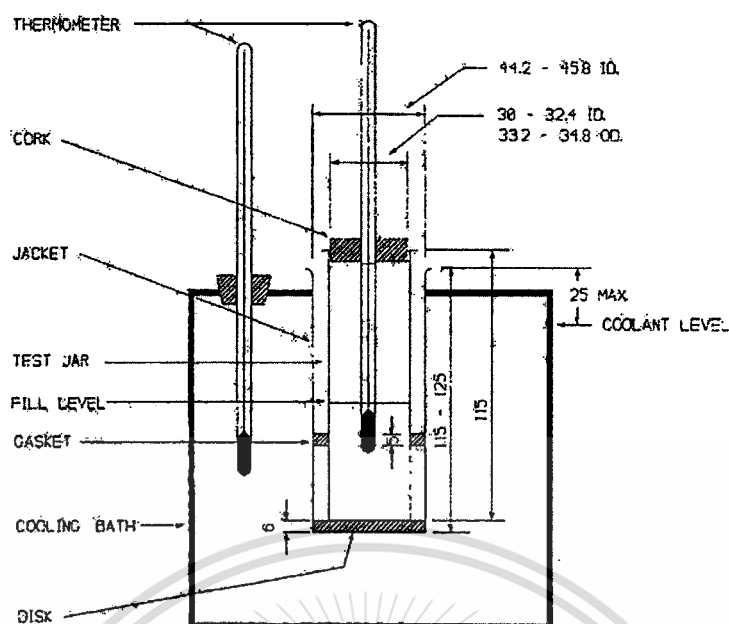


FIG. 1 **Apparatus for pour point test**

4. Summary of test method

- 4.1. After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

5. Significance and use

- 5.1. The pour point of petroleum specimen is an index of the lowest temperature of its utility for certain applications.

6. Apparatus

- 6.1. Test Jar, cylindrical, of clear glass, flat bottom, 33.2 to 34.8-mm outside diameter, and 115 to 125 mm in height. The inside diameter of the jar can range from 30.0 to 32.4 mm, within the constraint that the wall thickness be no greater than 1.6 mm. The jar shall have a line to indicate a sample height 54 ± 3 mm above the inside bottom. See Fig. 1.
- 6.2. Thermometers, having the following ranges and conforming to the requirements prescribed in Specification E1 for thermometers:

Thermometer	Temperature	Thermometer number	
	Range	ASTM	IP
High cloud and pour	-38 to +50°C	5C	1C
Low cloud and pour	-80 to +20°C	5C	2C
Melting point	+32 to +127°C	61C	63C

6.2.1. Since separation of liquid column thermometers occasionally occurs and may escape detection, thermometers should be checked immediately prior to the test and used only if they prove accurate within $\pm 1^\circ\text{C}$ (for example ice point).

- 6.3. Cork, to fit the test jar, bored centrally for the test thermometer.
- 6.4. Jacket, watertight, cylindrical, metal, flat-bottomed, 115 ± 3 -mm depth, with inside diameter of 44.2 to 45.8 mm. It shall be supported in a vertical position in the cooling bath (see 6.7) so that not more than 25 mm projects out of the cooling medium, and shall be capable of being cleaned.
- 6.5. Disk, cork or felt, 6 mm thick to fit loosely inside the jacket
- 6.6. Gasket, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.
- 6.7. Bath or Baths, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperature may be obtained by refrigeration if available, otherwise by suitable cooling mixtures. Cooling mixtures commonly used for bath temperatures down to those shown are as follows;

	Bath Temperature
Ice and water	$0 \pm 1.5^{\circ}\text{C}$
Crushed ice and sodium chloride crystals, or acetone or petroleum naphtha (see Section 7) with solid carbon dioxide added to give the desired temperature	$-18 \pm 1.5^{\circ}\text{C}$
Acetone or petroleum naphtha (see Section 7) with solid carbon dioxide added to give the desired temperature	$-33 \pm 1.5^{\circ}\text{C}$
Acetone or petroleum naphtha (see Section 7) with solid carbon dioxide added to give the desired temperature	$-51 \pm 1.5^{\circ}\text{C}$

7. Regents and materials.

7.1. The following solvents of technical grade are appropriate for low-temperature bath-media.

7.1.1. Acetone

7.1.2. Alcohol, ethanol

7.1.3. Alcohol, methanol

7.1.4. Petroleum naphtha,

7.1.5. Solid carbon dioxide,

8. Procedure

8.1. Pour the specimen into the test jar to the level mark. When necessary, heat the specimen in a bath until it is just sufficiently fluid to pour into the test jar.

8.1.1. Sample of residual fuels, black oils, and cylinder stocks which have been heated to a temperature higher than 45°C during the proceeding 24 h, or when the thermal history of these sample types is not known, shall be kept at room temperature for 24 h before testing. Samples which are known by the operator not to be sensitive to thermal history need not be kept at room temperature for 24 h before testing.

8.1.2. Experimental evidence supporting elimination of the 24-h waiting period for some sample types is contained in a research report.

8.2. Close the test jar with the cork carrying the high-pour thermometer (5.2). In the case of pour point above 36°C , use a higher range thermometer such as IP 63C or ASTM 61C.

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Adjust the position of the cork and thermometer so the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is immersed so the beginning of the capillary is 3 mm below the surface of the specimen.

8.3. For the measurement of pour point, subject the specimen in the test jar to the following preliminary treatment:

8.3.1. Specimens Having Pour Points above -33°C – Heat the specimen without stirring to 9°C above the expected pour point, but to at least 45°C , in a bath maintained at 12°C above the expected pour point, but at least 48°C . Transfer the test jar to a bath maintained at $24 \pm 1.5^{\circ}\text{C}$ and commence observations for pour point. When using a liquid bath, ensure that the liquid level is between the fill mark on the test jar and the top of the test jar.

8.3.2. Specimens Having Pour Points of -33°C and Below – Heat the specimen without stirring at least 45°C in a bath maintained at $48 \pm 1.5^{\circ}\text{C}$. Transfer the test jar to a bath maintained at $24 \pm 1.5^{\circ}\text{C}$. When using liquid bath, ensure that the liquid level is between the fill mark on the test jar and the top of the test jar. When the specimen temperature reaches 27°C , remove the high cloud and pour thermometer, and place the low cloud and pour thermometer in position. Transfer the test jar to the cooling bath (see 8.6.1).

8.4. See that that disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

TABLE 1 Bath and sample temperature ranges

Bath	Bath temperature setting, $^{\circ}\text{C}$	Sample temperature range, $^{\circ}\text{C}$
1	0 ± 1.5	Start to 9
2	-18 ± 1.5	9 to -6
3	-33 ± 1.5	-6 to -24
4	-51 ± 1.5	-24 to -42
5	-69 ± 1.5	-42 to -60

- 8.5. After the specimen has cooled to allow the formation of paraffin wax crystals, take great care not to disturb the mass of specimen nor permit the thermometer to shift in the specimen; any disturbance of the spongy network of wax crystals will lead to low and erroneous results.
- 8.6. Pour points are expressed in integers that are positive or negative multiple of 3 °C. Begin to examine the appearance of the specimen when the temperature of the specimen is 9 °C above the expected pour point (estimated as a multiple of 3 °C). At each test thermometer reading that is a multiple of 3 °C below the starting temperature remove the test jar from the jacket. To remove condensed moisture that limits visibility wipe the surface with a clean cloth moistened in alcohol (ethanol or methanol). Tilt the jar just enough to ascertain whether there is a movement of the specimen of the specimen in the test jar. If movement of specimen in the test jar is noted, then replace the test jar immediately in the jacket and repeat a test for flow at the next temperature, 3 °C lower. Typically, the complete operation of removal, wiping, and replacement shall require not more than 3 s.
- 8.6.1. If the specimen has not ceased to flow when its temperature has reached 27 °C, transfer the test jar to a jacket in a cooling bath maintained at $0 \pm 1,5$ °C. As the specimen continues to get colder, transfer the test jar to a jacket in the next lower temperature cooling bath in accordance with Table 1.
- 8.6.2. If the specimen in the jar does not show movement when tilted, hold the jar in a horizontal position for 5 s, as noted by an accurate timing device, and observe the specimen carefully. If the specimen shows any signs of movement before 5 s has passed, replace the test jar immediately in the jacket and repeat a test for flow at the next temperature, 3 °C lower.
- 8.7. Continue in this manner until a point is reached at which the specimen shows no movement when the test jar is hold in a horizontal position for 5 s. Record the observed reading of the test thermometer.
- 8.8. For black specimen, cylinder stock, and nondistillate fuel specimen, the result obtained by the procedure described in 8.1 through 8.7 is the upper (maximum) pour point. If required, determine the lower (minimum) pour point by heating the sample while

stirring, to 105 °C, pouring it into the jar, and determining the pour point as described in 8.4 through 8.7.

- 8.9. Some specifications allow for a pass/fail test or have pour point limits at temperatures not divisible by 3 °C. In these cases, it is acceptable practice to conduct the pour point measurement the appearance of the specimen when the temperature of the specimen is 9 °C above the specification pour point. Continue observations at 3 °C intervals as described in 8.6 and 8.7 until the specification temperature is reached. Report the sample as passing or failing the specification limit.

9. Calculation and report

- 9.1. Add 3 °C to the temperature recorded in 8.7 and report the results as the Pour Point, ASTM D97. For black oil, and so forth, add 3 °C to the temperature recorded in 8.7 and report the result as upper Pour Point, ASTM D97, or Lower Pour Point, ASTM D97, as required.

10. Precision and bias

- 10.1. Precision – The precision of this method as determined by the statistical examination of the interlaboratory test results is as follows:

10.1.1. Lubricating oil.

- 10.1.1.1. Repeatability – The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 6 °C only in one case in twenty. Differences greater than this should be considered suspect.

- 10.1.1.2. Reproducibility – The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 9 °C only in one case in twenty. Differences greater than this should be considered suspect.

- 10.1.1.3. The precision statement were derived from a 1998 interlaboratory test program using Practice D6300. Participants analyzed five sets of duplicate

base oils, three sets of duplicate multigrade lubricating oils, and one set each of duplicate hydraulic oils and automatic transmission fluid in the temperature range of -51 to -11 °C. Seven laboratories participate with the manual test method D97. Information on the type of sample and their average pour points are in research report D02-1499

10.1.2. Middle distillate and residual fuel:

10.1.2.1. Repeatability – The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 3 °C only in one case in twenty. Differences greater than this should be considered suspect.

10.1.2.2. Reproducibility – The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 9 °C only in one case in twenty. Differences greater than this should be considered suspect.

10.1.2.3. The precision statement was prepared with data on sixteen middle distillate and residual fuels tested by twelve cooperators. The fuels had pour points ranging from -33 to +51 °C.

11. Keywords

11.1. Petroleum products; pour point

**Standard test method for kinematic viscosity of transparent and opaque liquids
(and calculation of dynamic viscosity)**

1. Scope

- 1.1. This test method specified a procedure for the determination of the kinematic viscosity, V , of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η , can be obtained by multiplying the kinematic viscosity, V , by the density, ρ , of the liquid.
- 1.2. The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). If, however, the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters. The procedure and precision values for residual fuel oils, which under some conditions exhibit non-Newtonian behavior, have been included.
- 1.3. The range of kinematic viscosities covered by this test method is from 0.2 to 300000 mm²/s (see Table A1.1) at all temperatures (see 6.3 and 6.4). The precision has only been determined for those materials, kinematic viscosity ranges and temperatures as shown in the footnotes to the precision section.
- 1.4. The values stated in SI units are to be regarded as standard. The SI unit used in this test method for kinematic viscosity is mm²/s, and the SI unit used in this test method for dynamic viscosity is mPa·s. For user reference, 1 mm²/s = 10⁻⁶ m²/s = 1 cSt and 1 mPa·S = 1 cP = 0.001 Pa·S.
- 1.5 **WARNING**—Mercury has been designated by many regulatory agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website—<http://www.epa.gov/mercury/faq.htm>—for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.

- 1.6 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced documents

2.1. ASTM standards:

D446 Specifications and operating instructions for glass capillary kinematic viscometers

D1193 Specification for reagent water

D1217 Test method for density and relative density (specific gravity) of liquids by bingham pycnometer

D1480 Test method for density and relative density (specific gravity) of viscous materials by Bingham pycnometer

D1481 Test method for density and relative density (specific gravity) of viscous materials by Lipkin bicapillary pycnometer

D2162 Practice for basic calibration of master viscometers and viscosity oil standards

D2170 Test method for kinematic viscosity of asphalts (bitumens)

D2171 Test method for viscosity of asphalts by vacuum capillary viscometer

D6071 Test method for low level sodium in high purity water by graphite furnace atomic absorption spectroscopy

D6074 Guide for characterizing hydrocarbon lubricant base oils

D6299 Practice for applying statistical quality assurance and control charting techniques to evaluate analytical measurement system performance

D6617 Practice for laboratory bias detection using single test result from standard

material

E1 Specification for ASTM liquid-in-glass thermometers

E77 Test method for inspection and verification of thermometers

E1137/E1137M Specification for industrial platinum resistance thermometers

2.2. ISO standards:

ISO 3104 Petroleum Products—Transparent and opaque liquids—Determination of kinematic viscosity and calculation of dynamic viscosity

ISO 3105 Glass capillary kinematic viscometers—Specification and operating instructions

ISO 3696 Water for analytical laboratory use—Specification and test methods

ISO 5725 Accuracy (trueness and precision) of measurement methods and results.

ISO 9000 Quality management and quality assurance standards—Guidelines for selection and use

ISO 17025 General requirements for the competence of testing and calibration laboratories

2.3. NIST standards:

NIST technical note 1297 guideline for evaluating and expressing the uncertainty of NIST measurement results

NIST GMP 11 Good Measurement Practice for Assignment and Adjustment of Calibration Intervals for Laboratory Standards

NIST special publication 819 guide for the use of the international system of units (SI)

3. Terminology

3.1. See also international vocabulary of metrology.

3.2. Definitions:

3.2.1. digital contact thermometer (DCT), *n*—an electronic device consisting of a digital display and associated temperature sensing probe.

3.3. Definitions of terms specific to this standard:

3.3.1. automated viscometer, *n*—apparatus which, in part or in whole, has mechanized one or more of the procedural steps indicated in Section 11 or 12 without changing the principle or technique of the basic manual apparatus. The essential elements of the apparatus in respect to dimensions, design, and operational characteristics are the same as those of the manual method.

3.3.1.1. Discussion—Automated viscometers have the capability to mimic some operation of the test method while reducing or removing the need for manual intervention or interpretation. Apparatus which determine kinematic viscosity by physical techniques that are different than those used in this test method are not considered to be Automated Viscometers.

3.3.2. density, n —the mass per unit volume of a substance at a given temperature.

3.3.3. dynamic viscosity, η , n —the ratio between the applied shear stress and rate of shear of a material.

3.3.3.1. Discussion—It is sometimes called the coefficient of dynamic viscosity or absolute viscosity. Dynamic viscosity is a measure of resistance to flow or deformation which constitutes a material's ability to transfer momentum in response to steady or time-dependent external shear forces. Dynamic viscosity has the dimension of mass divided by length and time and its SI unit is pascal times second (Pa·s). Among the transport properties for heat, mass, and momentum transfer, dynamic viscosity is the momentum conductivity.

3.3.4. kinematic viscosity, ν , n —the ratio of the dynamic viscosity (η) to the density (ρ) of a material at the same temperature and pressure.

3.3.4.1. Discussion—Kinematic viscosity is the ratio between momentum transport and momentum storage. Such ratios are called diffusivities with dimensions of length squared divided by time and the SI unit is metre squared divided by second (m^2/s). Among the transport properties for heat, mass, and momentum transfer, kinematic viscosity is the momentum diffusivity.

3.3.4.2. Discussion—Formerly, kinematic viscosity was defined specifically for viscometers covered by this test method as the resistance to flow under gravity. More generally, it is the ratio between momentum transport and momentum storage.

3.3.4.3. Discussion—For gravity-driven flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ , if the density of air is negligible compared to that of the liquid. For any particular viscometer covered by this test method, the time of flow of a fixed volume of liquid is directly proportional to its kinematic viscosity, ν , where $\nu = \eta/\rho$, and η is the dynamic viscosity.

4. Summary of test method

- 4.1. The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity (determined value) is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values.

5. Significance and use

- 5.1. Many petroleum products, and some non-petroleum materials, are used as lubricants, and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity is essential to many product specifications.

6. Apparatus

- 6.1. Viscometers—Use only calibrated viscometers of the glass capillary type, capable of being used to determine kinematic viscosity within the limits of the precision given in the precision section.
- 6.1.1. Viscometers listed in Table A1.1, whose specifications meet those given in Specifications D446 and in ISO 3105 meet these requirements. It is not intended to restrict this test method to the use of only those viscometers listed in Table A1.1. Annex A1 gives further guidance.
- 6.1.2. Automated Viscometers—Automated apparatus may be used as long as they mimic the physical conditions, operations or processes of the manual apparatus. Any viscometer, temperature measuring device, temperature control, temperature controlled bath or timing device incorporated in the automated apparatus shall conform to the specification for these components as stated in section 6 of this test method. Flow times of less than 200 s are permitted, however, a kinetic energy correction shall be applied in accordance with section 7 on kinematic viscosity calculation of specifications D446. The kinetic energy correction shall not exceed

3.0 % of the measured viscosity. The automated apparatus shall be capable of determining kinematic viscosity of a certified viscosity reference standard within the limits stated in 9.2.1 and section 17. The precision shall be of statistical equivalence to, or better (has less variability) than the manual apparatus.

6.2. Viscometer Holders—Use viscometer holders to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions (see specifications D446 and ISO 3105).

6.2.1. Viscometers shall be mounted in the constant temperature bath in the same manner as when calibrated and stated on the certificate of calibration. See specifications D446, see operating instructions in Annexes A1–A3. For those viscometers which have tube L (see specifications D446) held vertical, vertical alignment shall be confirmed by using (1) a holder ensured to hold tube L vertical, or (2) a bubble level mounted on a rod designed to fit into tube L, or (3) a plumb line suspended from the center of tube L, or (4) other internal means of support provided in the constant temperature bath.

6.3. Temperature-controlled bath—Use a transparent liquid bath of sufficient depth such, that at no time during the measurement of flow time, any portion of the sample in the viscometer is less than 20 mm below the surface of the bath liquid or less than 20 mm above the bottom of the bath.

6.3.1. Temperature control—For each series of flow time measurements, the temperature control of the bath liquid shall be such that within the range from 15 to 100°C , the temperature of the bath medium does not vary by more than 0.02°C of the selected temperature over the length of the viscometer, or between the position of each viscometer, or at the location of the thermometer. For temperatures outside this range, the deviation from the desired temperature must not exceed 0.05°C .

6.4. Temperature measuring device in the range from 0 to 100°C —Use either calibrated liquid-in-glass thermometers (Annex A2) with an accuracy after correction of 0.02°C or better, or a digital contact thermometer as described in 6.4.2 with equal or better accuracy.

6.4.1. If calibrated liquid-in-glass thermometers are used, the use of two thermometers is recommended. The two thermometers shall agree within 0.04°C .

6.4.2. When using a digital contact thermometer (DCT) the following shall apply:

- (1) The only acceptable sensors are a resistance temperature device (RTD), such as a platinum resistance thermometer (PRT), or a thermistor.
- (2) A minimum display resolution of 0.01°C .
- (3) A combined (display and probe) minimum accuracy of $\pm 0.02^{\circ}\text{C}$.
- (4) A response time of less than 6 s as defined in specification E1137/E1137M.
- (5) A drift of less than 10 mK (0.01°C) per year.
- (6) mK over the range of intended use.
- (7) The DCT shall have a report of temperature calibration traceable to a national calibration or metrology standards body issued by a competent calibration laboratory with demonstrated competency in temperature calibration.
- (8) The calibration report shall include data for the series of test points which are appropriate for its intended use.

6.4.2.1. For a constant temperature bath employed in manual viscosity measurements, the probe shall be immersed at least 100 mm below the liquid level of the bath but no less than 3 times the sensor element length. see Fig. 1. The end of the probe sheath shall not extend past the bottom of the viscometer. It is preferable for the center of the sensing element to be located at the same level as the lower half of the working capillary as long as the minimum immersion requirements are met.

6.4.2.2. In the case of constant temperature baths used in instruments for automatic viscosity determinations, the user is to contact the instrument manufacturer for the correct DCT that has performance equivalence to that described here.

6.4.3. Outside the range from 0 to 100°C , use either calibrated liquid-in-glass thermometers of an accuracy after correction of $\pm 0.05^{\circ}\text{C}$ or better, or any other thermometric device of equal or better accuracy. When two temperature measuring devices are used in the same bath, they shall agree within $\pm 0.1^{\circ}\text{C}$.

6.4.4. When using liquid-in-glass thermometers, such as those in Table A2.1, use a magnifying device to read the thermometer to the nearest 1/5 division (for example, 0.01°C or 0.02°F) to ensure that the required test temperature and temperature control capabilities are met (see 10.1). It is recommended that thermometer readings (and any corrections supplied on the certificates of calibrations for the thermometers) be recorded on a periodic basis to demonstrate compliance with the test method requirements. This information can be quite useful, especially when investigating issues or causes relating to testing accuracy and precision.

6.5. Timing Device—Use any timing device that is capable of taking readings with a discrimination of 0.1 s or better and has an accuracy within $\pm 0.07\%$ (see Annex A3) of the reading when tested over the minimum and maximum intervals of expected flow times.

6.5.1. Electrical timing devices may be used if the current frequency is controlled to an accuracy of 0.05 % or better. Alternating currents, as provided by some public power systems, are intermittently rather than continuously controlled. When used to actuate electrical timing devices, such control can cause large errors in kinematic viscosity flow time measurements.

7. Reagents and materials

7.1. Chromic acid cleaning solution, or a nonchromium containing, strongly oxidizing acid cleaning solution. (**Warning**—Chromic acid is a health hazard. It is toxic, a recognized carcinogen, highly corrosive, and potentially hazardous in contact with organic materials. If used, wear a full face-shield and full-length protective clothing including suitable gloves. Avoid breathing vapor. Dispose of used chromic acid carefully as it remains hazardous. Nonchromium containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.)

7.2. Sample solvent, completely miscible with the sample. Filter before use.

7.2.1. For most samples a volatile petroleum spirit or naphtha is suitable. For residual fuels, a prewash with an aromatic solvent such as toluene or xylene may be necessary to remove asphaltenic material.

7.3. Drying solvent, a volatile solvent miscible with the sample solvent (see 7.2) and water (see 7.4). Filter before use.

7.3.1. Acetone is suitable. (**Warning**—Extremely flammable.)

7.4. Water, deionized or distilled and conforming to specification D1193 or Grade 3 of ISO 3696. Filter before use.

8. Certified viscosity reference standards

8.1. Certified viscosity reference standards shall be certified by a laboratory that has been shown to meet the requirements of ISO 17025 by independent assessment. Viscosity standards shall be traceable to master viscometer procedures described in Test Method D2162.

8.2. The uncertainty of the certified viscosity reference standard shall be stated for each certified value ($k = 2$, 95% confidence). See ISO 5725 or NIST 1297.

9. Calibration and verification

9.1. Viscometers—Use only calibrated viscometers, thermometers, and timers as described in Section 6.

9.2. Certified viscosity reference standards (Table A1.2)—These are for use as confirmatory checks on the procedure in the laboratory.

9.2.1. If the determined kinematic viscosity does not agree within the acceptable tolerance band, as calculated from Annex A4, of the certified value, recheck each step in the procedure, including thermometer and viscometer calibration, to locate the source of error. Annex A1 gives details of standards available.

9.2.1.1. As an alternative to the calculation in Annex A4, the approximate tolerance bands in Table 1 may be used.

9.2.2. The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors. It must be appreciated that a correct result obtained on a standard oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

9.2.3. The calibration constant, C , is dependent upon the gravitational acceleration at the place of calibration and this must, therefore, be supplied by the standardization

laboratory together with the instrument constant. Where the acceleration of gravity, g , differs by more than 0.1 %, correct the calibration constant as follows:

$$C_2 = (g_2/g_1) \times C_1 \quad (1)$$

where the subscripts 1 and 2 indicate, respectively, the standardization laboratory and the testing laboratory.

10. General procedure for kinematic viscosity

10.1. Adjust and maintain the viscometer bath at the required test temperature within the limits given in 6.3.1 taking account of the conditions given in Annex A2 and of the corrections supplied on the certificates of calibration for the thermometers.

10.1.1. Thermometers shall be held in an upright position under the same conditions of immersion as when calibrated.

10.1.2. In order to obtain the most reliable temperature measurement, it is recommended that two thermometers with valid calibration certificates be used (see 6.4).

10.1.3. They should be viewed with a lens assembly giving approximately five times magnification and be arranged to eliminate parallax errors.

10.2. Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time for manual viscometers shall not be less than 200 s or the longer time noted in Specifications D446. Flow times of less than 200 s are permitted for automated viscometers, provided they meet the requirements of 6.1.2.

10.2.1. The specific details of operation vary for the different types of viscometers listed in Table A1.1. The operating instructions for the different types of viscometers are given in Specifications D446.

10.2.2. When the test temperature is below the dew point, fill the viscometer in the normal manner as required in 11.1. To ensure that moisture does not condense or freeze on the walls of the capillary, draw the test portion into the working capillary and timing bulb, place rubber stoppers into the tubes to hold the test portion in place, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, and then remove the stoppers. When performing manual

viscosity determinations, do not use those viscometers which cannot be removed from the constant temperature bath for charging the sample portion.

10.2.2.1. The use of loosely packed drying tubes affixed to the open ends of the viscometer is permitted, but not required. If used, the drying tubes shall fit the design of the viscometer and not restrict the flow of the sample by pressures created in the instrument.

10.2.2.2. Viscometers used for silicone fluids, fluorocarbons, and other liquids which are difficult to remove by the use of a cleaning agent, shall be reserved for the exclusive use of those fluids except during their calibration. Subject such viscometers to calibration checks at frequent intervals. The solvent washings from these viscometers shall not be used for the cleaning of other viscometers.

TABLE 1 Approximate tolerance bands

Viscosity of reference material, mm ² /s	Tolerance band
< 10	±0.30%
10 to 100	±0.32%
100 to 1000	±0.36%
1000 to 10000	±0.42%
10000 to 100000	±0.54%
> 100 000	±0.73%

11. Procedure for transparent liquids

11.1.Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. If the sample is thought or known to contain fibers or solid particles, filter through a 75 μm screen, either prior to or during charging (see specifications D446).

11.1.1. In general, the viscometers used for transparent liquids are of the type listed in Table A1.1, A and B.

11.1.2. With certain products which exhibit gel-like behavior, exercise care that flow time measurements are made at sufficiently high temperatures for such materials to

flow freely, so that similar kinematic viscosity results are obtained in viscometers of different capillary diameters.

11.1.3. Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Where one bath is used to accommodate several viscometers, never add or withdraw, or clean a viscometer while any other viscometer is in use for measuring a flow time.

11.1.4. Because this time will vary for different instruments, for different temperatures, and for different kinematic viscosities, establish a safe equilibrium time by trial.

11.1.4.1. Thirty minutes should be sufficient except for the highest kinematic viscosities.

11.1.5. Where the design of the viscometer requires it, adjust the volume of the sample to the mark after the sample has reached temperature equilibrium.

11.2. Use suction (if the sample contains no volatile constituents) or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark, unless any other value is stated in the operating instructions for the viscometer. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. If this flow time is less than the specified minimum (see 10.2), select a viscometer with a capillary of smaller diameter and repeat the operation.

11.2.1. Repeat the procedure described in 11.2 to make a second measurement of flow time. Record both measurements.

11.2.2. From the two measurements of flow time, calculate two determined values of kinematic viscosity.

11.2.3. If the two determined values of kinematic viscosity calculated from the flow time measurements agree within the stated determinability figure (see 17.1.1) for the product, use the average of these determined values to calculate the kinematic viscosity result to be reported. Record the result. If not, repeat the measurements of flow times after a thorough cleaning and drying of the viscometers and filtering (where required, see 11.1) of the sample until the calculated kinematic viscosity determinations agree with the stated determinability.

11.2.4. If the material or temperature, or both, is not listed in 17.1.1, use 1.5% as an estimate of the determinability.

12. Procedure for opaque liquids

12.1. For steam-refined cylinder oils and black lubricating oils, proceed to 12.3 ensuring a thoroughly representative sample is used. The kinematic viscosity of residual fuel oils and similar waxy products can be affected by the previous thermal history and the following procedure described in 12.1.1-12.2.2 shall be followed to minimize this.

12.1.1. In general, the viscometers used for opaque liquids are of the reverse-flow type listed in Table A1.1, C.

12.1.2. Heat in the original container, in an oven, at $60 \pm 2^\circ\text{C}$ for 1 h.

12.1.3. Thoroughly stir the sample with a suitable rod of sufficient length to reach the bottom of the container. Continue stirring until there is no sludge or wax adhering to the rod.

12.1.4. Recap the container tightly and shake vigorously for 1 min to complete the mixing.

12.1.4.1. With samples of a very waxy nature or oils of high kinematic viscosity, it may be necessary to increase the heating temperature above 60°C to achieve proper mixing. The sample should be sufficiently fluid for ease of stirring and shaking.

12.2. Immediately after completing 12.1.4, pour sufficient sample to fill two viscometers into a 100-mL glass flask and loosely stopper.

12.2.1. Immerse the flask in a bath of boiling water for 30 min. (**Warning**—Exercise care as vigorous boil-over can occur when opaque liquids which contain high levels of water are heated to high temperatures.)

12.2.2. Remove the flask from the bath, stopper tightly, and shake for 60 s.

12.3. Two determinations of the kinematic viscosity of the test material are required. For those viscometers that require a complete cleaning after each flow time measurement, two viscometers may be used. A single viscometer in which an immediate, repeat flow time measurement can be made without cleaning may also be used for the two measurements of flow time and calculation of kinematic viscosity. Charge two

viscometers in the manner dictated by the design of the instrument. For example, for the cross-arm or the BS U-tube viscometers for opaque liquids, filter the sample through a 75- μm filter into two viscometers previously placed in the bath. For samples subjected to heat treatment, use a preheated filter to prevent the sample coagulating during the filtration.

12.3.1. Viscometers which are charged before being inserted into the bath may need to be preheated in an oven prior to charging the sample. This is to ensure that the sample will not be cooled below test temperature.

12.3.2. After 10 min, adjust the volume of the sample (where the design of the viscometer requires) to coincide with the filling marks as in the viscometer specifications (see Specifications D446).

12.3.3. Allow the charged viscometers enough time to reach the test temperature (see 12.3.1). Where one bath is used to accommodate several viscometers, never add or withdraw, or clean a viscometer while any other viscometer is in use for measuring flow time.

12.4. With the sample flowing freely, measure in seconds to within 0.1 s, the time required for the advancing ring of contact to pass from the first timing mark to the second. Record the measurement.

12.4.1. In the case of samples requiring heat treatment described in 12.1 through 12.2.1, complete the measurements of flow time within 1 h of completing 12.2.2. Record the measured flow times.

12.5. Calculate kinematic viscosity, V , in mm^2/s , from each measured flow time. Regard these as two determined values of kinematic viscosity.

12.5.1. For residual fuel oils, if the two determined values of kinematic viscosity agree within the stated determinability figure (see 17.1.1), use the average of these determined values to calculate the kinematic viscosity result to be reported. Record the result. If the calculated kinematic viscosities do not agree, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering of the sample. If the material or temperature, or both, is not listed in 17.1.1, for temperatures between 15 and 100°C use as an estimate of the determinability 1.0 %, and 1.5 % for temperatures outside this range; it must be

realized that these materials can be non-Newtonian, and can contain solids which can come out of solution as the flow time is being measured.

13. Cleaning of viscometer

13.1. Between successive determinations of kinematic viscosity, clean the viscometer thoroughly by several rinsings with the sample solvent, followed by the drying solvent (see 7.3). Dry the tube by passing a slow stream of filtered dry air through the viscometer for 2 min or until the last trace of solvent is removed.

13.2. Periodically clean the viscometer with the cleaning solution (**Warning**—see 7.1), for several hours to remove residual traces of organic deposits, rinse thoroughly with water (7.4) and drying solvent (see 7.3), and dry with filtered dry air or a vacuum line. Remove any inorganic deposits by hydrochloric acid treatment before the use of cleaning acid, particularly if the presence of barium salts is suspected. (**Warning**—It is essential that alkaline cleaning solutions are not used as changes in the viscometer calibration can occur.)

14. Calculation

14.1. Calculate each of the determined kinematic viscosity values, V_1 and V_2 , from the measured flow times, t_1 and t_2 , and the viscometer constant, C , by means of the following equation:

$$V_{1,2} = C \cdot t_{1,2} \quad (2)$$

where:

$V_{1,2}$ = determined kinematic viscosity values for V_1 and V_2 , respectively, mm^2/s ,

C = calibration constant of the viscometer, mm^2/s^2 , and

$t_{1,2}$ = measured flow times for t_1 and t_2 , respectively, s.

Calculate the kinematic viscosity result, n , as an average of V_1 and V_2 (see 11.2.3 and 12.5.1).

14.2. Calculate the dynamic viscosity, η , from the calculated kinematic viscosity, V , and the density, ρ , by means of the following equation:

$$\eta = V \times \rho \times 10^{-3} \quad (3)$$

where:

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η = dynamic viscosity, mPa·s,

ρ = density, kg/m³, at the same temperature used for the determination of the kinematic viscosity, and

ν = kinematic viscosity, mm²/s.

14.2.1. The density of the sample can be determined at the test temperature of the kinematic viscosity determination by an appropriate method such as Test Methods D1217, D1480, or D1481.

15. Expression of results

15.1. Report the test results for the kinematic or dynamic viscosity, or both, to four significant figures, together with the test temperature.

16. Report

16.1. Report the following information:

- 16.1.1. Type and identification of the product tested,
- 16.1.2. Reference to this test method or a corresponding international standard,
- 16.1.3. Result of the test (see Section 15),
- 16.1.4. Any deviation, by agreement or otherwise, from the procedure specified,
- 16.1.5. Date of the test, and
- 16.1.6. Name and address of the test laboratory.

17. Precision and bias

17.1. Comparison of determined values:

17.1.1. Determinability (d)—The difference between successive determined values obtained by the same operator in the same laboratory using the same apparatus for a series of operations leading to a single result, would in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C	0.0013 y	(0.13 %)
Formulated oils at 150°C	0.015 y	(1.5 %)

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Petroleum wax at 100°C	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C	0.011 ($y + 8$)	
Residual fuel oils at 50°C	0.017 y	(1.7 %)
Additives at 100°C	0.00106 y	
Gas oils at 40°C	0.0013 ($y+1$)	
Jet fuels at -20°C	0.0018 y	(0.18 %)

where: y is the average of determined values being compared.

17.2.Comparison of results:

17.2.1. Repeatability (r)—The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C	0.0026 x	(0.26 %)
Formulated oils at 150°C	0.0056 x	(0.56 %)
Petroleum wax at 100°C	0.0141 x	
Residual fuel oils at 80 and 100°C	0.013 ($x + 8$)	
Residual oils at 50°C	0.015 x	(1.5 %)
Additives at 100°C	0.00192 x	
Gas oils at 40°C	0.0043 ($x+1$)	
Jet fuels at -20°C	0.007 x	(0.7 %)

where: x is the average of results being compared.

17.2.2. Reproducibility (R)—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated below only in one case in twenty:

Base oils at 40 and 100°C	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C	0.0076 x	(0.76 %)
Formulated oils at 150°C	0.018 x	(1.8 %)
Petroleum wax at 100°C	0.0366 $x1.2$	

Residual fuel oils at 80 and 100°C	$0.04 (x + 8)$	
Residual oils at 50°C	$0.074 x$	(7.4 %)
Additives at 100°C	$0.00862 x 1.1$	
Gas oils at 40°C	$0.0082 (x+1)$	
Jet fuels at -20°C	$0.019 x$	(1.9 %)

where: x is the average of results being compared.

17.3. The precision for used oils has not been determined but is expected to be poorer than that for formulated oils. Because of the extreme variability of such used oils, it is not anticipated that the precision of used oils will be determined.

17.4. The precision for specific automated viscometers has not been determined. However, an analysis has been made of a large data set including both automated and manual viscometers over the temperature range of 40 to 100°C. The reproducibility of automated viscometer data is not statistically significantly different than the reproducibility of manual viscometer data. It is also shown that there is no bias of the automated data in comparison to the manual data.

18. Keywords

18.1. dynamic viscosity; kinematic viscosity; viscometer; viscosity

**Standard test method for
acid and base number by color-indicator titration**

1. Scope

- 1.1. This test method covers the determination of acidic or basic constituents (Note 1) in petroleum products² and lubricants soluble or nearly soluble in mixtures of toluene and isopropyl alcohol. It is applicable for the determination of acids or bases whose dissociation constants in water are larger than 10^{-9} ; extremely weak acids or bases whose dissociation constants are smaller than 10^{-9} do not interfere. Salts react if their hydrolysis constants are larger than 10^{-9} .
- 1.2. This test method can be used to indicate relative changes that occur in an oil during use under oxidizing conditions. Although the titration is made under definite equilibrium conditions, the method does not measure an absolute acidic or basic property that can be used to predict performance of an oil under service conditions. No general relationship between bearing corrosion and acid or base numbers is known.
- 1.3. The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.4. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced documents

2.1. ASTM standards:

D117 Guide for sampling, test methods, and specifications for electrical insulating oils of petroleum origin

D664 Test method for acid number of petroleum products by potentiometric titration

D1193 Specification for reagent water

D4175 Terminology relating to petroleum, petroleum products, and lubricants

D4739 Test method for base number determination by potentiometric hydrochloric acid titration

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3. Terminology

3.1. Definitions:

3.1.1. acid number, n —the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample to a specified end point.

3.1.1.1. Discussion—In this test method, the indicator is *p*-naphtholbenzein titrated to a green/green-brown end point in a toluene-water-isopropanol solvent.

3.1.2. base number, n —the quantity of acid, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample to a specified end point.

3.1.2.1. Discussion—In this test method, the indicator is *p*-naphtholbenzein titrated to an orange end point in a toluene-water-isopropanol solvent.

3.1.3. used oil, n —any oil that has been in a piece of equipment (for example, an engine, gearbox, transformer, or turbine) whether operated or not.

3.2. Definitions of terms specific to this standard:

3.2.1. strong acid number, n —the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a hot water extract of the sample to a golden-brown end point using methyl orange solution.

4. Summary of test method

4.1. To determine the acid or base number, the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end point indicated by the color change of the added *p*-naphtholbenzein solution (orange in acid and green-brown in base). To determine the strong acid number, a separate portion of the sample is extracted with hot water and the aqueous extract is titrated with potassium hydroxide solution, using methyl orange as an indicator.

5. Significance and use

- 5.1. New and used petroleum products can contain basic or acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with acids or bases. This number, whether expressed as acid number or base number, is a measure of this amount of acidic or basic substances, respectively, in the oil—always under the conditions of the test. This number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service; however, any condemning limits must be empirically established.
- 5.2. Since a variety of oxidation products contribute to the acid number and the organic acids vary widely in corrosive properties, the test cannot be used to predict corrosiveness of an oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils toward metals. Compounded engine oils can and usually do have both acid and base numbers in this test method.

6. Apparatus

- 6.1. Burets (with the following dimensions):
- 50-mL buret graduated in 0.1-mL subdivisions
 - 10-mL buret graduated in 0.05-mL or smaller subdivisions
 - 5-mL with 0.02-mL subdivisions

7. Reagents

- 7.1. Purity of reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 7.2. Purity of water—References to water shall be understood to mean reagent water that meets the requirements of either Type I, II, or III of specification D1193.

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- 7.3. Isopropyl alcohol, anhydrous (less than 0.9 % water). (**Warning**—Flammable.)
- 7.4. Hydrochloric acid solution, standard alcoholic —(0.1 *M*)—Mix 9 mL of concentrated hydrochloric acid (**Warning**— Corrosive, fumes cause irritation) (HCl, sp gr 1.19) with 1000 mL of anhydrous isopropyl alcohol (2-propanol) (**Warning**— See 7.3).
Standardize frequently enough to detect molarity changes of 0.0005 (Note 6), preferably by electrometric titration of approximately 8 mL (accurately measured) of the 0.1 *M* alcoholic KOH solution diluted with 125 mL of carbon dioxide-free water. When an electrometric titration is used for the standardization, the end point shall be a well-defined inflection point closest to the cell voltage for the acidic buffer solution. When a colorimetric titration is used for the standardization, titrate to the first stable appearance of the orange color with methyl orange indicator.
- 7.5. Methyl orange indicator solution—Dissolve 0.1 g of methyl orange in 100 mL of water.
- 7.6. *p*-Naphtholbenzein indicator^{5,6} solution—The *p*-naphtholbenzein shall meet the specifications given in Annex A1. Prepare a solution of *p*-naphtholbenzein in titration solvent equal to 10 ± 0.01 g/L.
- 7.7. Potassium hydroxide solution, standard alcoholic (0.1 *M*)—Add 6 g of solid KOH (**Warning**—Highly corrosive to all body tissue) to approximately 1 L of anhydrous isopropyl alcohol (containing less than 0.9 % water) in a 2-L Erlenmeyer flask. Boil the mixture gently for 10 to 15 min, stirring to prevent the solids from forming a cake on the bottom. Add at least 2 g of barium hydroxide (Ba(OH)₂) (**Warning**— Poisonous if ingested, strongly alkaline, causes severe irritation producing dermatitis) and again boil gently for 5 to 10 min. Cool to room temperature, allow to stand for several hours, and filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide (CO₂) during filtration. Store the solution in a chemically resistant dispensing bottle out of contact with cork, rubber, or saponifiable stopcock lubricant and protected by a guard tube containing soda lime or soda nonfibrous silicate absorbent (Ascarite, Carbosorb, or Indecarb).
- 7.7.1. Standardization of potassium hydroxide solution— Standardize frequently enough to detect changes of 0.0005 *M*. One way to do this is as follows: Weigh, to the nearest 0.1 mg approximately 0.2 g of potassium acid phthalate, which has been dried for at least 1 h at $110 \pm 1^\circ\text{C}$ and dissolve in 40 ± 1 mL of water, free of CO₂.

Titrate with the potassium hydroxide alcoholic solution to either of the following end points: (1) When the titration is electrometric, titrate to a well-defined inflection point at the voltage that corresponds to the voltage of the basic buffer solution, or (2) When titration is colorimetric, add six drops of phenolphthalein indicator solution and titrate to the appearance of a permanent pink color. Perform the blank titration on the water used to dissolve the potassium acid phthalate.

Calculate the molarity using the following equation:

$$\text{Molarity} = \frac{W_p}{204.23} \times \frac{1000}{V_2 V_b} \quad (1)$$

where:

W_p = weight of the potassium acid phthalate, g,

204.23 = molecular weight of the potassium acid phthalate,

V = volume of titrant used to titrate the salt to the specific end point, mL, and

V_b = volume of titrant used to titrate the blank, mL.

7.7.2. Prepare a 0.1 ± 0.01 m% solution of phenolphthalein by dissolving pure solid phenolphthalein in a 1:1 mixture of water, free of CO_2 , and ethanol.

7.8. Titration solvent—Prepare by mixing toluene, water, and anhydrous isopropyl alcohol in the ratio 100 : 1 : 99.

8. Preparation of used oil samples

8.1. Strict observance of the sampling procedure described in 8.2 is necessary, since the sediment itself is acidic or basic or has adsorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

8.2. Heat the sample (Note 9) of used oil to $60 \pm 5^\circ\text{C}$ in the original container and agitate until all sediment is homogeneously suspended in the oil (Note 10). If the original container is of opaque material, or if it is more than three-fourths full, transfer the entire sample to a clear glass bottle having a capacity at least one third greater than the volume of the sample, and transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container. After complete

suspension of all sediment, strain the sample or a convenient aliquot through a 100-mesh screen for the removal of large contaminating particles (Note 9).

TABLE 1 Size of sample

Acid number or base number	Size of sample, g	Sensitivity of weighing, g
New or light oils		
0.0 to 3.0	20.0 ± 2.0	0.05
Over 3.0 to 25.0	2.0 ± 0.2	0.01
Over 25.0 to 250.0	0.2 ± 0.02	0.001
Used or dark-colored oils		
0.0 to 25.0	2.0 ± 0.2	0.01
Over 25 to 250.0	0.2 ± 0.02	0.001

9. Procedure for acid number

- 9.1. Into an appropriate size Erlenmeyer flask or a beaker, introduce a weighed quantity of the sample as given in Table 1. Add 100 mL of the titration solvent and 0.5 mL of the indicator solution, and without stoppering, swirl until the sample is entirely dissolved by the solvent. If the mixture assumes a yellow-orange color, proceed as directed in 9.2; if it becomes green or green-black, proceed as directed in Section 10.
- 9.2. Without delay, titrate at a temperature below 30°C (Note 14). Add 0.1 M KOH solution in increments and mix to disperse the KOH as necessary (see Note 12). Shake vigorously near the end point, but avoid dissolving carbon dioxide (CO₂) in the solvent. (In the case of acidic oils, the orange color changes to a green or green-brown as the end point is approached.) When the solution first turns green or greenbrown, reduce the increment size to dropwise (manual burette) or between 0.01 and 0.05 mL (automated burette). Continue until a persistent green or green-brown end point is reached (see Note 13) and held for a minimum of 15 s after the addition of the last increment or if it reverses with two drops of 0.1 M HCl.
- 9.3. Blank—Perform a blank titration on 100 mL of the titration solvent and 0.5 mL of the indicator solution, adding 0.1-mL or less increments of the 0.1 M KOH solution.

9.3.1. The titration solvent usually contains weak acid impurities which react with the strongly basic components of the sample. To correct the base number for the sample, determine an acid number blank upon the solvent.

10. Procedure for base number

10.1. If the titration solvent containing the dissolved sample assumes a green or greenish-brown color after the indicator is added (9.1), carry out the titration as described in 9.2, but use 0.1 *M* HCl and titrate until the green-brown color changes to orange.

10.2. Blank—Perform a blank titration as directed in 9.3.

11. Procedure for strong acid number

11.1. Introduce approximately 25 g of a representative sample, weighed to the nearest 0.1 g, into a 250-mL separatory funnel and add 100 mL of boiling water. Shake vigorously and drain the water phase, after separation, into a 500-mL casserole. Extract the sample twice more with 50-mL portions of boiling water, adding both extracts to the casserole. To the combined extracts add 0.1 mL of methyl orange indicator solution and, if the solution becomes pink or red, titrate with 0.1 *M* KOH solution until the solution becomes golden brown in color. If the initial color is not pink or red, report the strong acid number as zero. (See Note 15.)

11.2. Blank—Into a 250-mL Erlenmeyer flask, introduce 200 mL of the same boiling water as used for the sample titration. Add 0.1 mL of methyl orange indicator solution. If the indicator color is yellow-orange, titrate with 0.1 *M* HCl to the same depth and shape of color obtained in the titration of the sample. If the indicator color is pink or red, titrate with 0.1 *M* KOH solution to the same end point as that used in the sample titration.

12. Quality control checks

12.1. Confirm the performance of the equipment or the procedure each day it is in use, by analyzing a quality control (QC) sample. It is advisable to analyze additional QC samples as appropriate, such as at the end of a batch of samples or after a fixed number of samples to ensure the quality of the results. Analysis of results from these QC samples can be carried out using control chart techniques. When the result of a test on a

QC sample exceeds the control limits of the laboratory, corrective action, such as instrument recalibration may be required. An ample supply of QC sample material shall be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions. If possible, the QC sample shall be representative of samples typically analyzed and the average value and control limits of the QC sample shall be determined prior to monitoring the measurements process. The precision for the QC sample must be compared against that given in the Precision and Bias section of this test method in order to verify that the instrument is functioning correctly.

13. Calculation

13.1. Calculate the acid number as follows:

$$\text{Acid number, mg of KOH/g} = [(A - B)M \times 56.1]/W \quad (2)$$

where:

A = KOH solution required for titration of the sample (9.2), mL,

B = KOH solution required for titration of the blank (9.3), mL,

M = molarity of the KOH solution, and

W = sample used, g.

13.2. Calculate the strong-acid number as follows:

13.2.1. If the blank titration is made with acid:

$$\text{Strong acid number, mg of KOH/g} = [(CM + Dm) \times 56.1]/W \quad (3)$$

where:

C = KOH solution required to titrate the water extract (11.1), mL,

M = molarity of KOH solution,

D = HCl solution required to titrate the blank solution (11.2), mL,

m = molarity of the HCl solution, and

W = sample used, g.

13.2.2. If the blank titration is made with base:

$$\text{Strong acid number, mg of KOH/g} = [(C - D)M \times 56.1]/W \quad (4)$$

where:

C = KOH solution required to titrate the water extract (11.1), mL,

D = KOH solution required to titrate the blank solution (11.2), mL,

M = molarity of the KOH solution, and

W = sample used, g.

13.3. Calculate the base number as follows:

$$\text{base number, mg of KOH/g} = [(Em + FM) \times 56.1]/W (5)$$

where:

E = HCl solution required for titration of the sample (Section 10), mL,

m = molarity of the HCl solution,

F = KOH required for titration of the acid number blank, mL,

M = molarity of the KOH solution, and

W = sample used, g.

14. Report

14.1. Report the result as acid number, strong acid number, or base number as follows:

Acid number (D974) = (result)

Strong acid number (D974) = (result)

Base number (D974) = (result)

15. Precision and bias

15.1. Precision—This precision section applies only to new, light-colored, straight mineral oils and new and used inhibited steam turbine oils. Insufficient data are available on other oils coming within the scope of this test method so that no precision is given for such oils.

15.1.1. Repeatability—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Acid base number	Repeatability
0.00 to 0.1	0.03
Over 0.1 to 0.5	0.05
Over 0.5 to 1.0	0.08
Over 1.0 to 2.0	0.12

15.1.2. Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Acid Base Number	Reproducibility
0.00 to 0.1	0.04
Over 0.1 to 0.5	0.08
Over 0.5 to 2.0	15 % of the neutralization number level

15.2.Bias—The procedures in this test method have no bias because the acid and base values can be defined only in the terms of the test method.

16. Keywords

16.1.acid number; base number; color indication titration; petroleum products

**Standard practice for calculating viscosity index from kinematic viscosity
at 40 °C and 100°C**

1. Scope

- 1.1. This practice covers the procedures for calculating the viscosity index of petroleum products, such as lubricating oils, and related materials from their kinematic viscosities at 40 and 100°C.
- 1.2. This practice does not apply to petroleum products with kinematic viscosities less than 2.0 mm²/s at 100°C. Table 1 given in this practice applies to petroleum products with kinematic viscosities between 2 and 70 mm²/s at 100°C. Equations are provided for calculating viscosity index for petroleum products having kinematic viscosities above 70 mm²/s at 100°C.
 - 1.2.1. In cases where kinematic viscosity data are not available at temperatures of 40 and 100°C, an estimate may be made of the viscosity index by calculating the kinematic viscosity at temperatures of 40 and 100°C from data obtained at other temperatures. Such viscosity index data may be considered as suitable for information only and not for specification purposes. See Test Method D341, Annex A1.
- 1.3. The kinematic viscosity values are determined with reference to a value of 1.0034 mm²/s at 20.00°C for distilled water. The determination of the kinematic viscosity of a petroleum product shall be carried out in accordance with Test Methods D445, D7042, IP 71, or ISO 3104.
 - 1.3.1. If Viscosity Index calculated for a given sample using kinematic viscosity measurements from different test methods are in disagreement, the values calculated from test method D445 measurements shall be accepted.
- 1.4. The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
 - 1.4.1. The values stated in SI units are to be regarded as the standard. For user reference,

$$1 \text{ mm}^2/\text{s} = 10^{-6} \text{ m}^2/\text{s} = 1 \text{ cSt}.$$
- 1.5. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate

safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced documents

2.1. ASTM standards:

D341 Practice for viscosity-temperature charts for liquid petroleum products

D445 Test method for kinematic viscosity of transparent and opaque liquids (and calculation of dynamic viscosity)

D1695 Terminology of cellulose and cellulose derivatives

D7042 Test method for dynamic viscosity and density of liquids by stabinger viscometer (and the calculation of kinematic viscosity)

E29 Practice for using significant digits in test data to determine conformance with specifications

2.2. ISO standards:

ISO 3104 Petroleum Products—Transparent and opaque liquids—Determination of kinematic viscosity and calculation of dynamic viscosity

2.3. Energy Institute Standard:

IP 71 Determination of kinematic viscosity and calculation of dynamic viscosity

3. Terminology

3.1. Definitions:

3.1.1. viscosity index, n —an arbitrary number used to characterize the variation of the kinematic viscosity of a petroleum product with temperature.

3.1.1.1. Discussion—For oils of similar kinematic viscosity, the higher the viscosity index the smaller the effect of temperature on its kinematic viscosity.

3.1.1.2. Discussion—Viscosity index is also used in Terminology D1695 in a definition unrelated to this one.

4. Significance and use

- 4.1. The viscosity index is a widely used and accepted measure of the variation in kinematic viscosity due to changes in the temperature of a petroleum product between 40 and 100°C.
- 4.2. A higher viscosity index indicates a smaller decrease in kinematic viscosity with increasing temperature of the lubricant.
- 4.3. The viscosity index is used in practice as a single number indicating temperature dependence of kinematic viscosity.
- 4.4. Viscosity index is sometimes used to characterize base oils for purposes of establishing engine testing requirements for engine oil performance categories.

5. Procedure

- 5.1. Determine the kinematic viscosity of the sample at 40 and 100°C in accordance with test method D445, test method D7042, ISO 3104, or IP 71.

5.2. Calculation:

5.2.1. If the kinematic viscosity of the sample at 100°C is less than or equal to 70 mm²/s, extract from Table 1 the corresponding values for L and H . Measured values that are not listed, but are within the range of Table 1, may be obtained by linear interpolation. The viscosity index is not defined and shall not be reported for oils with kinematic viscosity of less than 2.0 mm²/s at 100°C.

5.2.2. If the kinematic viscosity is greater than 70 mm²/s at 100°C, calculate the values of L and H as follows:

$$L = 0.8353 Y^2 + 14.67 Y - 216 \quad (1)$$

$$H = 0.1684 Y^2 + 11.85 Y - 97 \quad (2)$$

where:

L = kinematic viscosity at 40°C of an oil of 0 viscosity index having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated, mm²/s,

Y = kinematic viscosity at 100°C of the oil whose viscosity index is to be calculated, mm²/s, and

H = kinematic viscosity at 40°C of an oil of 100 viscosity index having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated, mm²/s.

5.2.3. If $U > H$, calculate the viscosity index, VI , of the oil as follows:

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$$VI = [(L - U)/(L - H)] \times 100 \quad (3)$$

where:

U = kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated, mm²/s.

5.2.3.1. Calculation example—Measured kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated = 73.30 mm²/s; kinematic viscosity at 100°C of the oil whose viscosity index is to be calculated = 8.86 mm²/s.

From Table 1 (by interpolation) $L = 119.94$

From Table 1 (by interpolation) $H = 69.48$

Substituting in Eq 3 and rounding to the nearest whole number:

$$VI = [(119.94 - 73.30)/(119.94 - 69.48)] \times 100 = 92.43 \quad (4)$$

$$VI = 92 \quad (5)$$

5.2.4. If $U < H$, calculate the viscosity index, VI , of the oil as follows:

$$VI = [((\text{antilog } N) - 1)/0.00715] + 100 \quad (6)$$

where:

$$N = (\log H - \log U) / \log Y \quad (7)$$

or

$$Y^N = H/U \quad (8)$$

5.2.4.1. Calculation example—Measured kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated = 22.83 mm²/s; kinematic viscosity at 100°C of the oil whose viscosity index is to be calculated = 5.05 mm²/s:

From Table 1 (by interpolation) $H = 28.975$ Substituting by Eq 7 (by logarithms):

$$N = [\log(28.975) - \log(22.83)] / \log(5.05) = 0.14719 \quad (9)$$

Substituting in Eq 6 and rounding to the nearest whole number:

$$\begin{aligned} VI &= [(\text{anti log}(0.14719) - 1)/0.00715] + 100 \\ &= [(1.40343 - 1)/0.00715] + 100 \\ &= [0.40343/0.00715] + 100 \\ &= 156.4235 \end{aligned} \quad (10)$$

$$VI = 156$$

5.2.4.2. Calculation Example—Measured kinematic viscosity at 40°C of the oil

whose viscosity index is to be calculated = 53.47 mm²/s; kinematic viscosity at 100°C of the oil whose viscosity index is to be calculated = 7.80 mm²/s:

From Table 1, $H = 57.31$

Substituting in Eq 7 (by logarithms):

$$N = [(\log 57.31 - \log 53.47)/\log 7.80] = 0.03376 \quad (11)$$

Substituting in Eq 6 and rounding to the nearest whole number:

$$\begin{aligned} VI &= [((\text{antilog } 0.03376) - 1)/0.00715] + 100 \\ &= [(1.08084 - 1)/0.00715] + 100 = 111 \end{aligned} \quad (12)$$

5.2.5. If $U = H$, the viscosity index, VI, of the oil equals 100.

5.3. ASTM D539b,7 is based on the above calculation and may be used instead of 5.2 through 5.2.5.

6. Report

- 6.1. Report the viscosity index to the nearest whole number, using the Rounding Method of E29. When the number is exactly halfway between the nearest two whole numbers, round to the nearest even number. For example, 116.5 shall be reported as 116.
- 6.2. The test report shall contain at least the following information:
 - 6.2.1. A reference to this standard
 - 6.2.2. The type and complete identification of the product tested,
 - 6.2.3. The result of the test,
 - 6.2.4. The test method used for the kinematic viscosity measurements,
 - 6.2.5. Any deviation, by agreement or otherwise, from the procedure specified, and
 - 6.2.6. The date of the test.

7. Keywords

- 7.1. kinematic viscosity; viscosity index

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