ไฮโดรจิเนชันของน้ำมันถั่วเหลืองโดยใช้ตัวเร่งปฏิกิริยา NiW/Al_2O_3 และ CoW/Al_2O_3

นางสาวอาภันดา พฤกษ์ชาติศิริ

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HYDROGENATION OF SOYBEAN OIL OVER NiW/Al_2O_3 AND CoW/Al_2O_3 CATALYSTS

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งานวิจัยนี้เป็นการศึกษาปฏิกิริยาไฮโดรจิเนชันน้ำมันถั่วเหลืองแบบบางส่วน และเลือกจำเพาะ โดยใช้ตัวเร่งปฏิกิริยา ซึ่งประกอบด้วยโลหะทรานซิชัน 2 ชนิด คือ 5%นิเกิล – 5%ทังสเตน, 5%นิเกิล – 10%ทังสเตน, 5%โคบอลต์ – 5%ทังสเตน และ 5%โคบอลต์ – 10%ทังสเตน บนตัวรองรับอลูมินา โดยทำการศึกษาถึงผลของอุณหภูมิ ความดัน และเวลาที่ใช้ในการทำปฏิกิริยา

จากการศึกษาพบว่า ตัวเร่งปฏิกิริยาที่ประกอบด้วย 5%นิเกิล – 10%ทังสเตน บนตัวรองรับอลูมินา เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพดีที่สุด ภาวะที่เหมาะสมในการเกิดกรดโอลิอิก คือ ที่อุณหภูมิ 150 องศาเซลเซียส ความดันไฮโดรเจน 150 ปอนด์ต่อตารางนิ้ว เวลาในการเกิดปฏิกิริยา 2 ชั่วโมง ความเร็วรอบของการกวน 500 รอบต่อนาที และใช้ปริมาณของตัวเร่งปฏิกิริยา 10% ของน้ำหนักของน้ำมันถั่วเหลือง ผลิตภัณฑ์ที่ได้มีค่าไอโอดีน 90 และมีส่วนประกอบของกรดปามิติก 9.09%, กรดสเตียริก 9.91%, กรดโอลิอิก 72.58% และกรดลิโนลิอิก 8.42% ของน้ำหนักของน้ำมันทั้งหมด ส่วนกรดลิโนลินิกถูกไฮโดรจิเนตจนหมด น้ำมันถั่วเหลืองภายหลังจากการทำไฮโดรจิเนชันแล้ว จะถูกแยกเป็น 2 ส่วน คือ ส่วนที่เป็นกรดไขมันที่อิ่มตัว และส่วนที่เป็นกรดไขมันไม่อิ่มตัว โดยวิธีวินเทอไรเซชัน พบว่าในส่วนที่เป็นกรดไขมันไม่อิ่มตัว จะมีปริมาณกรดโอลิอิก 87.58% ของน้ำหนักของกรดไขมันไม่อิ่มตัวทั้งหมด ปฏิกิริยาไฮโดรจิเนชันที่ใช้ตัวเร่งปฏิกิริยาที่มี 5%นิเกิล –10%ทังสเตน จะให้ปริมาณกรดโอลิอิกมากที่สุด เมื่อเปรียบเทียบกับผลิตภัณฑ์ที่ได้จากตัวเร่งปฏิกิริยาอื่น ภายใต้ภาวะการทดลองเดียวกัน

สาขาวิชา......**ปิโตเคมี และวิทยาศาสตร์พอลิเมอร์**.... ลายมือชื่อนิสิต..
หลักสูตร......**ปิโตรเคมี และวิทยาศาสตร์พอลิเมอร์**.... ลายมือชื่ออาจารย์ที่ปรึกษา..................................
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ARPANDA PRUCKCHARTSIRI : HYDROGENATION OF SOYBEAN OIL OVER NiW/Al_2O_3 AND CoW/Al_2O_3 CATALYSTS. THESIS ADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D., 132 pp. ISBN 974-347-132-4.

The study of the partial and selective hydrogenation of soybean oil was carried out using bimetallic catalysts. The catalysts were 5%Ni-5%W, 5%Ni-10%W, 5%Co-5%W, and 5%Co-10%W deposited on alumina support. The operating conditions, including temperature, hydrogen pressure, and reaction time, were studied.

It was found that the best catalyst was 5%Ni-10%W on alumina. The suitable condition to produce oleic acid using this catalyst were at the reaction temperature at 150 ^{o}C, hydrogen pressure at 150 psig, reaction time at 2 hours, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil. The product obtained from this condition, had iodine value at 90, consisting of 9.09% palmitic acid, 9.91% stearic acid, 72.58% oleic acid, and 8.42% linoleic acid by weight of oil. Meanwhile, linolenic acid was completely hydrogenated. The hydrogenated oil was separated into two parts; the saturated fatty acid part and the unsaturated fatty acid part, by winterization method. The unsaturated fatty acid part contained 87.58% oleic acid by weight of total unsaturated fatty acid part. The hydrogenation using 5%Ni-10%W on alumina provided the highest amount of oleic acid in the hydrogenated products compared to other catalysts under the same condition.

Department...**Petrochemistry and Polymer Science**. Student's signature…………………………..
Field of study**Petrochemistry and Polymer Science**. Advisor's signature……….....................…......
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ABBREVIATIONS

°C	:	Degree Celcius
^{13}C-NMR	:	Carbon-13 Nuclear Magnetic Resonance
Co	:	Cobalt
cm^{-1}	:	Unit of wave number
cm^3	:	Cubic centimeter
FTIR	:	Fourier Transform Infrared Spectrophotometer
GC-MS	:	Gas Chromatography – Mass Spectrometer
I.V.	:	Iodine Value
MHz	:	Megahertz
min.	:	Minute
ml.	:	Millilitre
ml/g	:	Millilitres per gram
Ni	:	Nickel
psi.	:	Pound per square inch
rpm.	:	Rounds per minute
rt.	:	Retention time
W	:	Tungsten
%wt	:	Percent by weight
w/v	:	Weight by volume

CHAPTER I

INTRODUCTION

Soybean oil consists of a complex mixture of glycerides, which contain several different fatty acids. It has more than 90 percent of 18 atom carbon fatty acid such as linolenic acid (C18:3), linoleic acid (C18:2), oleic aicd (C18:1) and stearic acid (C18:0). These make soybean oil an essential substance in food, cosmetic, and other industries. But because soybean oil contains unsaturated fatty acid, it may be rancid or rotten which easily leaves a sustainable odor. Partial hydrogenation process is one way to reduce double bond in soybean oil structure without affecting food nutrition. Nickel on kieseguhr and Nickel on silicate-diatomite were used for selective hydrogenation of soybean oil, of which the condition of hydrogenation was controlled to produce the required product. The hydrogenation of soybean oil is a very important operation in the chemical and food industry. The catalyst used in the industrial processes for the tallow and fat hydrogenation and in vegetable oils selective hydrogenation, is a nickel catalyst deposited on a silicates support [1].

Today, catalyst with two transition metals, nickel-molybdemun and nickel-tungsten tend to have high efficiency, which make them ideal for hydrogenation production in the petroleum oil industry. However, these catalysts have not been used in the hydrogenation of soybean oil or any vegetable oils. Therefore, it would be very interesting to apply these catalysts in the hydrogenation of soybean oil. Their activity and selectivity could be investigated.

The catalyst to be examined in this study includes two metals of the transition group, either nickel and tungsten or cobalt and tungsten. The understanding of the functions of two metals in the catalyst is expected to lead the way towards continuing research into catalysts consisting of several metals. In this project, a nickel and a cobalt catalyst are first prepared and then impregnated with tungsten. The reaction used to test the activity of this catalyst is the hydrogenation of soybean oil.

1.1 The objectives of this study

1.1.1 To prepare the bimetallic catalysts for the hydrogenation of soybean oil.

1.1.2 To study the optimum conditions for the hydrogenation of soybean oil and the chemical properties of soybean oil after the hydrogenation.

1.2 The scope of this study

1.2.1 Preparing several in-house catalysts by using the impregnation method.

1.2.2 Selecting the optimum operating conditions by varying these following parameters:

- kind of catalyst on the supporter (Ni, Co, and W)
- amount of catalyst (5 % and 10 %)
- reaction temperature
- reaction period
- hydrogen pressure

1.2.3 Comparing the results from different kinds of catalysts to those reported for the best commercial catalyst available.

1.2.4 Studying the chemical properties of soybean oil after the reaction.

- Iodine value
- Chemical composition

1.2.5 Separation of saturated fatty acids and unsaturated fatty acids.

CHAPTER II

THEORY AND LITTERATURE REVIEW

2.1 Fats and fatty oils [2-4]

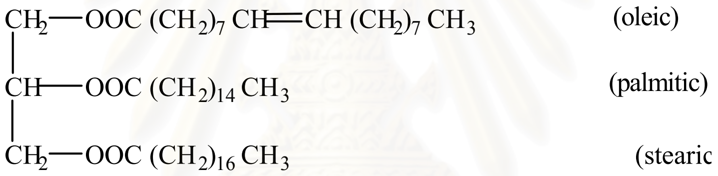
Fats and fatty oils are water-insoluble substances of plant or animal origin, which consist mainly of glyceryl ester of long-chain fatty acids. Depending on the composition of the fatty acid component, they may be liquid (oils) or solid (fats) at room temperature. However all become liquid at higher temperatures. Accordingly, the words oil and fat are used interchangeably in this thesis.

The main uses for fats and oils are: (a) for food (b) for soap and detergents, (c) for paint and other protective coatings, and (d) for other industrial purposes. Edible fats and oils are consumed either in the state in which they are obtained or after modification by such processes as hydrogenation and blending. Specific characteristics are important for each type of product, e.g., clarity and color in salad oils, consistency in margarine, and complex physical properties in shortenings. Oils for soap manufacture are required to have a certain fatty acid composition and to have a minimum content of constituents that may produce undesirable odor or color. Oils for paints and protective coatings require a minimum amount of color and a suitable balance of mono- and polyunsaturated fatty acids.

2.2 Composition and properties

As defined, fats and oils are essentially esters and, in the great majority of commercial oils, the alcohol component is glycerol. The nonester portion is usually less than 2 % of the total oil, and may contain sterols, hydrocarbons, and other organic compounds.

Triglycerides of a single fatty acid do occur in natural oils, but the great proportion of oils consist of “mixed” glycerides, Mixed glycerides contain either two or three different fatty acids esterified to glycerol, for example,



$$\begin{array}{lr}
CH_2\text{—}OOC\,(CH_2)_7\,CH{=}CH\,(CH_2)_7\,CH_3 & \text{(oleic)} \\
| & \\
CH\text{—}OOC\,(CH_2)_{14}\,CH_3 & \text{(palmitic)} \\
| & \\
CH_2\text{—}OOC\,(CH_2)_{16}\,CH_3 & \text{(stearic}
\end{array}$$

Figure 2.1 Structural formula of a typical triglyceride molecule.

Ordinary fats and oils consist of a complex mixture of such glycerides, containing several different major fatty acids and others in lesser amounts. The body fats of land animals are relatively simple in composition, in terms of the number of component acids. Vegetable oils are generally more complex, and appear to have the greatest number of components. There are about 150 different fatty acids that are known to occur in natural glycerides. A complete analysis of oil is seldom required except for research purposes. Determination of the fatty acid composition of an oil ordinarily consists of the identification and esterification of the four to six major fatty acids.

Natural fats and oils have the general properties of esters of high molecular weight, i.e., they are essentially neutral, relatively inert chemically, and of very low volatility. They are soluble in most organic solvents but insoluble in water. Some characteristics of common fats and oils are given in Table 2.1.

Table 2.1 Properties of common fats and oils

Fat or Oil	**Iodine value**	**Sponification value**	**Titer of fatty acids, ° C**
Coconut	7-10	255-260	20-22
Palm	51-58	196-210	36-45
Olive	79-88	188-195	17-21
Peanut	82-99	188-196	23-29
Castor	82-90	177-187	3
Rape	97-107	168-178	12-18
Cottonseed	103-113	192-196	33-38
Corn	103-125	188-193	21-24
Sunflower	120-140	186-194	17-20
Soybean	125-145	189-195	22-27

Long-chain fatty acids are commonly sold as mixtures with one or more major components. Properties of some pure individual acids are shown in Table 2.2.

Table 2.2 Properties of individual acid

Acid	**Formula**	**Molecular weight**	**Mp.,°C**	**Iodine value**
lauric	$C_{12}H_{24}O_2$	200.3	43.5	0
palmitic	$C_{16}H_{32}O_2$	256.4	62.9	0
stearic	$C_{18}H_{36}O_2$	284.5	69.6	0
oleic	$C_{18}H_{34}O_2$	282.5	16	89.9
eicosenoic	$C_{20}H_{38}O_2$	310.5	24	81.8
erucic	$C_{22}H_{42}O_2$	338.6	33.5	75
linoleic	$C_{18}H_{32}O_2$	280.4	-5	181
linolenic	$C_{18}H_{30}O_2$	278.4	-11	273.5
arachidonic	$C_{20}H_{32}O_2$	304.5	-	333.5
α-eleostearic	$C_{18}H_{30}O_2$	278.4	49	[a]
ricinoleic	$C_{18}H_{34}O_2$	298.5	5.5	85.2

[a] Varies with conditions of test.

Since the alcohol moiety is glycerol in all common oils and fats, the differences in chemical and physical properties of the glycerides are dependent on the nature of the fatty acid moiety. Fatty acids are classified mainly by chain length and degree of unsaturation. Thus the common acids are either short-chain (about C_4-C_8), medium-chain (C_{10}-C_{14}), and long-chain (C_{16} and longer). The melting point of the acids and their glycerol esters rises with chain length. The boiling point of the acids also rises but solubility in water and organic solvents decreases. Thus the short-chain acids have appreciable volatility and solubility in water whereas the long-chain acids are, for all practical purposes, nonvolatile at ordinary temperature and pressure, and are practically insoluble in water.

Fatty acids are classed as saturated (no double bonds), monounsaturated (one double bond), and polyunsaturated (two or more double bonds). The melting point of the acids and their glycerol esters decrease from saturated to polyunsaturated, solubility increases, but volatility and boiling point change only slightly. Special classes of unsaturated acids are those with one or more acetylenic (triple) bonds, and those with conjugated double and triple bonds.

2.3 Soybean oil [3-9]

Soybean is of the family *Leguminosae*, subfamily *Papilinaceae*, and the genus *Glycine max*. The soybean is a typical legume seed differing in color, size, and shape, depending upon variety. The common field varieties grown in the United States are nearly spherical and are yellow in color.

Soybean oil is the most important vegetable oil produced in the world because of its high quality and low cost. Favorable agronomic characteristics, reasonable returns to the farmer and processor, high-quality protein and edible oil products, and plentiful, dependable supply of soybeans available at a competitive price will enable soybean oil to maintain its dominance in both domestic and world markets.

The advantages include: (1) a high level of unsaturation is present; (2) the oil remains liquid over a relatively wide temperature range; (3) it can be hydrogenated selectively for blending with semisolid or liquid oils; (4) when partially hydrogenated, it can be used as a pourable, semisolid oil; (5) phosphatides, trace metals, and soaps in soybean oil can be removed without much difficulty to obtain a high-quality product; and (6) the presence of naturally occurring antioxidants.

2.3.1 Origin and systematic

The soybean oil is now the principal oilseed crop in the United States. They are believed to have been domesticated in the eastern half of northern China. Later, they were introduced and established in Japan and other parts of Asia, although the principal production areas are Brazil and Argentina. Soybean oil is used largely for edible purposes locally. It is used in articles of food, margarine and surfactant.

2.3.2 Composition and physical properties

Because of their high linoleic acid contents, unhydrogenated and partially hydrogenated soybean oil are good sources of this essential fatty acid. Soybean oil is the principal vegetable oil consumed and is partially hydrogenated to impart high temperature stability to cooking oil, extend shelf life, and improve flavor stability and physical and plastic properties. Linoleic and linolenic acid contents of soybean oil are reduced by hydrogenation, but more important from a nutritional viewpoint are migration of double bonds up and down the carbon chain and the conversion of cis to trans isomers, ie, positional and geometrical isomerization.

Physical properties of soybean oil depend on climate and variety. Processing the oil has an influence on the presence and level of the many minor constituents. The more important physical properties of soybean oil are summarized in Table 2.3. The values reported are not absolute because the composition and many of the properties depend on degree of unsaturation and other factor.

Table 2.3 The ranges of physical properties of soybean oil

Properties	**Value**
Specific gravity at 25°C	0.917-0.921
Refractive index at 25°C	1.470-10476
Iodine value (Wijs)	120-141
Viscosity, centipoises at 25°C	50.9
Solidification point (°C)	-10 to –16
Saponification number	189-195
Unsaponifiable matter, %	Not over 105

Except for minor amounts of impurities, some of which are removable by refining treatment, fats and oils consist of triglycerides, or esters of glycerol and high-molecular or long-chain aliphatic acids, both saturated and unsaturated, known as fatty acids. Because the fatty acid radicals constitute the greater part (usually about 95% by weight) of the glyceride molecule, mainly the reactive portion, the chemical and physical properties of a fat or oil are determined largely by the properties of the component fatty acids.

Owning to the complexity of glyceride structure and present impossibility of accurately determining the composition of fat in terms of all the component glycerides, chemical analyses of fats usually show only the relative proportions of the different fatty acids. The soybean oil consists of a complex mixture of glycerides which contains several different fatty acids. The composition of soybean oil is shown in Table 2.4.

Table 2.4 Fatty acid composition of soybean oil

Component acids	**Amount of fatty acid composition (wt%)**
Saturated	
palmitic	7-12
stearic	2-6
Unsaturated	
oleic	15-33
linoleic	35-60
linolenic	2-13

Due to glycerides present being mixed, which the glyceride containing two or three different acid radicals, the physical and chemical properties of soybean oil are depend on the nature of the fatty acid moiety.

The greater the degree of unsaturation in the fatty acids of the fat molecules the softer the fat, and the lower the melting point will be. When there is a considerable degree of unsaturation, the fat will be liquid at room temperature and will be called oil.

By chemical means, the hydrogen is added into oil, saturate its fatty acids, and thereby converts it to a solid. This is the process of hydrogenation that commonly converts a vegetable oil to a solid shortening. The partially hydrogenation gets an intermediate degree of solidification. Most natural fats do not contain only one kind of triglyceride molecule. Given fat will generally contain a mixture of triglyceride molecules, which will differ in the lengths and in the degrees of unsaturation of their fatty acids. Because of this, some molecules in the fat will be softer, while some will be harder. The overall fat may be in liquid form at room temperature but actually contain some solid fat molecules suspended in the liquid oil. Should the liquid fat be cooled, more of the fat molecules will solidify and they may form fat crystals which separate from the liquid oil portion. This is one property that is used in separating fats into liquid and solid fractions. The liquid fraction has a higher melting point than the original mixture, and both fractions will be suitable for different food uses.

Table 2.5 Melting points of fatty acids and their triglycerides present in soybean oil and partially hydrogenated soybean oils. [9]

Fatty acid		**Triglyceride**	
Name	**Melting point (°C)**	**Name or Composition**	**Melting Point (°C)**
Palmitic	62.9	Tripalmitin	56.0
Stearic	69.6	Tristearin	65.0
		18:0-16:0-16:0	59.5
		16:0-18:0-16:0	65
		18:0-16:0-18:0	64
Oleic	16.3	Triolein	-12
		16:0-18:1-16:0	30.4
		18:0-18:1-18:0	37.6
		16:0-18:1-18:1	-
		18:0-18:1-18:1	-
Elaidic	43.7	Trielaidin	37
Linoleic	-6.5	Trilinolein	-
Linolenic	-12.8	Trilinolenin	-

The melting point of triglycerides is usually determined by the component fatty acids. Melting points increase with increasing chain length and decrease with increasing concentrations of trans unsaturation. In some instances, melting points are also dependent on the position of double bonds, in that they rise as the double bond approaches either end of the molecule. In case of products with highly saturated fatty acids, the triglyceride melts above the fatty acid; with unsaturated-type products, the reverse is true (Table 2.5). Mixtures of triglycerides have depressed melting points compared to that for the homogeneous triglyceride.

2.3.3 Chemical reaction of soybean oil [10]

The chemical reactions of fats and fatty acids are important because they are employed in the manufacture of commercial products. Fats and fatty acids are organic chemicals and thus are subject to the numerous reactions available to the synthetic organic chemist. Because of double bonds and ester linkages in soybean oil provide reaction sites for the preparation of many useful derivatives. Chemical reactions commercially used to create important soybean oil derivatives are as follows in Table 2.6.

Table 2.6 Chemical reactions of soybean oil

Part of structure	**Nature of reaction**	**Type of products**
Ester linkage	(1) Hydrolysis	Fatty acids
		Glycerol
	(2) Esterification	Esters
	(3) Alcoholysis	Mono- and diglycerides, monoglycerol. etc.
	(4) Reduction	Alcohols
	(5) Saponification	Soluble soaps
		Insoluble soaps
	(6) Halogenation	Fatty acid halogens
Double bond	(7) Oxidative polymerization	Polymerized oils
	(8) Hydrogenation	Hydroxystearates
	(9) Halogenation	Halogenated oils
	(10) Epoxidation	Epoxidized oils
	(11) Sulfonation	Sulfonated oils

2.4 Hydrogenation [9-14]

Hydrogenation in the edible oils and fats industry is a chemical reaction in which hydrogen is added to the ethylenic linkages (double bond) found in naturally occurring triglycerides of vegetable. It is normally performed batch wise in a hydrogen pressurized stirred reactor. Hydrogenation is unique among the unit processes employed in oils and fats manufacture that it alters the molecular structure and composition of the glycerol ester. Other processes, except in a minor way for esterification, are principally for separation and/or purification.

While the hydrogenation reaction may appear straight forward, it is actually complicated. This is due to several factors. The esters may contain one, two, three, or more unsaturated bonds in each chain; and each double bond may be isomerized or hydrogenated at different rates, depending on its position or environment in the molecule. In addition, since oils are composed of triglyceride esters, the position of the ester on the glycerol also has some effect in determining the physical properties of the molecule. There are two reasons to hydrogenate oils. First, since the number of double bonds is reduced, the opportunity for oxidation is decreased, and thus the flavor stability is increased. Second, the physical characteristics are changed such as a raised melting point.

Hydrogenation with bimetallic catalysts has some limitations, however, in that the selectivity for linoleate is absolute. In other words, there is high selectivity for linolenic acid. Choice of conditions and equipments are mainly based on the exothermic heat of reaction and desorbed selectivity. Practical reaction conditions are usually at temperatures of 120-200 °C and at pressures from 50-200 psig.

2.4.1 General

The hydrogenation reaction requires a catalyst. Catalysts employed for triglyceride hydrogenation decrease in activity with use. The degree of inactivation principally depends on the purity of the feedstock. For hydrogenation to take place, the triumvirate of gaseous hydrogen, liquid oil, and solid catalyst must all be brought together (Figure 2.2). Using mechanical means, hydrogen is dissolved in the oil. The reaction is brought about by agitating the suspension of catalyst in hydrogen-laden oil in a closed vessel under hydrogen pressure. Agitation continuously renews the oil molecules at the active sites on the catalyst's surface. The solubility of hydrogen in oils increases linearly with temperature and pressure.

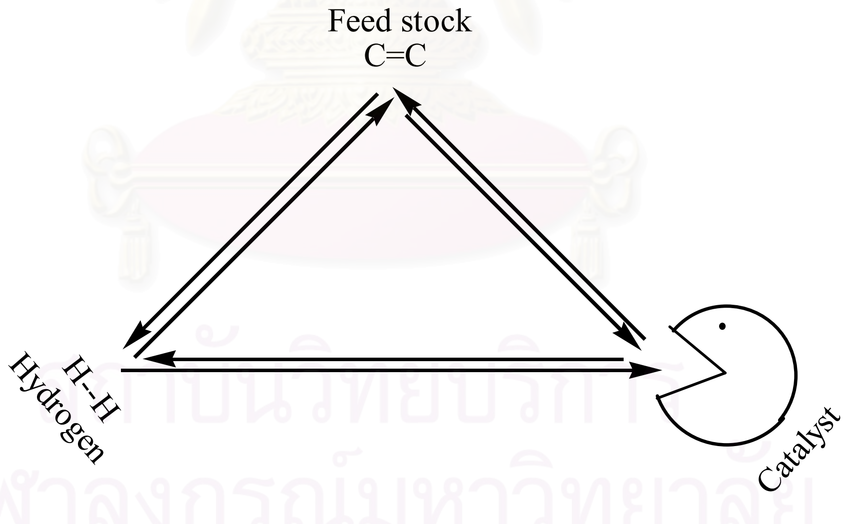


Figure 2.2 The triumvirate of hydrogen, double bond and catalytic site

The rate of hydrogenation depends on the rate at which hydrogen and unsaturated oil molecules are brought together on the catalyst's surface. This, in turn, depends on the pressure, temperature, and nature of the oil, activity of the catalyst, concentration and mixing of the triumvirate. The chemical composition and physical characteristics of partially hydrogenated triglyceride vary according to the positions on the molecule of those double bonds that are hydrogenated. In addition, the isomerization is usually to the lowest feasible iodine value, selectivity and isomerization are unimportant.

2.4.2 Mechanism and selectivity

The basic chemical equation for hydrogenation of an unsaturated carbon-carbon double bond is shown below.

$$-CH=CH- \quad + \quad H_2 \longrightarrow -CH_2-CH_2- \qquad \text{.......} \ (1)$$

While chemically and structurally simple, the reaction can be extremely complex in practice. As previously noted and as equation 1 indicates, hydrogenation can take place only when the liquid unsaturated oil, the solid catalyst, and the gaseous hydrogen have been brought together.

Each unsaturated group of the fatty ester chain can transfer back and forth between the main body of the oil and the bulk surface of the catalyst. These unsaturated groups can be adsorbed on the catalyst surface. Each adsorbed unsaturated group can react with a hydrogen atom to form an unstable complex that is a partially hydrogenated double bond. Some of the complexes may react with another hydrogen atom to complex the saturation of the double bond. If the complex does not react with another atom of hydrogen, hydrogen is removed from the adsorbed molecule and the “new” unsaturated bond is desorbed. Both the saturated and the unsaturated bonds are desorbed from the catalyst surface and diffused into the main body of the oil. Thus not only are some of the bonds saturated but some are also isomerized to new positions or new geometric forms. The addition of a single hydrogen atom allows free rotation around the carbon-carbon single bond.

The term selectivity, as used in the edible oils and fats industry has had two meanings, as applied to the hydrogenation reaction and to products. The term originally was defined as the conversion of a diene to a monomer compared with the conversion of a monomer to a saturate. Another type of selectivity was applied to catalysts. If a catalyst had “selectivity”, it produced an oil of softer consistency or lower melting point at a given iodine value. The model (equation 2) shown below could be used to measure the relative reaction rate constants for each hydrogenation step during batch hydrogenation of soybean oils.

$$\text{Linolenic} \longrightarrow \text{Linoleic} \longrightarrow \text{Oleic} \longrightarrow \text{stearic} \qquad \text{........ (2)}$$

2.4.3 Catalyst and catalysis [15-17]

2.4.3.1 Definition of catalyst

A catalyst, according to the classical definition of Ostwald, is a substance that alters the rate of a chemical reaction without affecting the energy factors of the reaction or being consumed in the reaction. Properly speaking, therefore, a catalyst cannot initiate but can only accelerate a reaction. In numerous instances, however, including the hydrogenation of fats and oils, the reaction rate is so imperceptibly slow in the absence of a catalyst that the latter must be considered an essential element of the reacting system.

The fact that a catalyst cannot initiate a reaction does not mean that its introduction into a reacting system may not influence the composition of the reaction products or that different catalysts may not yield different products. In many cases, reaction follows a number of alternative courses. Hence, the composition of the final products will depend on the relative rate of the various alternative reactions. Where a number of different reactions occur together, the addition of a catalyst to the system may accelerate some of them to a far greater extent than others.

Catalysts increase the reaction rate through their influence on the activation energy. A catalyst breaks the reaction up into two successive steps: the combination of catalyst and reactants to form an unstable intermediate compound, and the breakdown of this compound to yield a new product and the free catalyst. This has the effect of permitting the energy barrier to be surmounted in two small steps, rather than one large one (Figure 2.3). In other words, two reactions with relatively low activation energies are substituted for a single reaction with high activation energy.

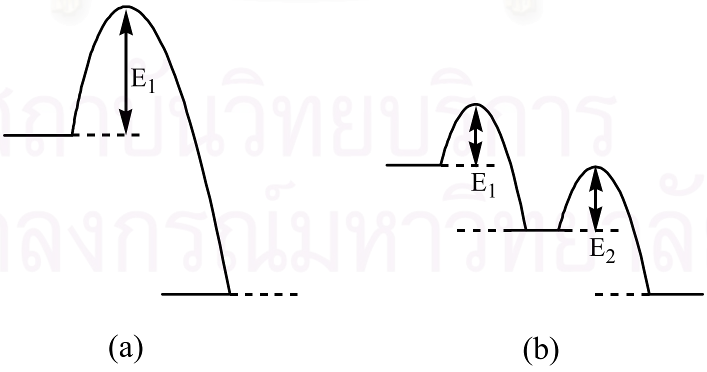


Figure 2.3 Graphical representation of the activation energy factor in **(a)** uncatalyzed and **(b)** catalyzed reaction

In the past it has been generally assumed that a single collision of an unsaturated fatty acid chain with hydrogen and an active catalyst is sufficient to hydrogenate only one double bond. In other words, hydrogenation is assumed to occur stepwise in the case of a polyunsaturated fatty acid chain, for example, linolenic → linoleic → oleic → stearic, with breakdown of the above-mentioned complex and desorption of the fatty acid occurring at the end of each step [18]. This may be the case in the sequence linoleic → oleic → stearic; or in any analogous progression from two isolated double bonds, to one, to none. There is evidence, however, that the hydrogenation of linolenic acid chains may precede in part directly to the formation of oleic acid, without intermediate desorption of linoleic acid from the catalyst. Evidently, two of the three double bonds in triethenoid conjugated fatty acid chains also hydrogenate simultaneously.

2.4.3.2 Classification of catalysts

The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation. Here the catalysts shall be classified according to the state of aggregation in which they act. There are two large groups: heterogeneous catalysts (solid-state catalysts) and homogeneous catalysts. There are also intermediate forms such as homogeneous catalysts attached to solids (supported catalysts), also known as immobilized catalyst. The well known biocatalysts (enzymes) also belong to this class.

In supported catalysts the catalytically active substance is applied to a support material that has a large surface area and is usually porous. By far the important catalysts are the heterogeneous catalysts.

Whereas for heterogeneous catalysis, phase boundaries are always present between the catalyst and the reactants, in homogeneous catalysis, catalyst, starting materials, and products are present in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts since in theory each individual atom can be catalytically active. In heterogeneous catalysts only the surface atoms are active.

Table 2.7 Comparison of homogeneous and heterogeneous catalysts

Homogeneous	**Heterogeneous**
1. Catalyst and reactants are in the same phase.	1. Catalyst and reactants are in different phase, which separated by a phase boundary.
2. Catalyst is uniformly distributed throughout the system and the mobility of catalyst is the same as that of the other components.	2. Catalyst is not uniformly distributed throughout the system and the mobility of catalyst is different from that of the other components.
3. Catalyst acts by it mass and the rate of reaction is proportional to the concentration of catalyst.	3. Catalyst acts by its surface and the rate of reaction is proportional to the catalyst surface area exposed for the reaction and the concentration on the catalyst surface of various adsorbed species.
4. High cost of catalyst losses.	4. Low cost of catalyst losses.

The major disadvantage of homogeneous transition metal catalysts is the difficulty of separating the catalyst from the product. Heterogeneous catalysts are either automatically removed in the process, or they can be separated by simple methods such as filtration or centrifugation. Table 2.7 summarizes the differences of the two classes of catalysts. Heterogeneous catalysts are generally the most important in industry, and in edible oil hydrogenation they are used exclusively. In the hydrogenation of soybean oil, a heterogeneous catalyst was used in this experiment.

2.4.3.3 Heterogeneous catalysis

The type of catalysis that operates the fat hydrogenation is the heterogeneous catalysis. By definition, a heterogeneous system is one in which the catalyst and the reactants exist in different physical states. Heterogeneous catalysis is to be somewhat sharply distinguished from homogeneous catalysis, in which the catalyst and the reactants comprise a single phase. In homogeneous catalysis the catalyst functions in the form of individual molecules, which are uniformly distributed through the reaction system. Thus the question of catalyst structure or of surface phenomena does not enter. On the other hand, in heterogeneous catalysis it is the question surface, which performs the catalytic function; hence the nature of the surface is of extreme importance. A catalyst operating in a homogeneous system is defined simply in terms of its chemical constitution and its concentration in the system. With all other factors controlled, the effect of a homogeneous catalyst of definite composition is exactly predictable upon the basis of its concentration. If the catalyst is a solid, however, its behavior will depend not only both the nature and extent of its surface. The fact that, by and large, the submicroscopic character of its surface determines the characteristics of a solid catalyst renders the study and control of such catalysts very difficult. Apparently similar catalysts may differ enormously in their activity and specific action.

In the catalytic heterogeneous reaction, Figure 2.4, there is a reaction occurring between fluid and porous solid catalysts. In order for the reaction to occur, the reactants in the fluid must first be transported to the outer surface of the solid, and then they must diffuse through the pores of the solid to the catalytic active site. At least one of the reactant species must usually be chemisorbed onto the surface of the solid. Subsequently, the reaction occurs among chemisorbed species or between a chemisorbed species and another species that is either physically adsorbed or that collides with the chemisorbed species directly from the fluid phase. After the reaction, products are desorbed and diffuse out through the pores various steps, which respond in a different way to experimental variables such as pressure, temperature. For bulk-fluid velocity, and the chemical and physical structure of the catalyst, it is convenient to classify then as follows:

1. External mass transfer of reactants from the bulk fluid to the external surface of the catalyst particle.
2. Internal diffusion of reactants to active sites within the particle.
3. Adsorption of reactants on active sites.
4. Surface reaction.
5. Desorption of products.
6. Internal diffusion of products to surface of particle.
7. External mass transfer of products to bulk fluid.

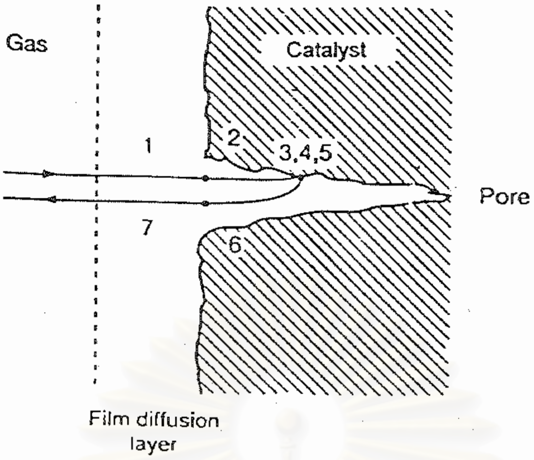


Figure 2.4 Individual steps of a heterogeneously catalyzed gas-phase reaction

2.4.3.4 Preparation of heterogeneous catalysts [15,19-20]

Preparation of the catalyst is a very important step in the study of heterogeneous catalysts. Heterogeneous catalysts are necessary to keep the properties of high reactivity, stability, and prevention of side reactions. These properties depend on the preparation technique. In the past, preparation of catalyst was an art. Properties of the catalyst may not be the same in each batch of preparation even if the same technique is used. It is according to difficulty in the control of the reaction condition. Testing instruments of catalyst give reproducibility of reaction.

There are many catalyst preparation techniques used in industry. Each catalyst has some selectivity on the preparation method. The most popular technique is impregnation.

Impregnation is the most popular and the easiest technique. A support, such as alumina, was added into metal salt solution such as nitrate salt. After dispersion of the metal salt in order to equilibrium, heating is applied to convert metal salt on the surface of support to metal oxide.

Impregnation can be done by two techniques.

1. Wet Impregnation

The support was added into an excess amount of metal salt solution. The amount of metal salt can be calculated from the different amount of metal salt in solution before and after the impregnation process. This process is too complicated and inconvenient to carry out in the laboratory.

2. Dry Impregnation

This is the most convenient technique for laboratory scale work. In this technique, it is necessary to prepare the solution, which the amount of metal salt is equal to the surface of support.

Dry impregnated catalysts became commercially available for use in the hydrogenation reaction. Their combination of performance characteristics (i.e., good activity, excellent selectivity, and superior filterability compared with wet impregnation catalysts) made them attractive to edible oil hydrogenators. They currently constitute essentially 100% of commercial catalysts consumed worldwide in the edible oil industry. In this experiment, dry impregnation was used for preparing catalysts because this method is a convenient technique and easy to work in laboratory.

These catalysts are, in most, generally used today because they have proven to be highly selective, easy to regenerate, and resistant to poison.

2.4.3.5 Metallic component [21-22]

Catalysts developed for hydrogenating, especially hydrogenating catalysts which can be suitably applied for production of soybean oil, are comprises of at least one or more metal, metal oxide or group VIB and VIII on a carrier support which comprises one or more oxide of elements of groups II, III, and IV.

Generally, the metals employed will be chromium (Cr), molybdenum (Mo) or tungsten (W), metals of group VI and iron (Fe), cobalt (Co) or nickel (Ni), metals of group VIII. Ni or Co is regarded as the active hydrogenation component, with W acting as a promoter, which increases the catalytic activity. The metallic component can be employed either as the metals or as the oxide of such a metal.

The critical factor for catalytic activity is that transition metals have valency (i.e. outer) electrons in their atoms, which are d-orbitals. These electrons are available for sharing into chemisorption bonds. The general predictions for chemisorption on transition metals are summarized as follows:

(a) The strength of the M-H bond decreases with an increase in the atomic number of the metal (M) along a particular transition series in the periodic table.

(b) The number of M-H bonds per unit area surface at maximum surface coverage increases with increasing atomic number.

2.4.3.6 Supported catalysts

Supported catalysts represent the largest group of heterogeneous catalysts and are of major economic importance, especially in refinery technology and the chemical industry. Supported catalysts are heterogeneous catalysts in which small amounts of catalytically active materials, especially metals are applied to the surface of porous, mostly inert solids – the so-called supports. The supports can have special forms such as pellets, rings, extrudates, and granules.

The main function of the catalyst support is to increase the surface area of the active component. Catalytic activity generally increases with increasing catalyst surface area, but a linear relationship cannot be expected since the reaction rate is often strongly dependent on the structure of the catalyst surface. However, in many reactions, the selectivity decreases when the catalytic surface is enlarged. The choice of the appropriate catalyst support for a particular active component is important because in many reactions the support can significantly influence the reaction rate and the course of the reaction. The nature of the reaction system largely determines the type of catalyst support. Typical catalyst supports are porous solids such as aluminum oxides, silica gel, MgO, TiO_2, ZrO_2, aluminosilicates, zeolites, activated carbon, and ceramics.

The term alumina is used to describe various hydrated and anhydrous aluminium oxides. Most commercially available aluminas are prepared from the mineral bauxite (a mixture of hydrated aluminas and several non-alumina impurities) and are available at > 99% purity. Thermally stable high-surface-area forms of alumina can be prepared, with acidic or basic surfaces. These may be used as acid or base catalysts or supports for other catalytic materials.

Alumina (Al_2O_3), the acidic component in a dual function catalyst, exists in several distinct forms: the gamma form or the alpha form, depending on the method of preparation and subsequent treatment. Activated aluminas are amphoteric, containing either acidic or basic sites of various strength. As shown in Figure 2.7, if γ-alumina is heated above 800 K, the residual water is driven off to generate a catalytically inactive form known as α-alumina. Activated alumina is often used as supports, where they provide a large surface area on which catalysts (metal) can be highly dispersed.

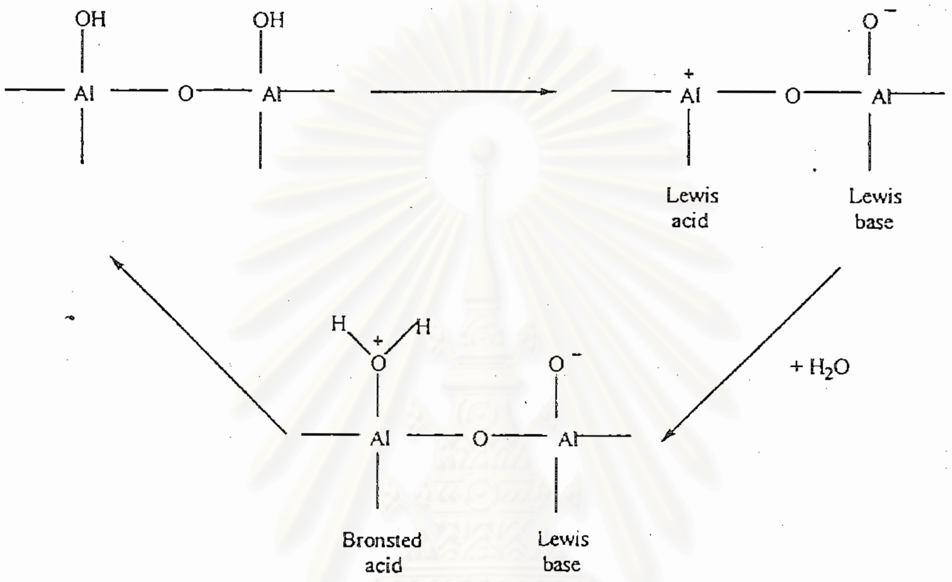


Figure 2.5 Acidic and basic sites on alumina

2.4.4 Characteristics of hydrogenated soybean oil

The characteristic of soybean oil most directly affected by hydrogenation is the iodine value, which decreases in direct proportion to the amount of hydrogen absorbed. The free fatty acid content of absolutely dry oil is only slightly affected by hydrogenation. However, even small amounts of water, from either the oil or hydrogen, will cause an increase in the fatty acids by hydrolysis. Hydrogenation reduces the iodine value of oils. The relationship depends largely on the average molecular weight of the glycerides.

It is necessary to know the characteristics of the starting oil and the hydrogenated products. This is done by gas chromatography [23]. In GC they can be separated in the free from as methyl ester. Free fatty acids often show adsorption and tailing on the columns and quantitative results are not reliable, especially for long-chain unsaturated fatty acids. GC of free acids is sometimes used for the analysis of short-chain saturated fatty acids. Mostly, fatty acid methyl esters are prepared for GC separation.

2.4.5 Separation of hydrogenated soybean oil [9, 24-25]

The art of fractional crystallization for the purification of many organic and inorganic substances is well recognized as an integral part of both laboratory and commercial practice. However, application to fatty acid substances on a commercial scale is a relatively recent innovation. Although some processes are generally applicable to the separation of a broad range of classes, most of the literature is directed to the separation of triglycerides or fatty acids. The scope of this section is confirmed for the most part to commercially practiced processes employed in the fractionation of edible-grade fats and oils and to special products derived form them. However, a few interesting experimental processes or modifications that may have future commercial application also have been included.

The method to purify the hydrogenated soybean oil is winterization, inwhich the materials responsible for clouding and solidification in the partially hydrogenated soybean oil will be removed after subjecting the oil to cold environment.

The winterization will achieve the following goals: (1) removes waxes and other nontriglyceride constituents, (2) removes naturally occuring high-melting triglycerides; and (3) removes high-melting triglycerides formed during partial hydrogenation.

The term “winterization” is applied to the dry fractional process wherein oils are cooled to remove small quantities of solid fat fractions that would normally cloud when oil that is in the liquid form at room temperature is held at refrigerator temperature. When the solid fat fraction is complete, it is usually separated from liquid oil by filtration. The quality of oil is normally determined by means of a cool test, which by definition is the length of time required for fat to develop a cloud at 0 °C under specific, defined conditions.

2.5 Literature reviews

The invention related to the catalytic hydrogenation of soybean oil and other substances, are the followings:

In 1979, Cahen [26] studied the process for partially and selectively hydrogenating soybean oil, which comprises the step of treating soybean oil in the presence of nickel catalyst on kieselguhr and a mixture of aliphatic amines. The hydrogenation of soybean oil was carried out at 140 °C and a hydrogen flow rate of 4 m^3/hour was maintained during the reaction. After the reaction, liquid hydrogenation products were obtained and the formation of trans-isomers or conjugated dienes or saturated compounds was substantially reduced.

In 1997, Yoshimura et al. [27] studied the hydrogenation of tetralin over sulfided nickel-tungstate on alumina and nickel-molybdate on alumina catalysts. The hydrogen sulfide was added to control its pressure. The sulfided NiMo/Al_2O_3 catalyst was advantageous in hydrogenating tetralin under low H_2S partial pressure. On the other hand, the sulfided NiW/Al_2O_3 catalyst was advantageous in hydrogenating tetralin under high H_2S partial pressure. It was found that the sulfided NiMo/Al_2O_3 catalyst under low H_2S partial pressure was less stable than the sulfided NiW/Al_2O_3 catalyst.

In 1998, Jovanovic et al. [1] prepared catalyst to be used for selective hydrogenation of vegetable oil. The catalyst was a nickel deposited on a natural silicate support (diatomite). This catalyst was used in hydrogenation of soybean oil and sunflower oil. The reaction was operated at a temperature of 195 °C, hydrogen pressure of 1.5 MPa and process duration time of 180 min. This catalyst has good catalytic properties and high selectivity but is difficult to regenerate.

In 1999, Caceres et al. [28] prepared the NiMo and NiW catalysts supported on carbon obtained from peach stones. The catalysts were prepared using two different impregnation techniques: pore filling and excess of solution. This research studied the positive influence of phosphorus on hydrodesulfurization and hydrodenitrogenation activity of both molybdenum and tungsten based catalysts, The PNiW and PNiMo catalysts on carbon prepared by impregnation with heteropolyanion solutions were as or more active for hydrodenitrogenation reaction than those obtained from the classical isopolyanions.

In 1999, Chaiphasert [29] studied a catalytic hydrotreatment of used automotive lubricating oil by using bimetal catalysts. These catalysts were NiWF and NiMoF on supported alumina. It was found that the suitable conditions for the bimetal catalysts were at 350 °C, hydrogen pressure of 500 psig, reaction time of 150 min, and catalyst concentration of 30% wt. The hydrotreated oil obtained from these conditions had good properties such as high viscosity index, low acidity, sulfur and metal content and could be used as a lube base oil.

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

1. Soybean oil was obtained commercially.
2. Industrial hydrogen gas

   Thai Industrial Gas Trading Ltd., TIG
3. Nickel (II) nitrate hexahydrate ($Ni\,(NO_3)_2 \cdot 6H_2O$)

   Analytical grade; BDH chemicals Ltd.
4. Cobalt (II) nitrate hexahydrate ($Co\,(NO_3)_2 \cdot 6H_2O$)

   Analytical grade; Fluka
5. Sodium tunstate dihydrate ($Na_2O_4W \cdot 6H_2O$)

   Chemical grade; Fluka
6. Alumina support (CS331-3 1/16″ Extrudate)

   United catalyst Inc.; USA
7. Methyl alcohol

   Analytical grade; Merck
8. Sulfuric acid (98% w/w)

   Analytical grade; J.T. Baker
9. Glacial acetic acid

   Analytical grade; Carlo Erba

10. Carbon tetrachloride

    Analytical grade; Merck

11. Iodine trichloride (IOI$_3$)

    Analytical grade; Fluka

12. Iodine (I$_2$)

    Chemical grade; Fluka

13. Potassium iodide (KI)

    Analytical grade; Merck

14. Sodium thiosulfate (Na$_2$S$_2$O$_3$)

    Analytical grade; M&B

15. Starch granule

    Reagent grade; Sigma Chemicals Company

16. Sodium hydrogen carbonate (CHNaO$_3$)

    Chemical grade; Fluka

17. Potassium dichromate (K$_2$Cr$_2$O$_7$)

    Chemical grade, M&B

3.2 Apparatus and instruments

1. High Pressure Reactor

All experiments for the hydrogenation study of soybean oils were carried out in a hydrogenation apparatus, which consisted of four parts as follows:

1.1 Reactor (Figure 3.1)

The hydrogenation reactor was a batch high pressure stirred autoclave model from the Parr Instrument Company, consisting of 1,000 ml stainless steel, cylindrical bomb, bomb head, bomb heater, two stirrers and a cooling coil. The reactor could work at a pressure range of 0-2,000 psig and a temperature range of 0-350 °C.

Figure 3.1 High pressure reactor

1.2 Reactor Fitting (Figure 3.2)

The stirred unit of the reactor was supplied with convenient fittings for hanging the various functions. The parts are indicated with the following letters.

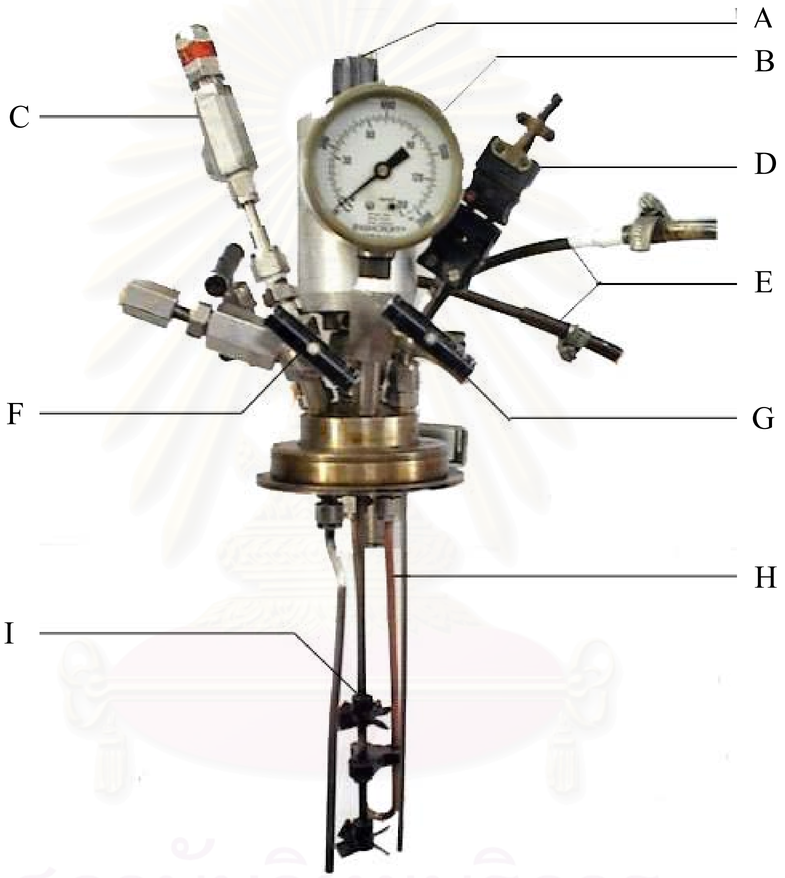


Figure 3.2 Reactor Fitting

A. A stirrer magnetic drive system

B. A pressure gauge

C. A safety rupture disc

D. A dual thermocouple

E. A water cooling channel

F. A gas inlet value

G. A gas release value

H. A heating rod

I. A stirring shaft with 6-blade turbine type impeller

1.3 High-speed motor

This part was attached to the reactor fitting.

1.4 Manual temperature controller

The temperature controller was model 4242 from the Parr Instrument Company. It was operated in association with a dual thermocouple. There were various improvability modules to support with monitoring and controlling of the temperature. A temperature setting on the controller established a set point temperature within the range of 0-350 °C.

1.5 Gas controller system

The system consisted of a hydrogen tank with regulator (0-2,000 psig).

1.6 Cooling system

It is composed of two parts, one for cooling the reaction and one for cooling the stirrer. It was found that at the beginning of the reaction, the rate of hydrogenation was so fast that the temperature controller could not keep the temperature at the desired value. Therefore, it had to be cooled by water in the cooling coil. The cooling coil was connected to the water pipe in the laboratory. The cooling system for the stirrer was connected to the reactor fitting.

2. Calcinator

   Carbolite Furnaces, model GSM

3. Apparatus for determining the Iodine value (I.V.) of the oil

   3.1 Burette in 50 ml.

   3.2 Graduate pipette in 1, 5, 10 ml.

   3.3 Glass stopper volumetric flask

   3.4 Stand and clamp for supporting burette

4. Gas Chromatography – Mass Spectrometer (GC-MS)

   Fisons Instruments, GC 800 Series; MS VG TRIO 2000

5. Fourier Transform Infrared Spectrophotometer (FTIR)

   Perkin Elmer, Nicolet (Impect 410)

6. X-ray fluorescence (XRF)

   Oxford E.D. 2000

7. Nuclear Magnetic Resonance Spectrometer

   Bruker, model AC-F 200

3.3 Procedure

1. Catalyst preparation

A standard α-alumina support was used for all preparations. The support was in the form of 1-6 mm extrudated with a maximum pore volume of about 0.64

ml·g^{-1}. Nickel nitrate, cobalt nitrate and sodium tungstate dihydrate were normally used to impregnate the support.

1.1 Hydrogenating catalyst: containing 5%Ni-10%W on alumina support

- Nickel nitrate (33.18 g) was dissolved in water (126 ml). The alumina support (200 g) was poured into the solution, which was left at room temperature for 1 hour and stirred occasionally. Then the mixture was first dried at 120 °C for 16 hours and then continually calcined at 520 °C for 2 hours to obtain the calcined solid.
- The calcined solid was reimpregnated with the solution of sodium tungstate dihydrate (24.04 g) in water (126 ml) which was left at room temperature for 2 hours, dried at 120 °C for 16 hours and then calcined at 520 °C for 2 hours.

1.2 Hydrogenating catalyst: containing 5%Ni-5%W on alumina support

The preparation procedure was carried out as in 1.1 but the amount of tungsten was reduced by half. So, after nickel impregnation, the calcined solid was reimpregnated with the solution of sodium tungstate (12.02 g) in water (126 ml). Then, the catalyst was dried and calcined.

1.3 Hydrogenating catalyst: containing 5%Co-10%W on alumina support

The preparation procedure was carried out as in 1.1 but cobalt nitrate (33.08 g) was used in place of nickel nitrate.

1.4 Hydrogenating catalyst: containing 5%Co-5%W on alumina support

The preparation procedure was carried out as in 1.2 but cobalt nitrate (33.08 g) was used in place of nickel nitrate.

1.5 Activation of catalysts

The catalysts were activated by reduction before use. The condition, which activates catalyst, was 300 psig hydrogen pressure in a stainless steel reactor and 300 °C for 6 hours to obtain the activated catalysts.

1.6 Regeneration of catalysts

The used catalysts were washed three times with hexane. The washed catalysts were dried at 120 °C for 16 hours, calcined at 500 °C for 4 hours and then activated with hydrogen gas following the procedure according to 2.3 to obtain the reusable catalysts.

1.7 Characterization of catalysts

The catalysts were characterized by X-ray fluorescence.

2. Hydrogenating process

The soybean oil was charged into the reactor and the required quantities of catalysts were added. The reactor was closed. After a thermocouple was inserted into the reactor, the stirring motor was connected and water passed into the cooling tube. Before starting the process, hydrogen gas was compressed into the reactor until desired pressure was obtained. The required conditions were set. After the reaction took place, heating was stopped and the reaction mixture was stirred until the mixture cooled to room temperature. The pressure was released and the catalyst was separated by filtration to give the hydrogenated soybean oil.

2.1 The effect of catalyst type on hydrogenating process

The experiment using NiW catalysts and CoW catalysts on an alumina supporter was carried out. For each experiment the reaction mixture was worked up in the same way as above to produce the wax products. To select the best hydrogenating catalysts, the hydrogenation condition was set at a temperature of 200 °C, hydrogen pressure of 200 psig, agitation speed of 500 rpm, catalyst concentration of 10% (weight by weight), and reaction time of 3 hours.

2.2 The effect of temperature on hydrogenating process

The described procedure was operated at various temperatures (100, 120,150, and 200 °C) by using the prepared catalysts. The reaction mixture was worked up in the same way as above to give the desired products.

2.3 The effect of pressure on hydrogenating process

The hydrogen solubility in oil is directly proportional with pressure. Therefore, reaction rate could increase when hydrogen pressure is increased. The described procedure was operated at various pressures (100, 150, and 200 psig) using the optimum temperature to produce the hydrogenated products.

2.4 The effect of reaction time on hydrogenating process

The described procedure was operated at various reaction times (60, 100, 120, and 140 minutes) using the optimum temperature and the optimum pressure.

Table 3.1 Various operating conditions for hydrogenation reaction

Studied parameters	Reaction temperature (°C)	Hydrogen pressure (psig)	Reaction time (min.)	Agitation speed (rpm)
Reaction Temperature	100	150	60	500
	120	150	60	500
	150	150	60	500
	200	150	60	500
Hydrogen Pressure	150	100	60	500
	150	150	60	500
	150	200	60	500
Reaction time	150	150	60	500
	150	150	100	500
	150	150	120	500
	150	150	140	500

3. Esterification of soybean fatty acids

Soybean oil fatty acids (10 g) were placed into a round bottom flask. Methanol (14.56 g) and concentrated sulfuric acid (0.32 ml., 5% by weight of alcohol) were added. Then, the reaction flask was fitted with a condenser, stirred by a magnetic bar. The mixture was heated to 70 °C for 360 min. Then, it was poured into the separatory funnel to separate oil from methanol. The excess acid was washed out from the oil by 5% sodium hydrogen carbonate solution. Then, dried with sodium sulfate anhydrous. The product was called soybean oil methyl ester.

Methyl ester was used in the analysis of the hydrogenated soybean oil by the gas chromatographic method.

4. Analysis of the hydrogenated soybean oil

4.1 Gas chromatograph – Mass spectrometer (GC-MS)

Gas chromatograph – mass spectrometer was used to identify and quantitatively determination of the fatty acid components. The GC-MS was performed using DB wax capillary column. The general conditions can be summerized as follows:

Column : 60 m.; 0.25 mm.
column packing : PEG (polyethyleneglycol); 0.25 microns
temperature of
  injection port : about 20 °C higher than the colume temperature
  colume : 150 °C – 210 °C
pressure : flow rate 5 psig
sample size : 1 μl (splitless)

4.2 Iodine Value (I.V.)

Iodine value is defined as the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed). The method and reagents are shown in Appendix A.

4.3 Separation of soybean oil fatty acids

After the hydrogenation reaction, the hydrogenated soybean oil was separated into saturated and unsaturated fatty acids using the winterization method. This separation was carried out on the basis of the difference of melting points of individual fatty acids.

In this method, substances were cooled to about 20-25 °C and then the temperature was controlled for separation of unsaturated and saturated soybean oil fatty acids. At this point, the mixture was then ready for filtration. The filtration would separate the saturated oil from the unsaturated oil. The saturated oil would be wax and the unsaturated oil would be liquid.

CHAPTER IV

RESULTS AND DISCUSSION

The hydrogenation of triglyceride oils is obviously a complicated reaction. It involves not only several simultaneous and consecutive chemical steps but also physical transfer steps of reaction and products on the catalyst surface. The experiment relating to the hydrogenation of soybean oil was performed under the best conditions of elevated temperature and pressure in the presence of prepared catalysts. The hydrogenating catalyst was made up of the combination of group VI metal and group VIII metal supported on alumina.

The goal of this research is the investigation of catalysts that are more effective in selective hydrogenation of soybean oil by using catalysts such as nickel, cobalt, and tungsten. The temperature, pressure, and reaction time were optimized in order to achieve the required product.

4.1 Properties of prepared catalysts

The catalysts were prepared by impregnation of nickel, cobalt, and tungsten on alumina support, which had a pore volume of about 0.64 ml/g. They were characterized by X-ray fluorescence. The result gave information on the amount of elemental composition of catalysts. It showed that the prepared catalyst on alumina support had the amount of metal composition corresponding to the amount of impregnation metal as shown in Figures B1-B4. The amounts of metal composition after metal impregnation are presented in Table 4.1.

Table 4.1 Analytical results of the prepared catalysts.

Catalyst types	**Amount of metal (%wt)**		
	Ni	**Co**	**W**
NW I	5.76	-	6.84
NW II	5.05	-	10.21
CW I	-	5.43	4.95
CW II	-	4.83	11.11

4.2 Hydrogenation process

The aim of this study was to choose the suitable condition and the effective catalyst for selective hydrogenation of soybean oil. The original soybean oil was characterized as shown in Table 4.2 and Figure C1.

Table 4.2 Fatty acid composition and iodine value of the original soybean oil.

Properties	**Soybean oil (%wt)**
Iodine Value (I.V.)	132
% Fatty acid composition	
C16:0 palmitic acid	9.65
C18:0 stearic acid	5.80
C18:1 oleic acid	27.22
C18:2 linoleic acid	51.55
C18:3 linolenic acid	5.79

This experiment was designed to find the optimum conditions for selective hydrogenation. While the oil was contacting to the hydrogenation catalyst, some of the double bonds might be hydrogenated at different rates. All of the hydrogenation reactions occurred simultaneously with different relative rates. The oleic selectivity was simply the ratio of the hydrogenation rate of linoleic acid compared to the hydrogenation rate of oleic acid.

4.3 Screening of catalyst types

The hydrogenation condition was chosen based on prior experiment [1]. This condition was 200 psig of hydrogen pressure, 200 °C of reaction temperature, 180 min of reaction time, 500 rpm of agitation speed, and 10% by weight of oil. The properties of hydrogenated soybean oil are shown in Table 4.3 and in Figures C2-C5 by chromatogram.

Table 4.3 Analytical results of hydrogenated soybean oil using various catalyst types: reaction temperature at 200 °C, hydrogen pressure at 200 psig, reaction time at 180 min, agitation speed at 500 rpm, and catalyst concentration at 10 % by weight of oil.

Properties	**Soybean oil**	**Catalyst types**			
		NW I	**NW II**	**CW I**	**CW II**
Iodine value (I.V.)	132	98	76	101	87
%Fatty acid composition					
C16:0 palmitic acid	9.65	10.41	10.57	10.70	10.24
C18:0 stearic acid	5.80	11.64	87.64	11.11	11.03
C18:1 oleic acid	27.22	49.99	1.79	48.63	50.53
C18:2 linoleic acid	51.55	25.04	0.00	27.25	26.67
C18:3 linolenic acid	5.79	3.11	0.00	3.30	1.51

Where NW I 5%Ni-5%W

NW II 5%Ni-10%W

CW I 5%Co-5%W

CW II 5%Co-10%W

From this experiment, it was concluded that the prepared NW II catalyst gave better performance than the other catalysts. With this catalyst, stearic acid increased from 5.80% to 87.64% by weight of oil. While the other catalysts gave stearic acid content at 11.64%, 11.11%, and 11.03% by weight of total fatty acid, respectively. However, this condition was not aimed to produce oleic acid. The experiment were 3-times conducted for validity, which are shown in Appendix E.

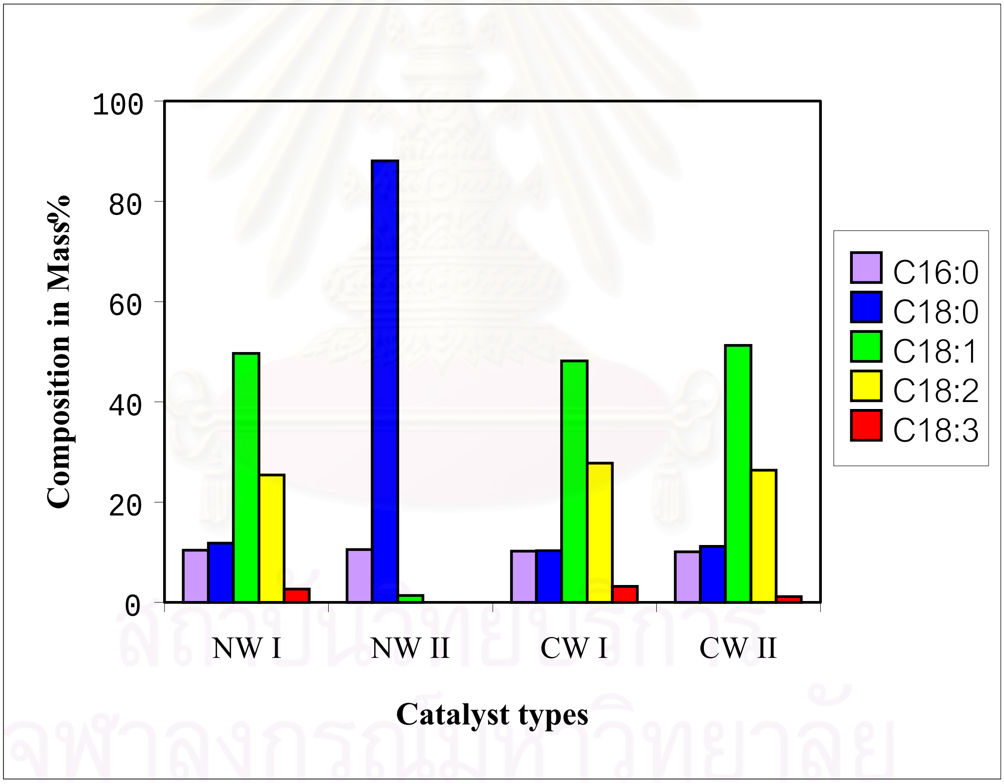


Figure 4.1 Relation of fatty acid concentration (mass%) and catalyst types.

A comparison of the results obtained when the hydrogenation was carried out at the same condition with different catalysts is presented in Figure 4.1. The most active catalyst that was selected for a process of partially and selectively hydrogenation of soybean oil was NW II catalyst on alumina support. So this catalyst was used in order to find the optimized condition to produce oleic acid, which was the required product.

4.4 Selection of the optimum operating condition

The 5%Ni-10%W catalyst (NW II) and the 5%Co-10%W catalyst (CW II) were selected for determining the optimum operating condition by varying these parameters: reaction temperature, hydrogen pressure, and reaction time.

4.4.1 Effect of the reaction temperature

The effect of temperature on the rate of the reaction has been studied for a variety of hydrogenation. The exact observation is dependent on the nature of the substrate being hydrogenated and on the types of catalyst being used. But for almost all hydrogenation the rate will approximately double for every ten to twenty degree increase in temperature.[11]

In this section, the temperature of the experiments on hydrogenation of soybean oil was varied at different temperature of 100 °C, 120 °C, 150 °C, and 200 °C for both NW II and CW II catalysts.

4.1.1.1 Effect of reaction temperature on hydrogenation process using NW II catalyst

The results of the experiment at different temperature are shown in Table 4.4. In the chromatograms, Figures B6-B9, showed the fatty acids content changes as a function of the time lapse during the soybean oil hydrogenation reaction.

Table 4.4 Analytical results of hydrogenated soybean oil using NW II as a catalyst at various temperatures: hydrogen pressure at 150 psig, reaction time at 60 min, agitation speed at 500 rpm, catalyst concentration at 10% by weight of oil.

Properties	**Soybean oil**	**Reaction temperature (°C)**			
		100	**120**	**150**	**200**
Iodine value (I.V.)	132	123	120	97	99
%Fatty acid composition					
C16:0 palmitic acid	9.65	12.45	12.09	9.01	10.90
C18:0 stearic acid	5.80	5.77	5.61	8.26	8.10
C18:1 oleic acid	27.22	27.37	27.99	54.82	54.16
C18:2 linoleic acid	51.55	48.40	48.91	25.78	25.60
C18:3 linolenic acid	5.79	6.04	5.40	2.12	1.24

From 4.4, it is observed that the increasing reaction temperature from 100 °C to 200 °C decreased the iodine value from 123 to 99, while oleic acid increased from 27.37% to 54.16%. Stearic acid increased from 5.77% to 8.10% which linolenic acid decreased from 6.04% to 1.24%.

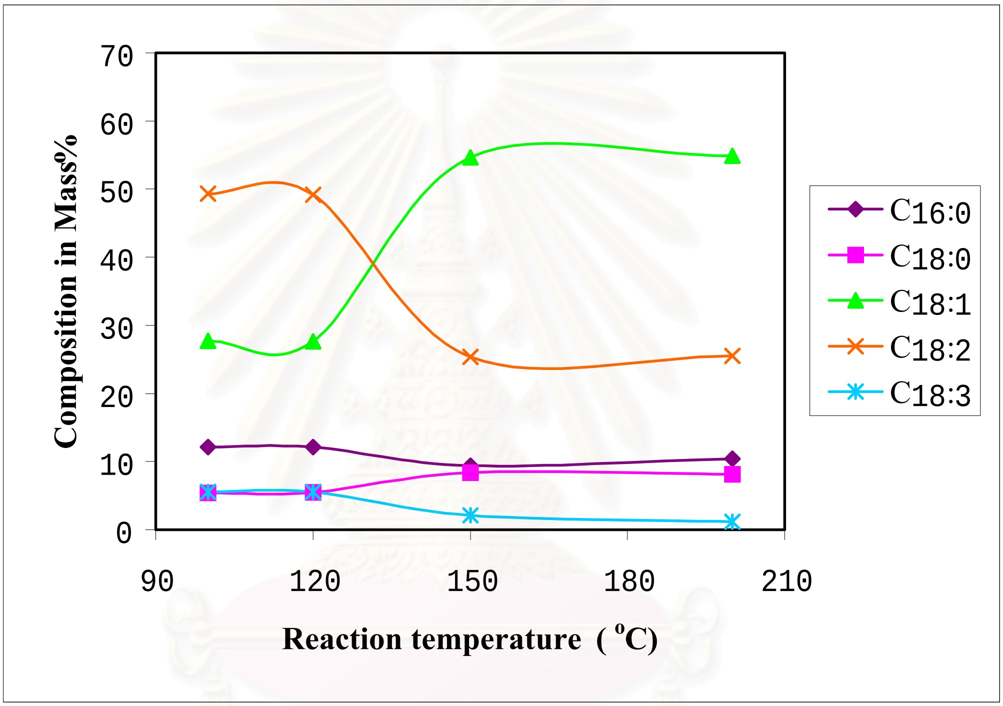


Figure 4.2 Relation of fatty acid concentration (mass%) and reaction temperature. (NW II catalyst)

From the experiment, it is observed that the fatty acid composition is important to change the iodine value. In other words, the iodine value decreased with increasing temperature. From Figure 4.2, the amount of linoleic acid slightly decreased at 100 °C and 120 °C. But between 120 °C and 150 °C, the amount of linoleic acid was decreased by half while oleic acid content rapidly increased, which was ideal for the required product. At 200 °C, the ratio of acid compositions was similar to the composition at 150 °C. It can be concluded that the optimum temperature for NW II catalyst should be 150 °C because it gave the highest amount of the oleic acid. Although, the amount of oleic acid at 200 °C was slightly different from that at temperature of 150 °C. The temperature at 150 °C was selected in this study because of energy saving.

4.1.1.2 Effect of reaction temperature on hydrogenation process using CW II catalyst

The results of this experiment were derived from the test under the same conditions with NW II catalyst. The reaction temperature was varied from 100, 120, 150, and 200 °C, respectively. The operating conditions were carried out at hydrogen pressure at 150 psig, reaction time at 60 min, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil. The properties of hydrogenated oil are shown in Table 4.5 and Figures C10-C13.

Table 4.5 Analytical results of hydrogenated soybean oil using CW II as a catalyst at various reaction temperatures: hydrogen pressure at 150 psig, reaction time at 60 min., agitation speed at 500 rpm, and catalyst concentration at 10% weight of oil.

Properties	**Soybean oil**	**Reaction temperature (°C)**			
		100	**120**	**150**	**200**
Iodine value (I.V.)	132	125	125	110	108
%Fatty acid composition					
C16:0 palmitic acid	9.65	10.51	9.76	10.18	10.32
C18:0 stearic acid	5.80	5.06	5.69	6.21	7.70
C18:1 oleic acid	27.22	29.56	31.80	40.26	52.25
C18:2 linoleic acid	51.55	48.52	46.71	38.25	26.23
C18:3 linolenic acid	5.79	6.36	6.03	5.11	3.50

The result showed that oleic acid in the hydrogenated oil increased when the temperature was increased from 150 °C to 200 °C. The reaction was operated at a higher temperature to increase the rate of hydrogenation and also to increase the higher molecular weight component.

In term of iodine value, the increasing of reaction temperature increased the rate of hydrogenation resulting in the increasing of higher molecule weight fatty acid. The hydrogenated soybean oil obtained from higher temperature had lower iodine value than the one at lower temperatures.

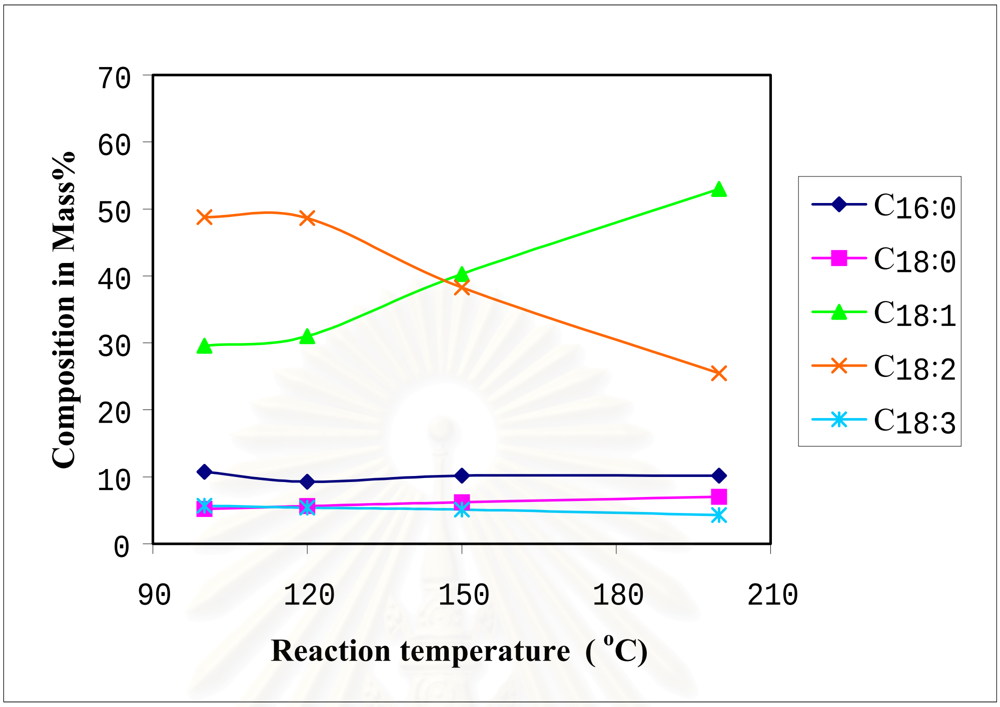


Figure 4.3 Relation of fatty acid concentration (mass%) and reaction temperature. (CW II catalyst)

This result revealed that by using CW II catalyst, hydrogenated oil obtained at a higher temperature had less amount of oleic acid than that at a lower temperature. It was expected that linoleic acid would be hydrogenated to oleic acid during hydrogenating process. But, the temperature at 200 °C when using CW II catalyst, the amount of oleic acid was less than the reaction at 150 °C when using NW II catalyst. The details are shown in Figure 4.3 and from the chromatograms in Figures C10-C13.

From Tables 4.4 and 4.5, it was obvious that NW II catalyst had better efficiency than CW II catalyst in oleic acid production. The selectivity of the hydrogenating soybean oil is also dependent on the reaction temperature at which it was operating. The lower the temperature, the more selective the reaction was. The hydrogenation of soybean oil, over NW II catalyst at 120 °C, slightly converted linoleic acid to oleic acid. At 150 °C, linoleic acid was hydrogenated to be oleic acid and at higher temperature, all double bonds were hydrogenated.

4.4.2 Effect of the hydrogen pressure

The second parameter in the hydrogenating process was the hydrogen pressure. Generally, an increase in hydrogen pressure also results in a decrease in reaction selectivity. The hydrogen pressure on the hydrogenation of soybean oil with NW II and CW II catalysts was varied at different pressures of 100, 150, and 200 psig. The operating conditions were carried out at the optimum temperature at 150 °C, reaction time at 60 min, agitation speed at 500 rpm, and catalyst concentration at 10% weight of oil.

4.4.2.1 Effect of hydrogen pressure on hydrogenation process using NW II catalyst

The results of this experiment at different hydrogen pressure are shown in Table 4.6 and Figures C14-C16. It was evident from the figures that hydrogenation rate increased with increasing hydrogen pressure. The increasing of hydrogen pressure affected the selectivity of soybean oil hydrogenation.

From the analytical results of the hydrogenated products, it was observed that some amount of oleic acid was converted to stearic acid. However the iodine value decreased from 120 to 92 when the hydrogen pressure was raised from 100 psig to 200 psig.

Table 4.6 Analytical results of hydrogenated soybean oil using NW II as a catalyst at various hydrogen pressures: reaction temperature at 150 °C, reaction time at 60 min., agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil.

Properties	**Soybean oil**	**Hydrogen pressure (psig)**		
		100	**150**	**200**
Iodine value (I.V.)	132	120	97	92
%Fatty acid composition				
C16:0 palmitic acid	9.65	10.70	9.01	10.26
C18:0 stearic acid	5.80	5.19	8.26	11.83
C18:1 oleic acid	27.22	27.17	54.82	50.61
C18:2 linoleic acid	51.55	51.05	25.78	24.65
C18:3 linolenic acid	5.79	5.89	2.11	2.65

In Figure 4.4, it showed that the amount of linoleic acid decreased in contrary to the increasing of oleic acid content. As hydrogen solubility in oil was directly in correlation to pressure, it was not surprising to see the more rapid reaction rate from 100 psig to 150 psig. This is due to the fact that when hydrogen pressure increases, selectivity decreases, and hydrogenation rate increases.

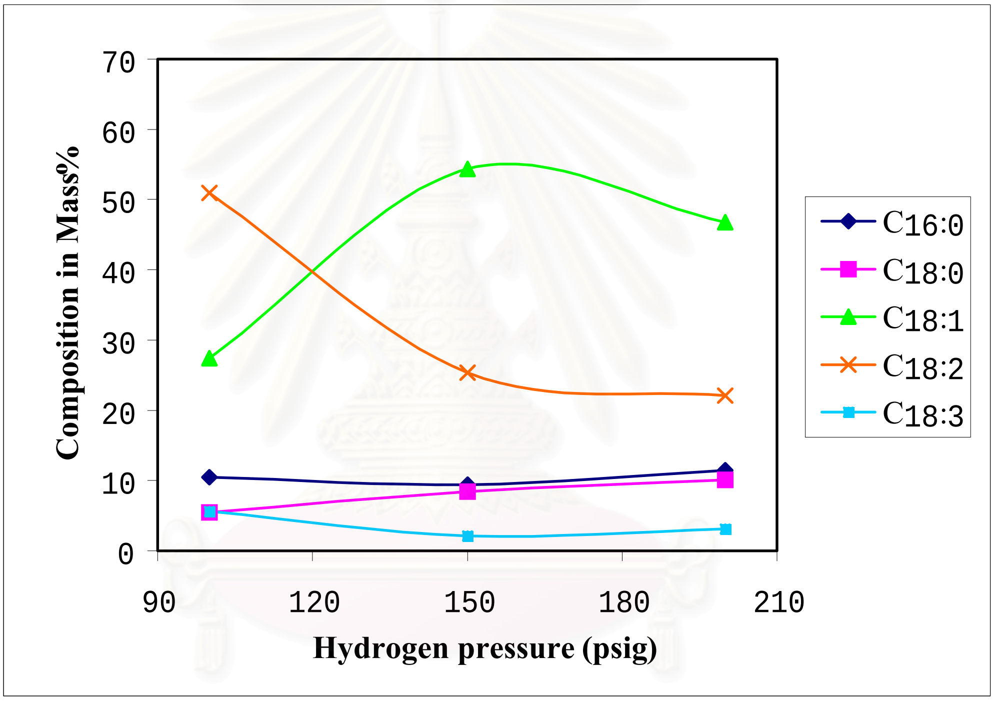


Figure 4.4 Relation of fatty acid concentration (mass%) and hydrogen pressure. (NW II catalyst)

In this research, for the higher amount of required product and the economic consideration, the suitable hydrogen pressure is 150 psig.

4.2.2.2 Effect of hydrogen pressure on hydrogenation process using CW II catalyst

This parameter was studied for the hydrogenation process of soybean oil using CW II catalyst. The reactions were performed with identical conditions with NW II catalyst. The results and the chromatograms are shown in Table 4.7, Figures 4.5, and C17-C19.

Table 4.7 Analytical results of hydrogenated soybean oil using CW II as a catalyst at various hydrogen pressures: reaction temperature at 150 °C, reaction time at 60 min, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil.

Properties	Soybean oil	Hydrogen pressure (psig)		
		100	150	200
Iodine value (I.V.)	132	129	110	107
%Fatty acid composition				
C16:0 palmitic acid	9.65	10.42	10.18	9.78
C18:0 stearic acid	5.80	5.21	6.21	8.19
C18:1 oleic acid	27.22	28.05	40.26	40.82
C18:2 linoleic acid	51.55	51.00	38.25	36.12
C18:3 linolenic acid	5.79	5.32	5.11	5.09

From Figure 4.5, the properties of soybean oil were slightly changed between 150 psig to 200 psig. It was observed that when increasing the hydrogen pressure, the rate of hydrogenation of the unsaturated oil was increased, but was lower than those using NW II.

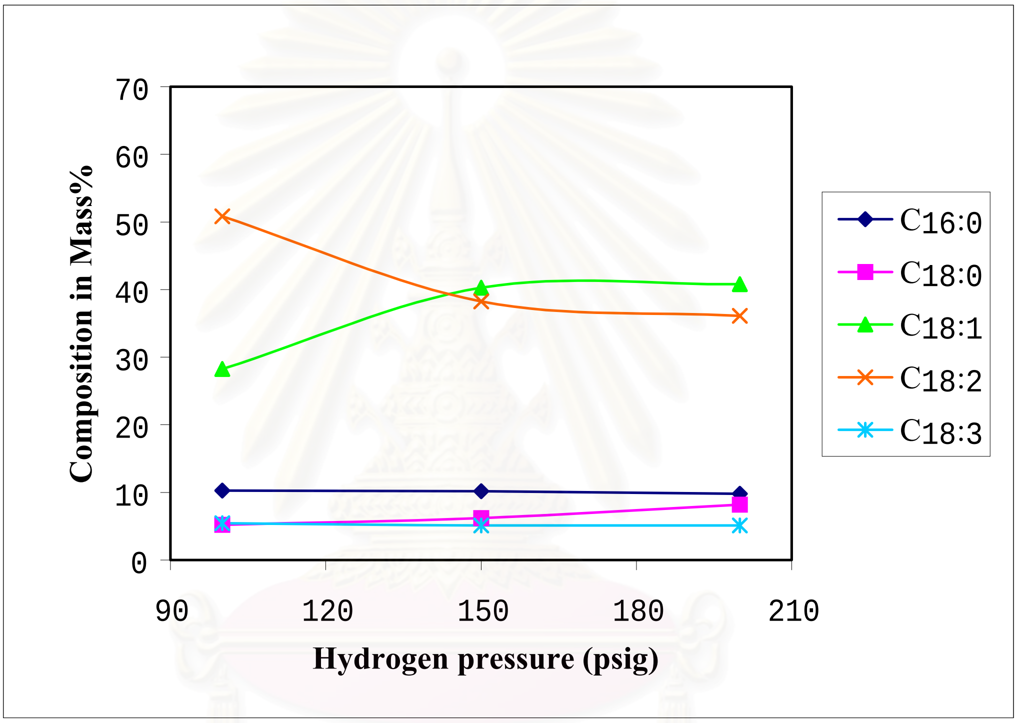


Figure 4.5 Relation of fatty acid concentration (mass%) and hydrogen pressure. (CW II catalyst)

In some cases even a slight pressure increase was sufficient to destroy the selectivity of the reaction. The hydrogenation of acetylenes to olefin over NW II and CW II catalysts proceeds smoothly under suitable pressure, but no selectivity between the hydrogenation of the acetylene and the olefin is observed when the pressure is increased to 200 psig. [11]

4.4.3 Effect of the reaction time

The hydrogenation time was varied from 60, 100, 120, and 140 min, respectively. The NW II and CW II catalysts on alumina support were used and the reaction was operated at 150 °C and 150 psig.

4.4.3.1 Effect of reaction time on hydrogenation process using NW II catalyst

The results of this experimental section at different reaction times are shown in Table 4.8, Figure 4.6, and Figures C20-C23.

Table 4.8 Analytical results of hydrogenated soybean oil using NW II as a catalyst at various reaction times: 150 °C, 150 psig, 500 rpm, and 10% catalyst by weight of oil.

Properties	**Soybean oil**	**Reaction time (min)**			
		60	**100**	**120**	**140**
Iodine value (I.V.)	132	97	95	90	87
%Fatty acid composition					
C16:0 palmitic acid	9.65	9.01	9.71	9.09	9.00
C18:0 stearic acid	5.80	8.26	9.31	9.91	15.67
C18:1 oleic acid	27.22	54.82	60.73	72.58	66.76
C18:2 linoleic acid	51.55	25.78	20.17	8.42	8.57
C18:3 linolenic acid	5.79	2.11	0.08	0.00	0.00

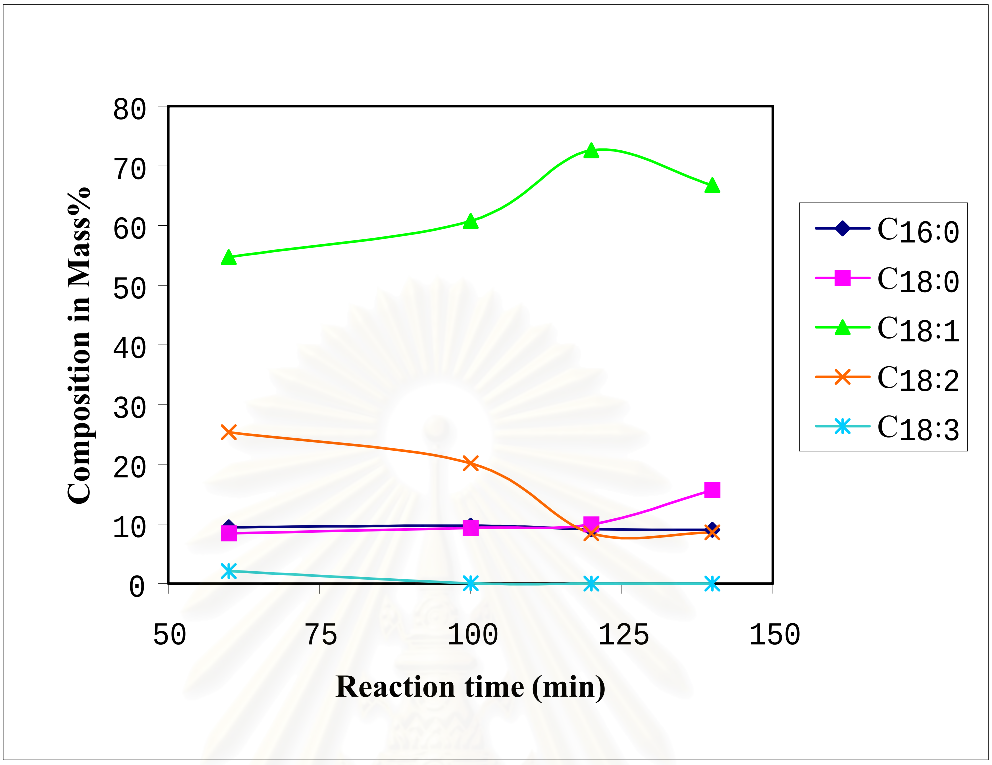


Figure 4.6 Relation of fatty acid concentration (Mass%) and reaction time. (NW II catalyst)

The results from Table 4.8 and Figure 4.6 showed that the increasing of the reaction time from 60 to 100 min increased the amount of oleic acid. Meanwhile, the linolenic acid content still remained in the hydrogenated oil. At 120 min, the increasing of hydrogenation rate was higher than the rate of reaction time, which increased from 60 to 100 min. This shows that at a longer period of time, the increasing of reaction time caused much increase in the hydrogenating rate. However, if a longer reaction time was used (at 120 min), the required product would occur in high quantity, while all of linolenic acid would be reduced to nil. However, at the reaction time of 140 min., some of oleic acid was hydrogenated to stearic acid. It was observed that the amount of stearic acid was slightly increased while the ratio of other fatty acid compositions was changed similarly. The iodine value decreased in accordance with the reaction time and the weight of oil.

4.4.3.2 Effect of reaction time on hydrogenation process using CW II catalyst

The CW II catalyst was used in the hydrogenation of soybean oil. At identical conditions as in the case of using NW II as catalyst, the results are shown in Table 4.9, Figures 4.7, and C24-C27.

Table 4.9 Analytical results of hydrogenated soybean oil using CW II as a catalyst at various reaction times: reaction temperature at 150 °C, hydrogen pressure at 150 psig, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil.

Properties	**Soybean oil**	**Reaction time (min)**			
		60	**100**	**120**	**140**
Iodine value (I.V.)	132	110	100	98	90
%Fatty acid composition					
C16:0 palmitic acid	9.65	10.18	9.84	9.99	9.71
C18:0 stearic acid	5.80	6.21	9.06	9.24	11.33
C18:1 oleic acid	27.22	40.26	42.32	53.12	60.54
C18:2 linoleic acid	51.55	38.25	34.90	25.01	17.33
C18:3 linolenic acid	5.79	5.11	3.88	2.64	1.09

In term of iodine value, the decreasing of reaction time increased the iodine value. This resulted in decreasing of lower molecular weight fatty acid components. Therefore, the hydrogenated soybean oil operated at a short reaction time had more iodine value than at long reaction time. Oleic acid was increased when the reaction was performed at a longer reaction time. It was expected that the longer reaction time had a greater amount of oleic acid when CW II was used as a catalyst. But when comparing to the one with NW II catalyst, the oleic acid contents in reaction with CW II were lower at every reaction time.

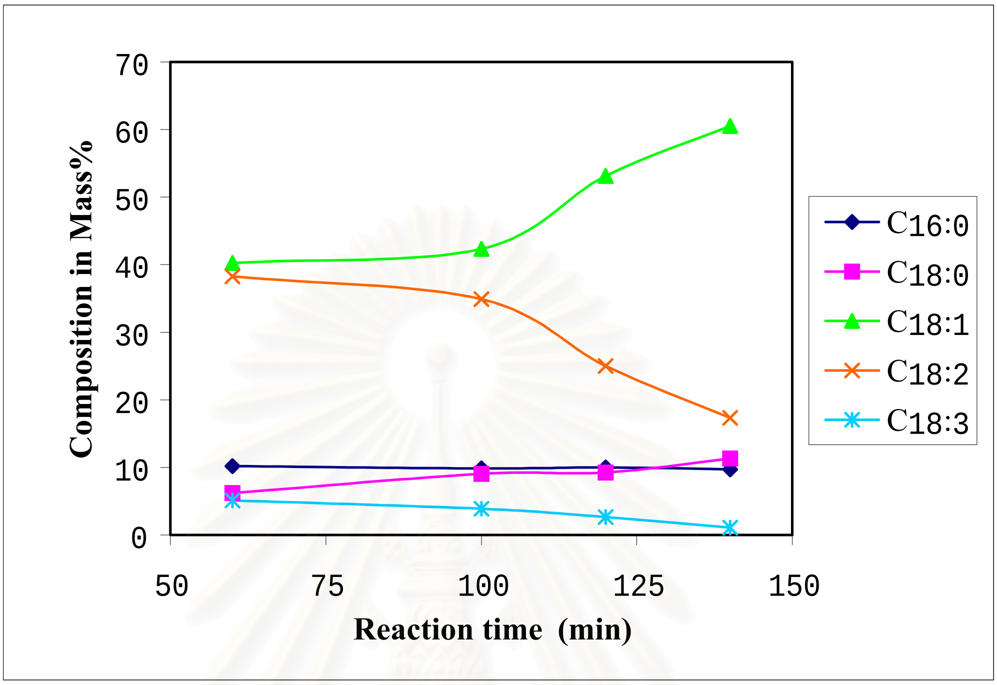


Figure 4.7 Relation of fatty acid concentration (mass%) and reaction time. (CW II catalyst)

The observed data from Figure 4.7 indicated that the suitable reaction time was 140 min. If the reaction time was higher, the rate of hydrogenation would be increased.

The goal of this study was to find the minimum reaction time, which gave oil with high content of oleic acid. These observations suggested that the suitable reaction time was 120 min.

4.4.4 Effect of the catalyst types

The effect of catalyst types on hydrogenation of soybean oil was studied using four types of catalysts under the same preparation conditions. The impregnated catalysts were 5%Ni-5%W (NW II), 5%Ni-10%W (NW II), 5%Co-5%W (CW I), and 5%Co-10%W (CW II) on alumina support.

The four types of catalysts were employed in the hydrogenation of soybean oil under the same condition including a temperature at 150 °C, hydrogen pressure at 150 psig, reaction time at 120 min, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil. The results of the experiment at different catalyst types are shown in Table 4.10, Figures 4.8, and C28-C31.

Table 4.10 Analytical results of hydrogenated soybean oil using various catalyst types: reaction temperature at 150 °C, hydrogen pressure at 150 psig, reaction time at 120 min, agitation speed at 500 rpm, and catalyst concentration at 10 % by weight of oil.

Properties	**Soybean oil**	**Catalyst types**			
		NW I	**NW II**	**CW I**	**CW II**
Iodine value (I.V.)	132	121	90	123	98
%Fatty acid composition					
C16:0 palmitic acid	9.65	9.64	9.09	9.58	9.99
C18:0 stearic acid	5.80	7.48	9.91	6.11	9.24
C18:1 oleic acid	27.22	48.77	72.58	46.02	53.12
C18:2 linoleic acid	51.55	30.06	8.42	33.41	25.01
C18:3 linolenic acid	5.79	4.05	0.00	4.88	2.64

where NW I 5%Ni - 5%W

NW II 5%Ni - 10%W

CW I 5%Co - 5%W

CW II 5%Co - 10%W

From the comparative results of the hydrogenation using different catalyst from Figure 4.8, it was evident that the hydrogenation using cobalt catalyst was slower than nickel catalyst. Therefore, nickel was the prefer catalyst in hydrogenation of soybean oil. As a result from gas chromatography, NW I catalyst could give 48.77% oleic acid, but CW I catalyst gave only 46.02%. At the same time, NW II catalyst gave more oleic acid than CW II catalyst. From the comparison of NW I and NW II catalysts, it was obvious that the hydrogenation reaction using NW II catalyst was better than NW I catalyst because it gave high percentage of oleic acid which indicated higher selectivity. This trend was observed as well in the reaction using CW I and CW II catalysts. The CW II catalyst was better than CW I catalyst because of the different ratio of tungsten content. It is obvious that the increase of tungsten content from 5% to 10% increased the hydrogenation reaction and decreased the iodine value from 120 to 107.

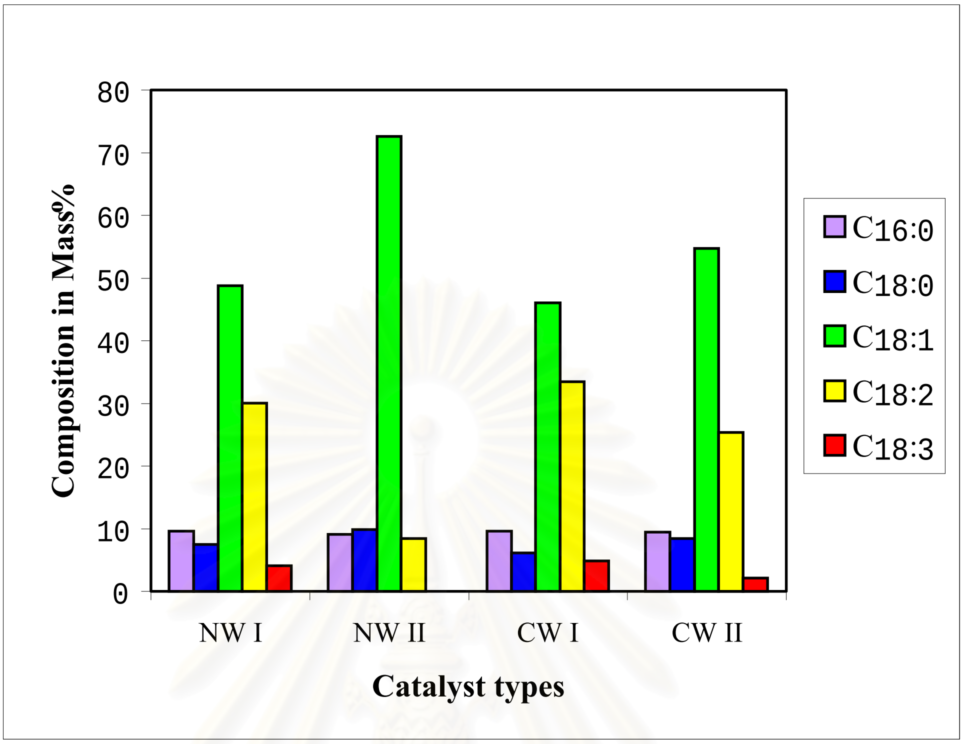


Figure 4.8 Relation of fatty acid concentration (mass%) and catalyst types at the optimum condition.

The difference of catalytic efficiency may be due to the metal and the composition ratio of the two metals. It should be noted that the composition ratio is based on the total concentrations of metals on the support and that the different metal distribution could also influence the activity. The result indicated that the catalyst with nickel / tungsten weight ratio of 1:2 gave higher activity than at the ratio of 1:1.

From this study, it could be seen that the prepared NW II catalyst had better selectivity in hydrogenation of soybean oil than the other prepared catalysts. Therefore, the NW II catalyst was suitable for a process of partially and selectively hydrogenation of soybean oils.

In the study of Jovanovic et. at.[1], they prepared catalyst that was a nickel deposited on a natural silicate support (diatomite) used for selective hydrogenation of soybean oil. The optimized condition to produce oleic acid is presented in Table 4.11.

Table 4.11 Comparison of the optimized condition to produce oleic acid between this work with Jovanovic's work.

Subject	**Reaction temperature (°C)**	**Hydrogen pressure (psig)**	**Reaction time (min)**	**%wt of oleic acid**
Jovanovic	195	200	180	52.00
This work	150	150	120	87.58

Table 4.11 indicated that the amount of oleic acid obtained from this work was more than that obtained from Jovanovic's work, even though the condition of this work was less than that of Jovanovic's work. Because this work used bimetallic catalysts, but Jovanovic's work used monometallic catalyst.

4.4.5 Effect of the regenerated catalyst (NW II)

This experiment studied the activity of the used catalyst by using NWII catalyst under optimum condition: reaction temperature at 150 °C, hydrogen pressure at 150 psig, reaction time at 120 min, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil. The operating reaction was varied to find the efficiency of the regenerated catalyst.

From Table 4.11, it indicated that the prepared catalyst (NW II) could be reused twice. The efficiency of catalyst from the first time of regeneration decreased at about 30 % of the fresh catalyst. After second of regeneration, the catalyst was less active because the fatty acid compositions of hydrogenated oil was slightly changed when comparing with the original oil. This was a result from decreasing the surface area of active site of catalyst, which was due to the accumulation of oil and by products on the catalyst. Therefore, the rate of hydrogenation was deceased.

Table 4.12 Analytical results of hydrogenated soybean oil using regenerated catalyst.

Properties	**Soybean oil**	**Number of times to regenerate**		
		#1	**#2**	**#3**
Iodine value (I.V.)	132	90	108	125
%Fatty acid composition				
C16:0 palmitic acid	9.65	9.09	10.08	9.53
C18:0 stearic acid	5.80	9.91	7.82	7.71
C18:1 oleic acid	27.22	72.58	51.16	31.02
C18:2 linoleic acid	51.55	8.42	25.52	45.71
C18:3 linolenic acid	5.79	0.00	5.42	6.03

4.5 Separation of soybean oil fatty acids

Winterization is used to separate saturated oil and unsaturated oil. The oil was chilled rapidly. Then, the oil was separated into two parts, each part would contain the different fatty acids as shown in Table 4.11 and Figures C32-C33.

From Table 4.11, it indicated that the winterization could separate the unsaturated fraction rich in oleic acid (87.58%), which was the required product. Therefore, partial hydrogenation in combination with winterization was employed to make oleic acid from soybean oil.

Table 4.13 Analytical result of the separation between saturated oil and unsaturated oil.

Acid components	**Soybean oil**	**Fatty acid composition (%wt)**	
		Part I	**Part II**
Saturated			
C16:0 palmitic acid	9.65	56.02	5.94
C18:0 stearic acid	5.80	32.97	3.42
Unsaturated			
C18:1 oleic acid	27.22	7.61	87.58
C18:2 linoleic acid	51.55	3.40	3.06
C18:3 linolenic acid	5.79	0.00	0.00

Where Part I is a saturated fraction.

Part II is a unsaturated fraction.

4.6 Determination of spectroscopic properties

The soybean oil was converted to fatty acid methyl esters and they were determined by FTIR and ^{13}C-NMR as well as GC and GC-MS.

4.6.1 Infrared spectra

The IR spectra were used to characterize original soybean oil and soybean oil fatty acid methyl ester (FAME). Their IR spectra are given in Figures D1 and D2 and the characteristic peaks are shown in Tables 4.12 and 4.13.

Table 4.14 The characteristic absorption of original soybean oil.

Absorption frequency (cm^{-1})	**Vibration assignment**
3010	=C–H stretching
2921,2854	aliphatic C–H stretching
1741	carbonyl (C=O) of triglyceride
1650	C=C bending
1461,1379	C–H bending
1160,1230	C–O stretching

Table 4.15 The characteristic absorption of soybean oil fatty acid methyl ester.

Absorption frequency (cm^{-1})	**Vibration assignment**
3004	=C–H stretching
2923,2852	aliphatic C–H stretching
1742	carbonyl C=O stretching
1460-1366	C–H bending
1245-1119	C–O stretching

4.6.2 ^{13}C-NMR spectra

Bruker, ACF 200 MHz nuclear magnetic resonance spectrometer was used for the characterization of original soybean oil fatty acid methyl ester. The ^{13}C-NMR spectra are shown in Figures D3 and D4, respectively.

The ^{13}C-NMR spectrum of original soybean oil is shown in Figure D3. It indicated the signals of triglycerides ($-CH_2-O-$) of soybean oil at 61.80 and 68.69 ppm, the signals of parafinic carbons (CH_2, CH_3) at 13.82 to 33.89 ppm, the signals of olefinic carbons (C=C) at 126.88 to 133.55 ppm, and the signal of olefinic carbons (C=O) appeared at 172.32 to 172.73 ppm.

The ^{13}C-NMR spectrum of soybean oil fatty acid methyl ester shown in Figure D4 demonstrated the important signals of methyl ester ($O-CH_3$) and carbonyl (C=O) of methyl ester product at 51.39 and 173.67 ppm, respectively. The signals of parafinic carbons (CH_2, CH_3) were at 14.05 to 34.06 ppm and olefinic carbons (C=C) were at 127.87 to 130.16 ppm.

4.6.3 GC-MS technique

The composition and amount of fatty acid methyl esters at various conditions were determined by GC-MS. The GC-MS was performed using DB wax capillary column and the GC-MS chromatograms are shown in Figure series C and mass spectra are shown in Figures D1-D4.

From Figure C1, GC chromatogram indicated that methyl ester of original soybean oil was a mixture of methyl ester of long chain fatty acid (C16 and C18). The main composition was methyl oleate at retention time 12.15 min. The total compositions of soybean oil fatty acid ester are shown in Table 4.14.

Table 4.16 The retention time of each fatty acid methyl ester.

Retention time (min)	**Fatty acid methyl ester**
9.50	Hexadecanoic acid
11.87	Octadecanoic acid
12.15	9-octadecanoic acid
12.81	9,12-octadecanoic acid
13.88	9,12,15-octadecanoic acid

The peak area ratio of the GC-MS chromatogram was determined and converted into the percentage of each composition of fatty acid.

CHAPTER V

CONCLUSION

This research aimed to study the effects of bimetallic catalysts in the hydrogenation of soybean oil. The objective for accomplishment was a process for the partial and selective hydrogenation of soybean oil using, NiW and CoW catalysts, on alumina support. The operating condition was studied for each type of catalysts, in order to produce oleic acid and/or stearic acid.

The suitable catalyst for hydrogenation of soybean oil to give good yield of oleic acid was NW II (5%Ni-10%W). The suitable operating condition for the hydrogenation of soybean oil using the NW II catalyst to produce oleic acid was the reaction temperature at 150 ^{o}C, hydrogen pressure at 150 psig, reaction time 120 minutes, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil. Under this condition, the hydrogenation of soybean oil at the selected condition provided the hydrogenated product was composed of 72.58 %w/w of oleic acid. The iodine value was 90.

The winterization method was used to separate the unsaturated fraction out of saturated fraction and the amount of oleic acid in the final product was increased to 87.58 % and gave the desired product in 85% yield. The hydrogenation of soybean oil at temperature at 200 ^{o}C, hydrogen pressure at 200 psig, reaction time at 180 minutes, agitation speed at 500 rpm, and catalyst concentration at 10% by weight of oil gave waxy product with stearic acid was the main constituent.

Suggestion for further work

1) The impregnated catalysts should be prepared on various supports in order to study the effects of sintering in the hydrogenation.

2) The prepared catalysts, which incorporated promoters, should be prepared. The activity and the stability of the hydrogenation catalyst, which would be affected to a certain degree by promoters, should be studied.

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APPENDIX

Appendix A

Iodine Value

Wijs method

A.O.A.C. official Method Cd 1-25

Definition:

The iodine value is a measure of the unsaturation of fats and oils and is expressed in term of the number of centigram of iodine adsorbed per gram of sample (% iodine absorbed).

A. Apparatus

1. Glass stoppered bottle or wide-mouth Erlenmeyer flasks, 500 ml.
2. Glass stoppered volumetric flask, conforming to Bureau of Standards tolerances and accurately calibrated to contain 1000 ml.
3. Pipette 1, 5, 10, and 20 ml.
4. Bottles, Pyrex, actinic, glass stoppered, 1000 ml.
5. Bulet, 25 ml.

B. Reagents

a) Wijs'solution.

Wijs'solution is more stable if iodine is contained in slightly excess and it often gives high result of iodine value if chlorine is contained in excess. This solution shall be stored in a brown bottle, or a dark place. When it might freeze in winter, it shall be heated to a temperature not higher than 40 °C prior to use.

Dissolve 13 g of iodine in 1000 ml of acetic acid. Pipette 20 ml of the solution and titrate with N/10 sodium thiosulfate solution to determine the concentration of iodine. After dried chlorine is introduced in the solution, pipette 20 ml of the solution, add 15 ml of potassium iodide solution (10 w/v%) and 1000 ml of water, and titrate with N/10 sodium thiosulfate solution so that the titre measure twice the initial titre. The titration shall be made after chlorine gas is introduced in the solution until the color of liberated iodine disappears, reserving small portions of the solution aside before introducing chlorine. If chlorine is present excessively, it shall be removed by adding appropriated amount of iodine solution reserved.

b) Potassium iodide solution (10 w/v%).

Dissolve 100 g of potassium iodide in 1000 ml of water.

c) N/10 Sodium thiosulfate solution.

Dissolve 24.8 g of sodium thiosulfate in water and dilute it with water to 1000 ml. This solution shall be standradized as follows.

Standardization: Take 10 ml of potassium iodide solution (w/v%) into a glass-stoppered Erlenmeyer flask and add 5 ml of hydrochloric acid and shake well. Add exactly 25 ml of N/10 potassium dichlomate solution (primary standrad substance), tightly stopper with a glass stopper wet with potassium iodide solution (10 w/v%) and gently shake the flask. Add 100 ml of water, shake and titrate with N/10 sodium thiosulfate solution until the yellow color almost disappears. Add 1 ml of starch solution and continue the titration until the blue color of iodine-strach changes to green.

Run the blank titration and calculate the factor of N/10 sodium thiosulfate solution, f, by the following formula:

$$f = \frac{25}{A - B}$$

A: volume of N/10 sodium thiosulfate solution consumed in actual titration (ml.)

B: volume of N/10 sodium thiosulfate solution consumed in blank titration (ml.)

d) Starch solution.

Dissolve 1 g of soluble starch with small amount of water an pour slowly, with constant stirring, into 200 ml of boiling water. Cool it down to room temperature and the supernatant liquid or the filtrated shall be used for test.

e) N/10 Potassium dichromate solution.

Pulverize potassium dichromate specified in JIS K 8005 and heat at 100 to 110 °C for 3 to 4 hours. Dissolve 4.9035 g (on the basis of 100%) of this reagent in water. Transfer the solution to a 1000 ml volumetric flask and dilute with water to the mark.

C. Procedure

Weight accurately proper amount of the sample into a ground-stoppered 500 ml of Erlemmeyer flask and add 10 ml of carbon tetrachloride to dissolve the sample. Add exactly 25 ml of wijs'solution and tightly stopper with a glass stopper wet with potassium iodide solution (10 w/v%) in order to prevent volatilization of iodine and chlorine and gently swirl the flask. If the clear solution is not obtained, carbon tetrachoride shall be added additionally until the solution becomees clear. Place the flask in a dark place kept a temperature of 20 to 30 °C for suitable priod (30 minutes for the sample having iodine value not more than 100, 1 hour for iodine value 100 ml over, and 2 hours for tung oil) and swirl the flask occasionally. Add 20 ml of potassium iodine solution (10 w/v%) and 100 ml of water, swirl the flask and titrate with N/10 solution until the solution colors pale yellow. Add 1 ml of strach solution and continue the titration, with swirling, until the bule color of iodine-strach disappears.

Run the blank titration

The sample shall be taken as directed below in such amount that not more than one half of wijs'solution is consumed.

Expected iodine value	**Weight of sample to be take (g)**
Less than 5	2.00 (to 2 significant digits)
5 to 30 excl.	1.00 (to 3 significant digits)
30 to 50 excl.	0.60 (to 3 significant digits)
50 to 100 excl.	0.30 (to 3 significant digits)
100 to 150 excl.	0.20 (to 3significant digits)
150 to 200 excl.	0.15 (to 4 significant digits)
200 and over	0.10 (to 4 significant digits)

D. calculation of iodine value

$$\text{Iodine value} = \frac{(B-C) \times f \times 1.269}{S}$$

B: volume of N/10 sodium thiosulfate solution consumed in blank titration (ml)

C: volume of N/10 sodium thiosulfate solution consumed in actual titration (ml)

f : factor of N/10 sodium thiosulfate solution

S: weight of sample (g)

Appendix B

Analyst	Concentration Units
Co	98.95 ppm
Ni	5.76 Wt %
W	6.84 Wt %

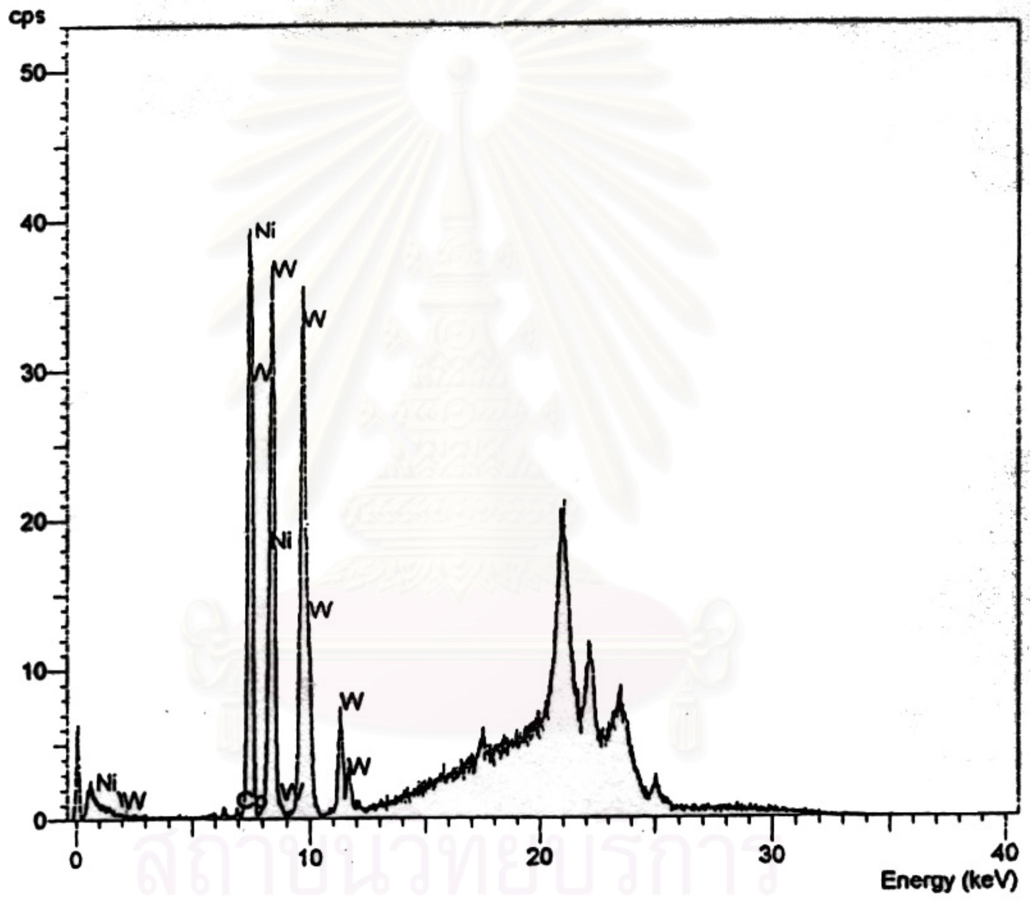

Figure B1 A plot of X-ray fluorescence data of 5%Ni-5%W prepared catalyst.

Analyst	Concentration	Units
Co	68.47	ppm
Ni	5.05	Wt %
W	10.21	Wt %

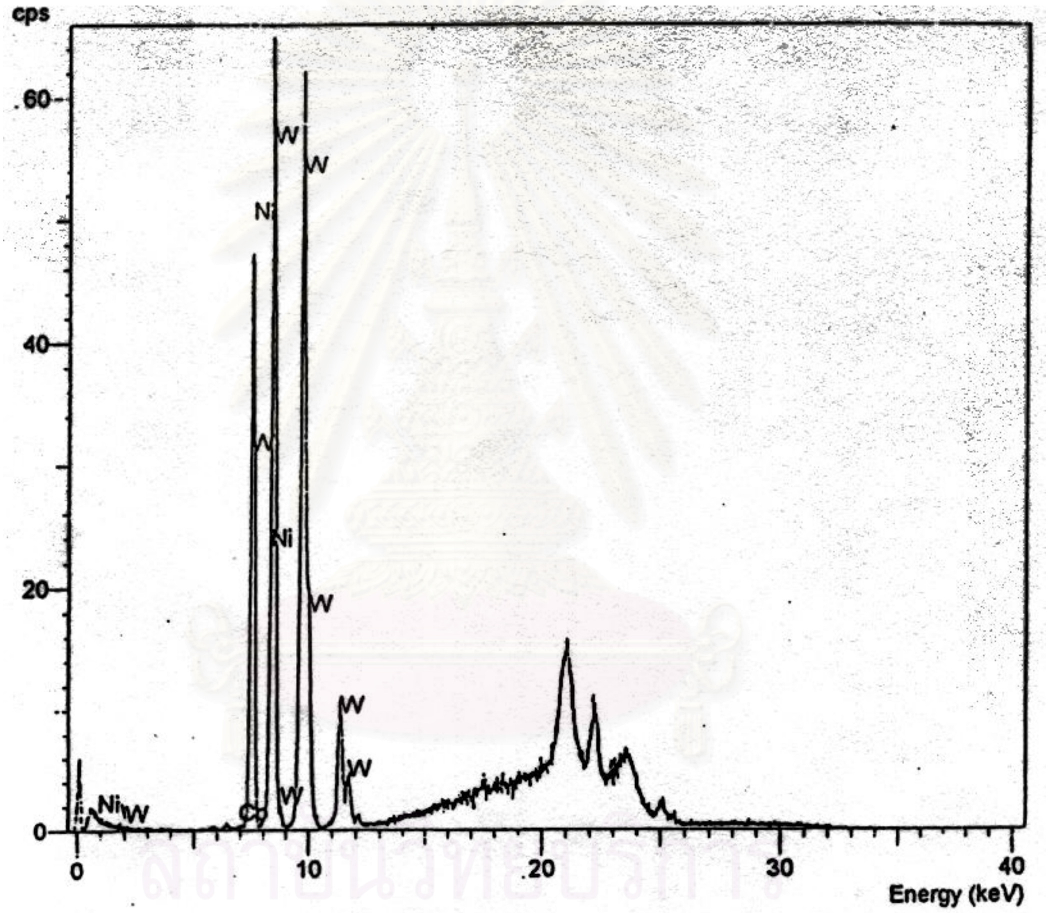

Figure B2 A plot of X-ray fluorescence data of 5%Ni-10%W prepared catalyst.

Analyst	Concentration	Units
Co	5.43	Wt %
Ni	0.00	Wt %
W	4.95	Wt %

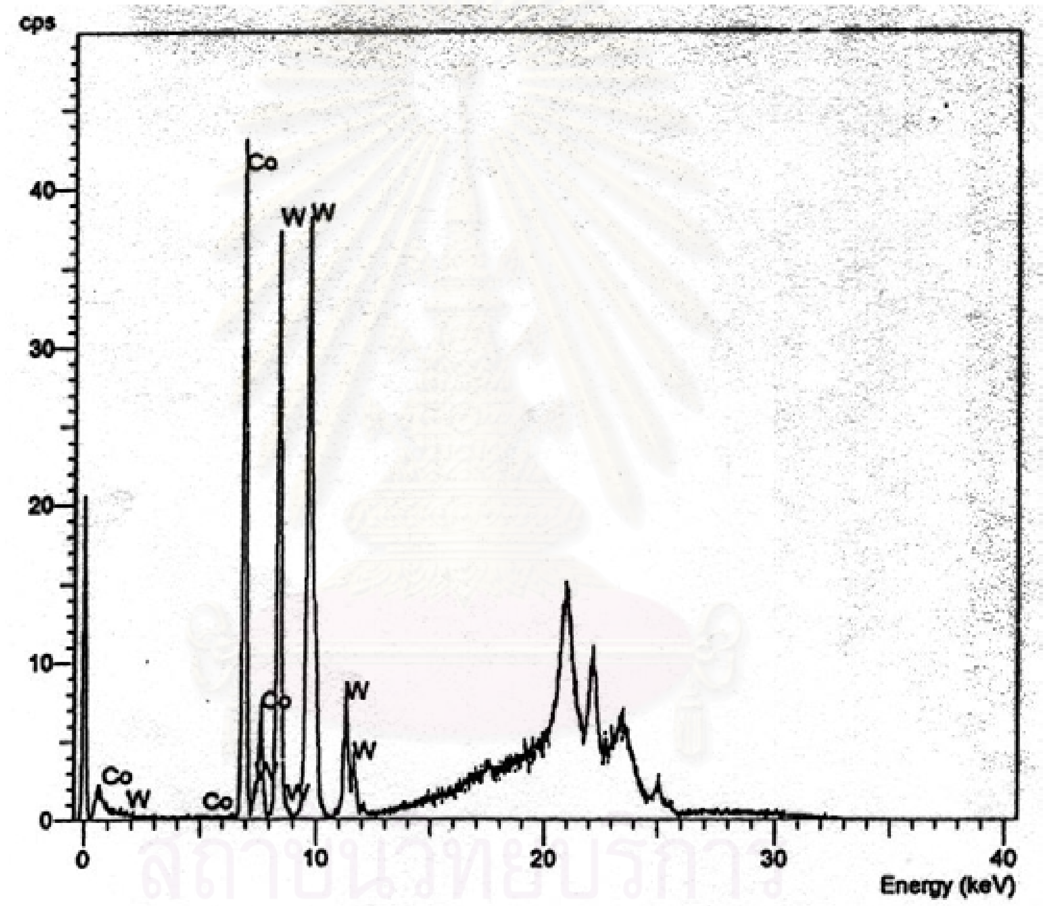

Figure B3 A plot of X-ray fluorescence data of 5%Co-5%W prepared catalyst.

Analyst	Concentration	Units
Co	4.83	Wt %
Ni	0.00	Wt %
W	11.11	Wt %

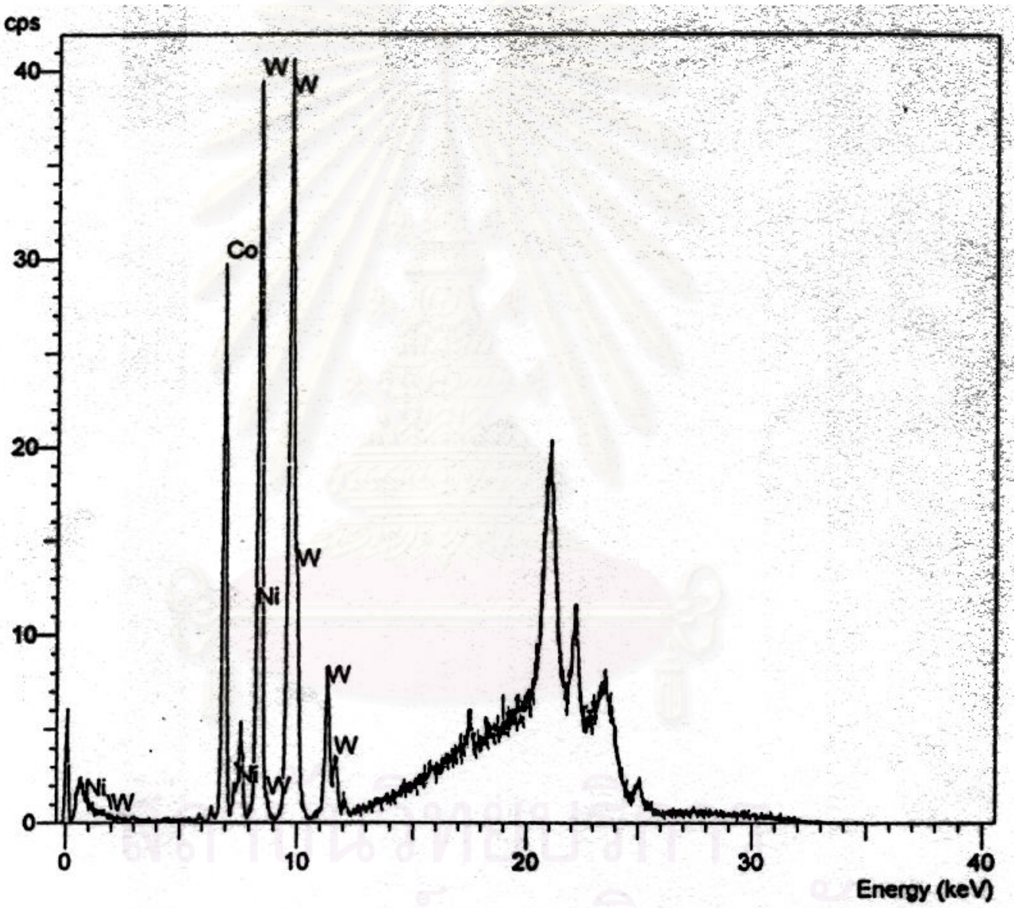

Figure B4 A plot of X-ray fluorescence data of 5%Co-10%W prepared catalyst.

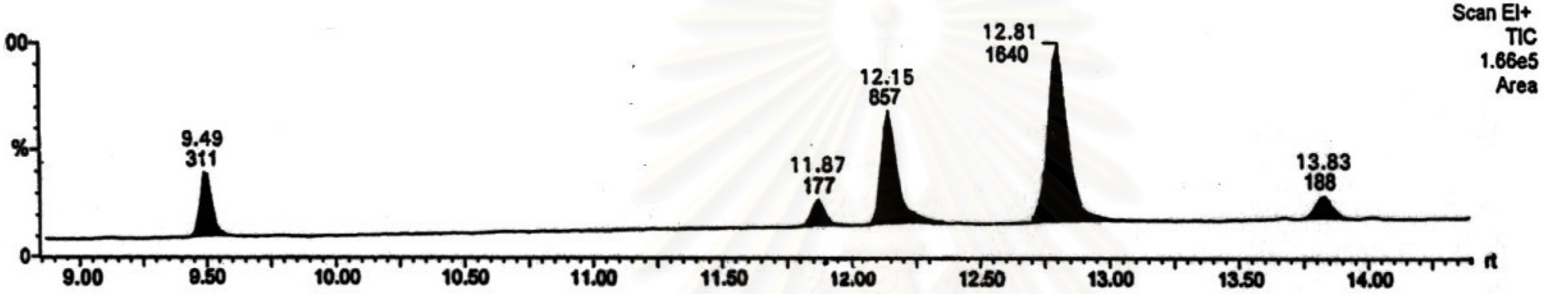

Figure C1 The gas chromatogram of original soybean oil methyl ester.

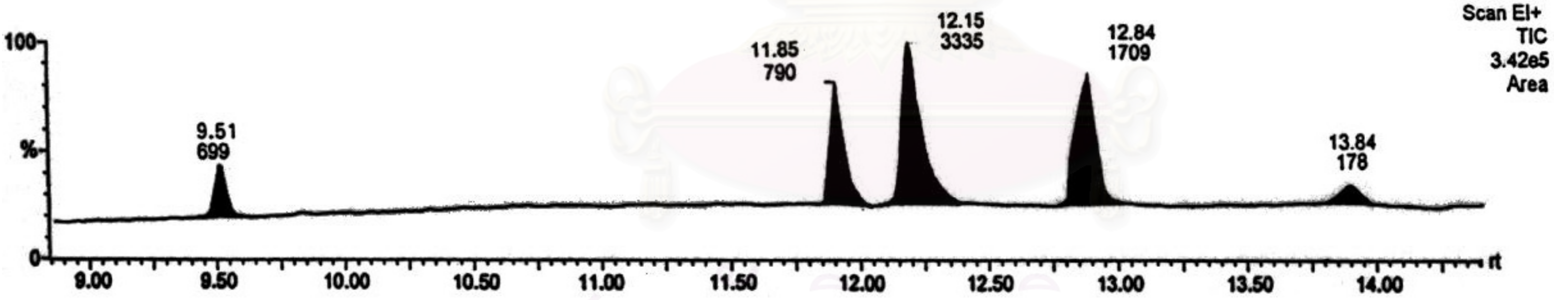

Figure C2 The gas chromatogram of hydrogenated soybean oil methyl ester using NW I catalyst.

At condition: 200 °C, 200 psig, and 180 min.

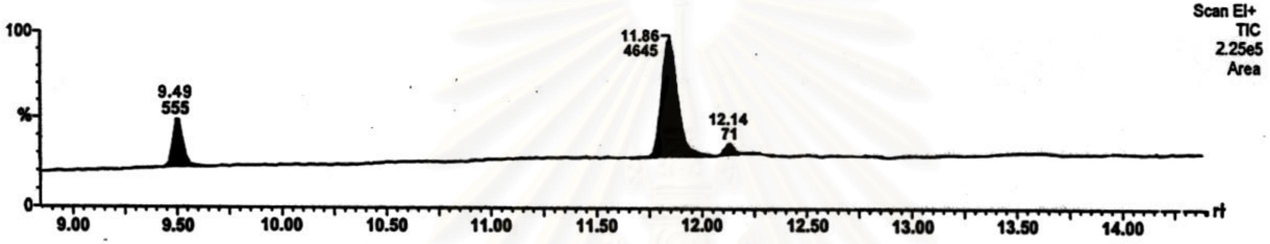

Figure C3 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 200 °C, 200 psig, and 180 min.

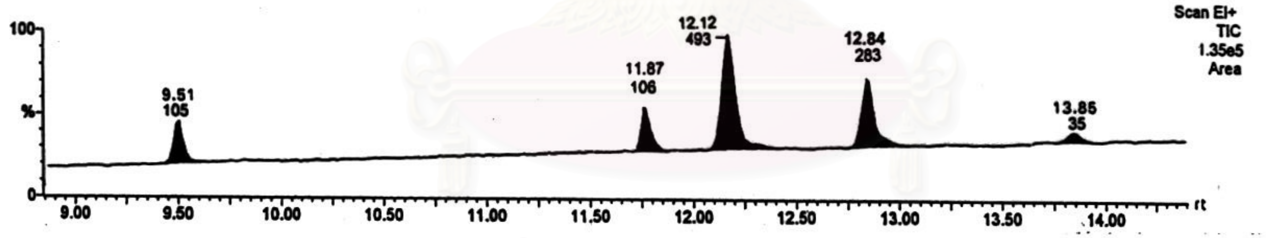

Figure C4 The gas chromatogram of hydrogenated soybean oil methyl ester using CW I catalyst. At condition: 200 °C, 200 psig, and 180 min.

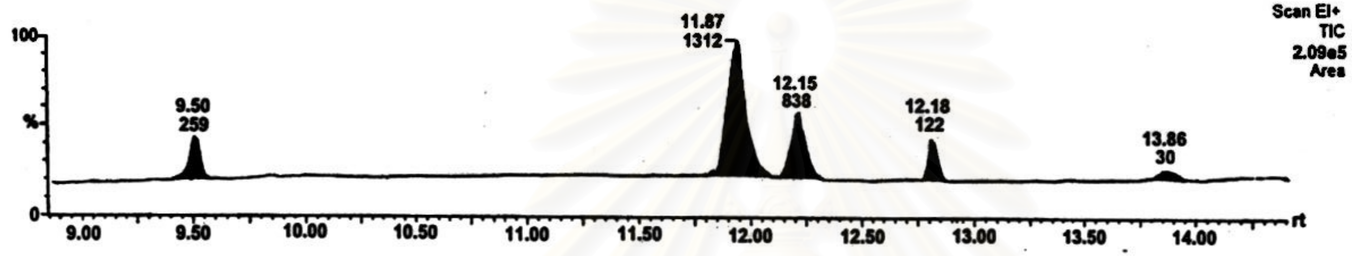

Figure C5 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 200 °C, 200 psig, and 180 min.

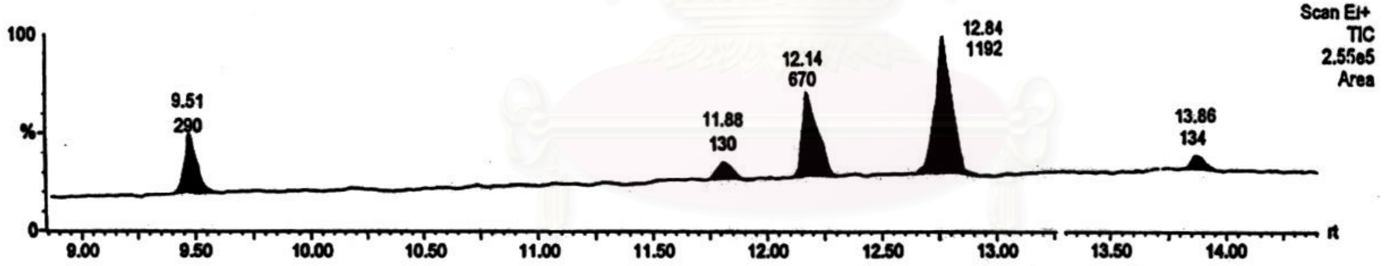

Figure C6 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 100 °C, 150 psig, and 60 min.

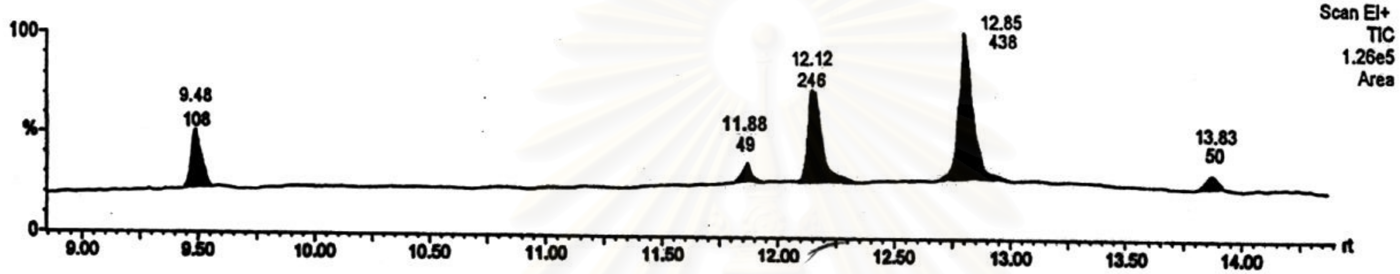

Figure C7 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 120 °C, 150 psig, and 60 min.

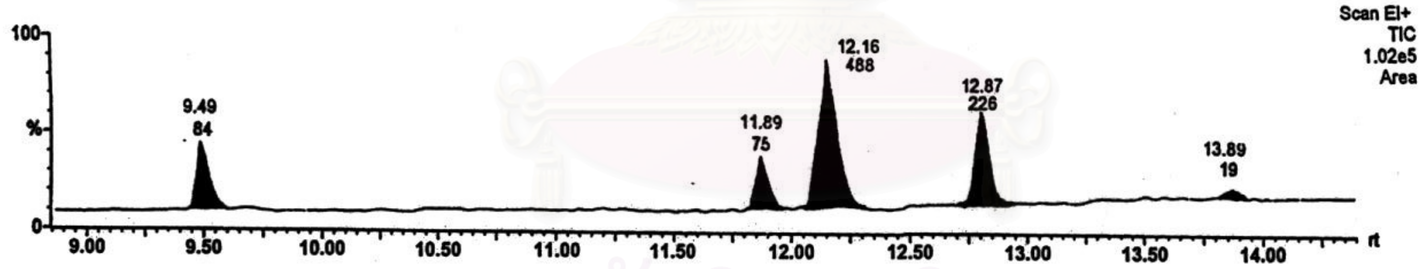

Figure C8 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 60 min.

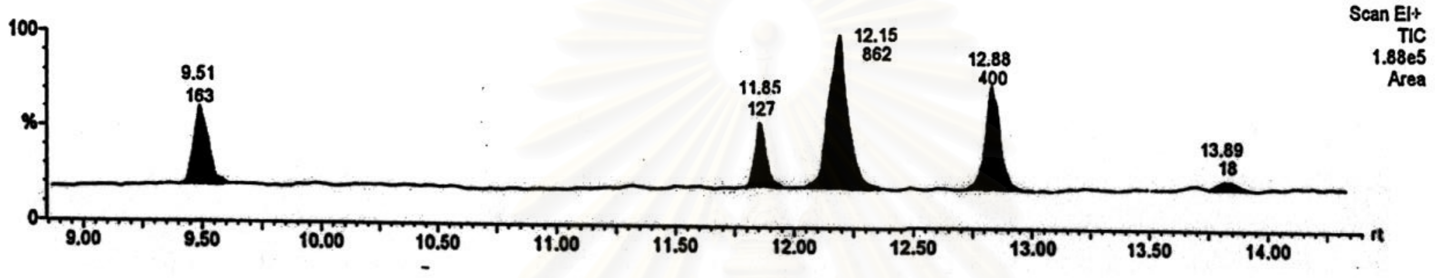

Figure C9 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 200 °C, 150 psig, and 60 min.

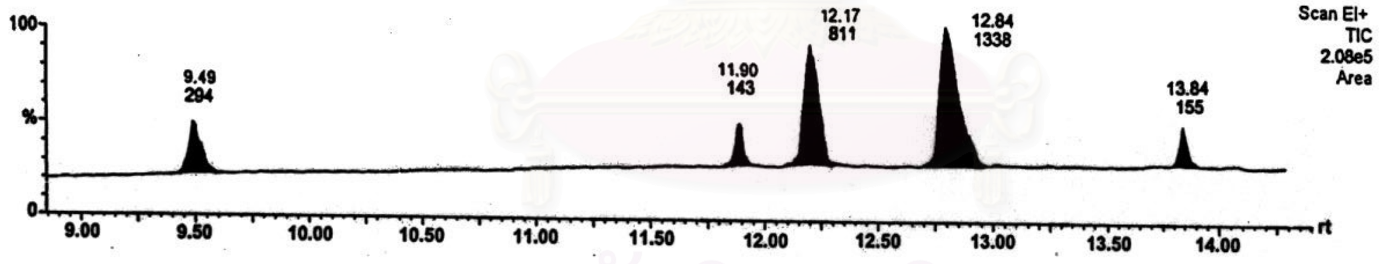

Figure C10 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 100 °C, 150 psig, and 60 min.

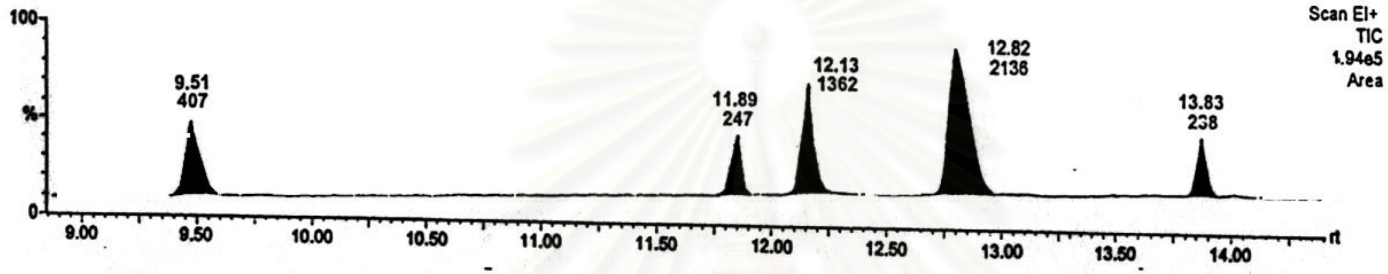

Figure C11 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 120 °C, 150 psig, and 60 min.

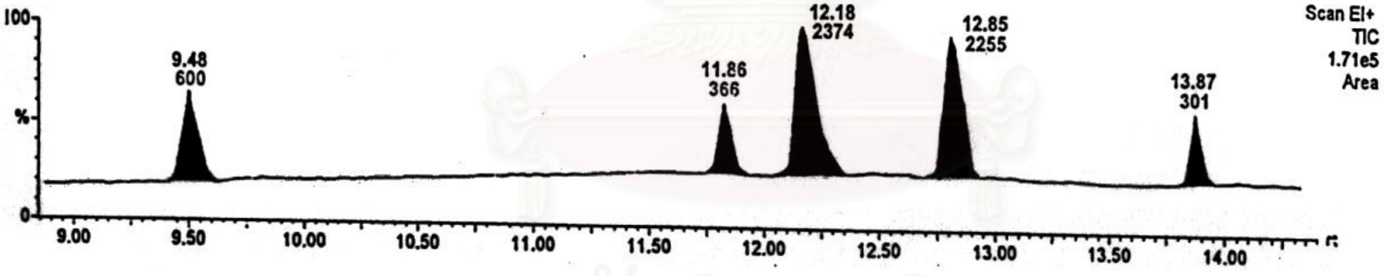

Figure C12 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 150 psig, and 60 min.

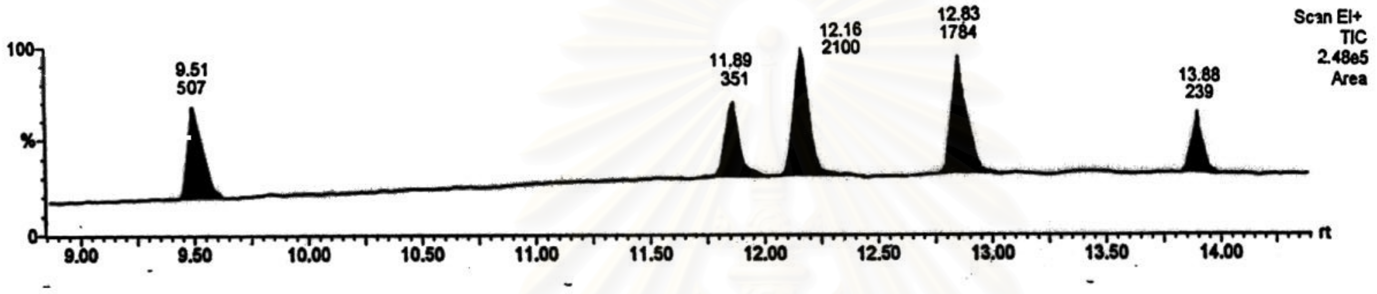

Figure C13 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 200 °C, 150 psig, and 60 min.

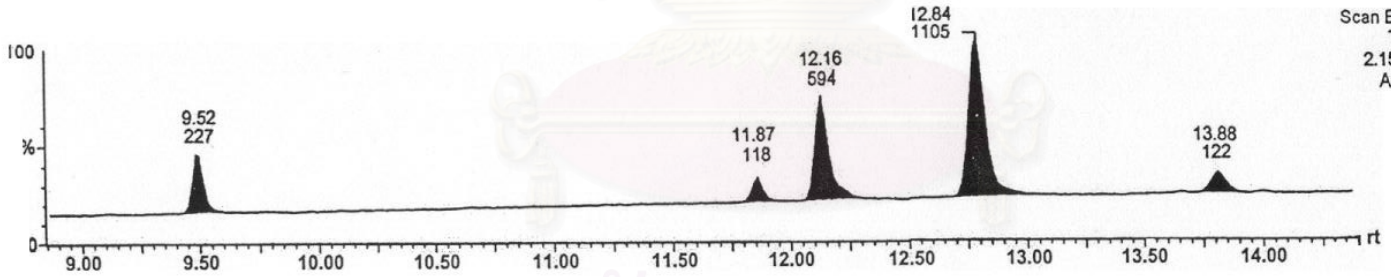

Figure C14 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 100 psig, and 60 min.

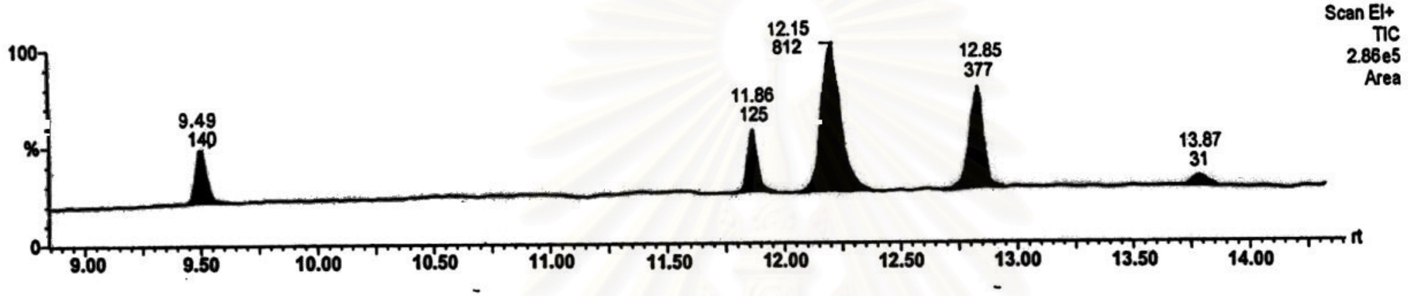

Figure C15 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 60 min.

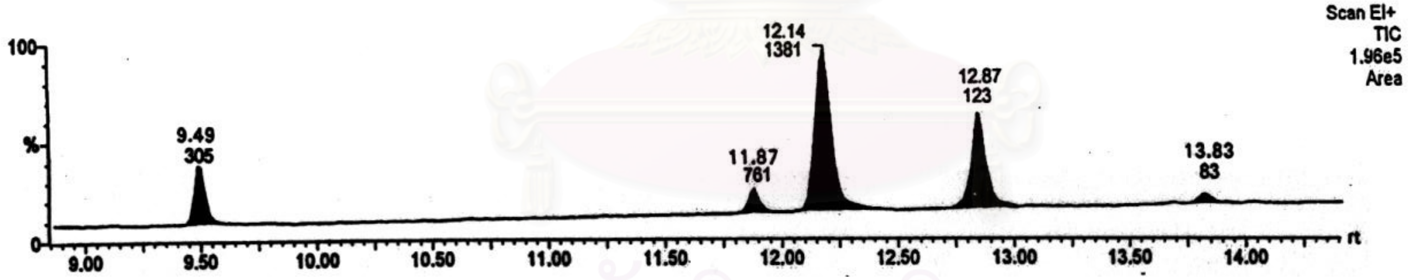

Figure C16 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 200 psig, and 60 min.

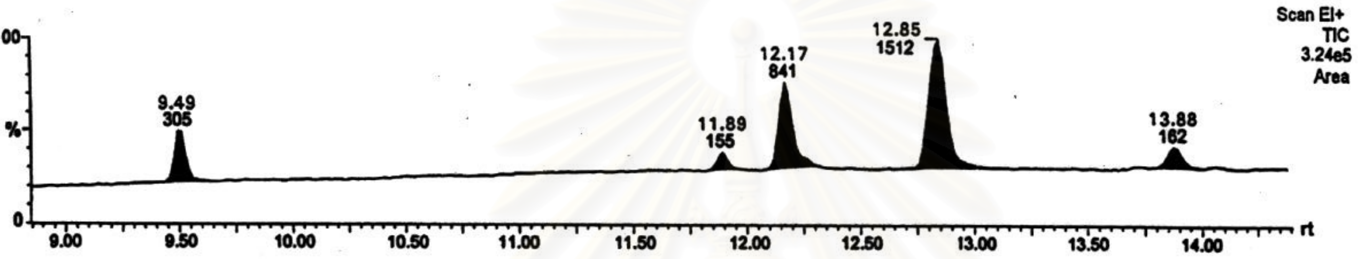

Figure C17 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 100 psig, and 60 min.

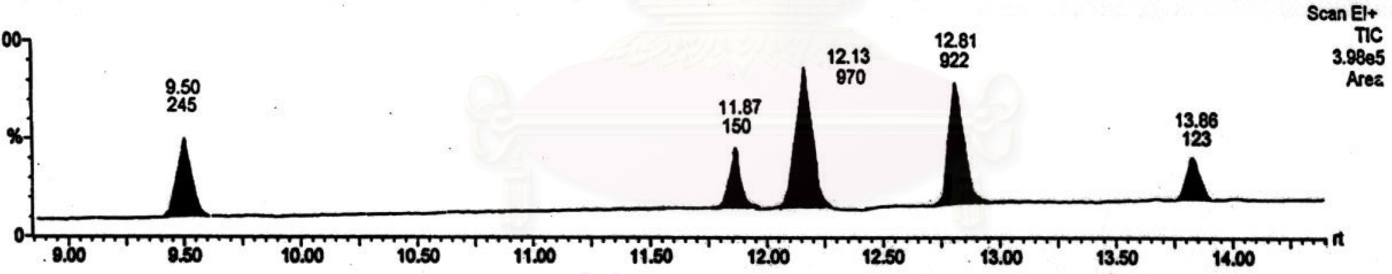

Figure C18 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 150 psig, and 60 min.

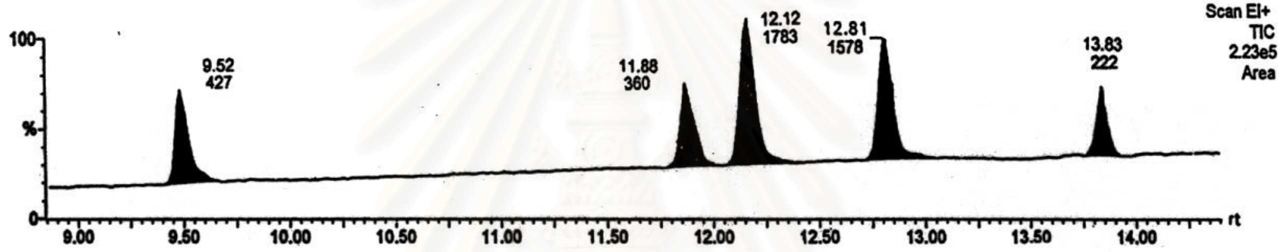

Figure C19 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 200 psig, and 60 min.

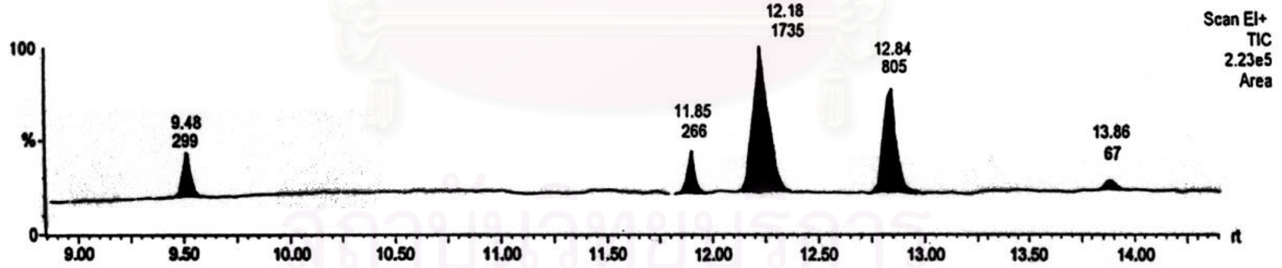

Figure C20 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 60 min.

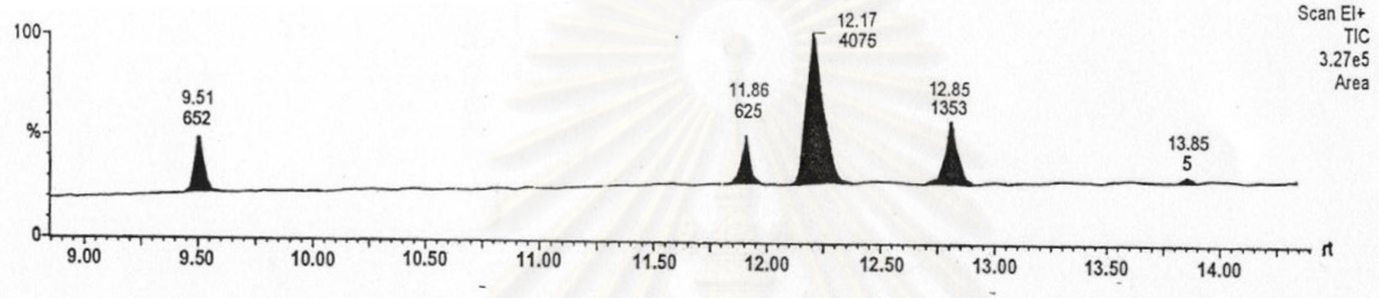

Figure C21 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 100 min.

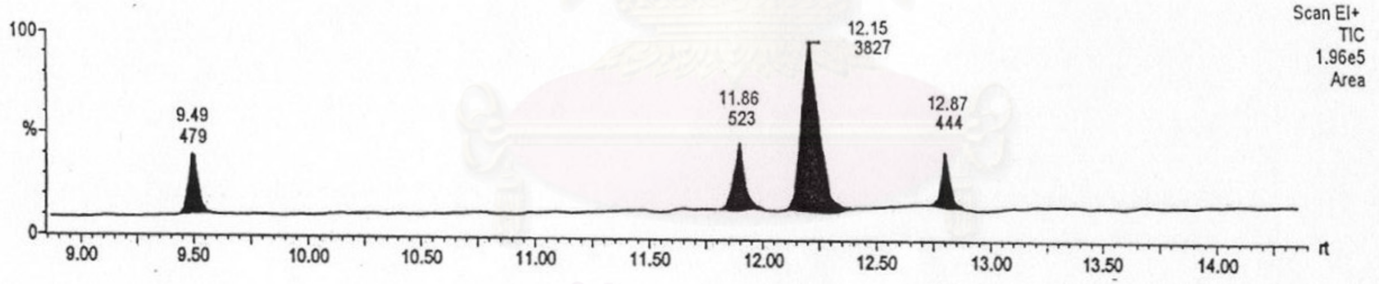

Figure C22 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 120 min.

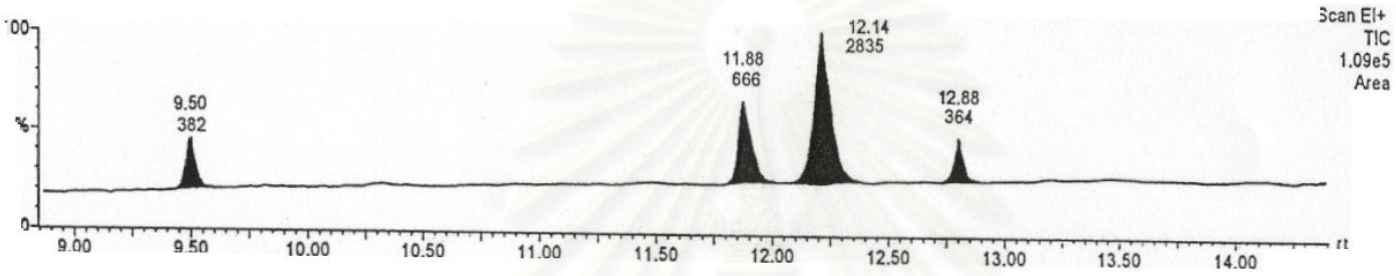

Figure C23 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 140 min.

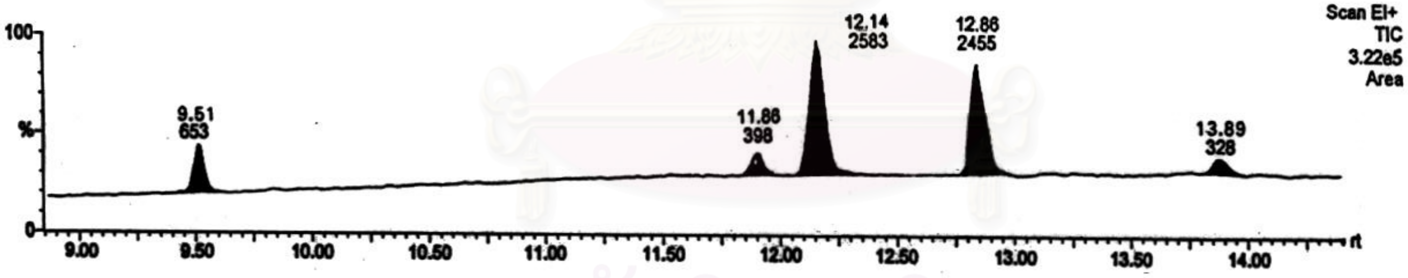

Figure C24 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 150 psig, and 60 min.

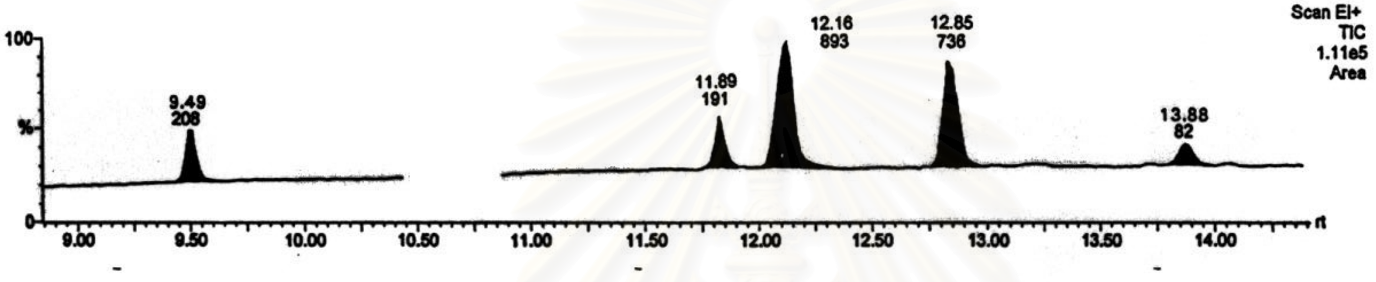

Figure C25 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 150 psig, and 100 min.

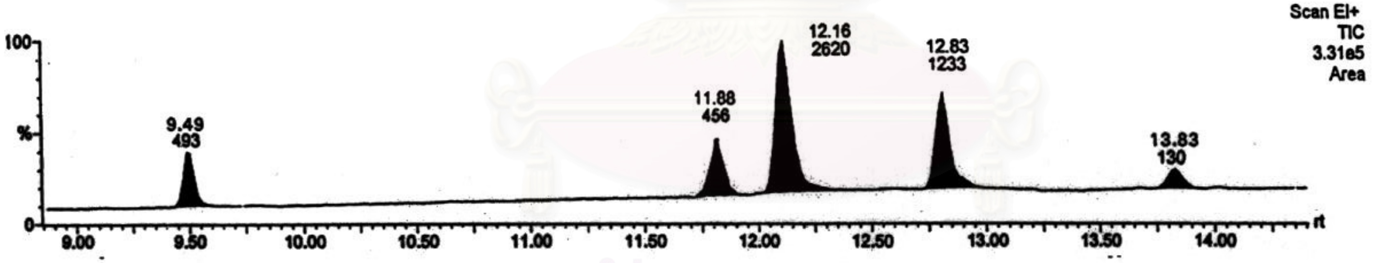

Figure C26 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 100 psig, and 120 min.

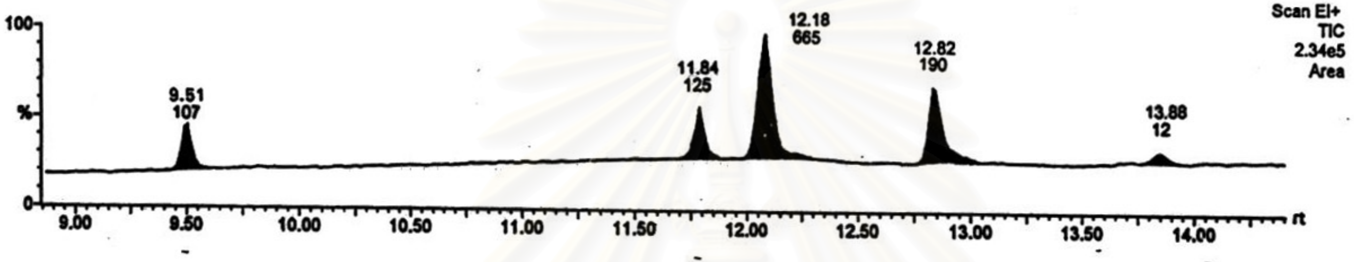

Figure C27 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 150 psig, and 140 min.

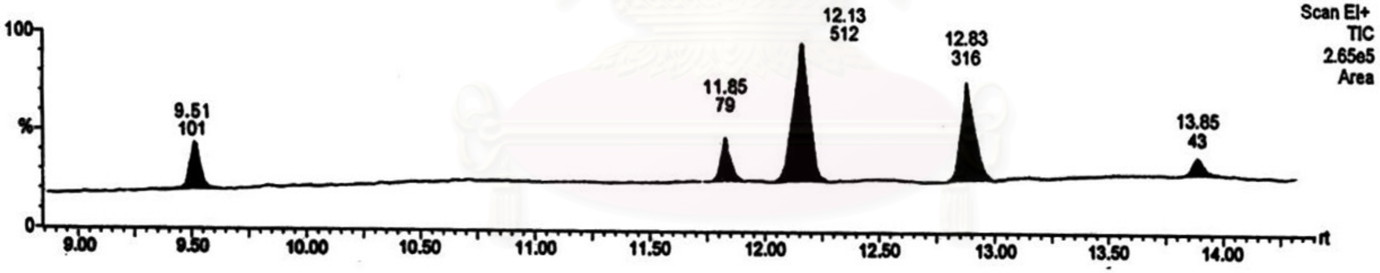

Figure C28 The gas chromatogram of hydrogenated soybean oil methyl ester using NW I catalyst. At condition: 150 °C, 150 psig, and 120 min.

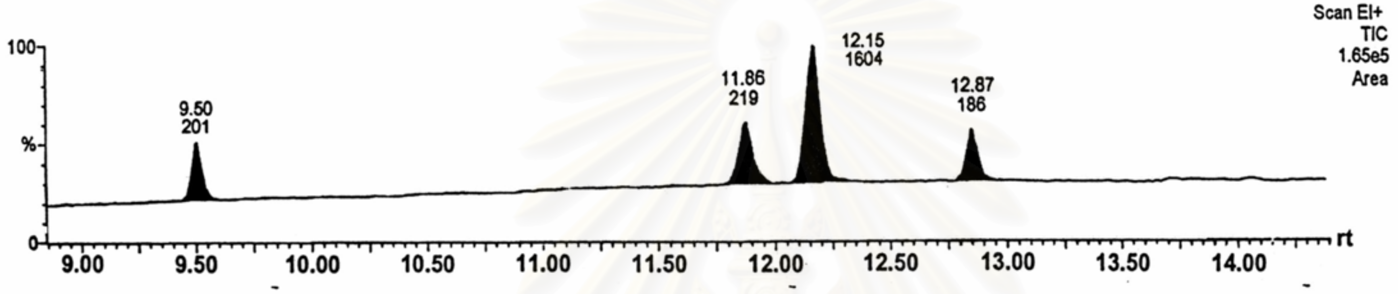

Figure C29 The gas chromatogram of hydrogenated soybean oil methyl ester using NW II catalyst. At condition: 150 °C, 150 psig, and 120 min.

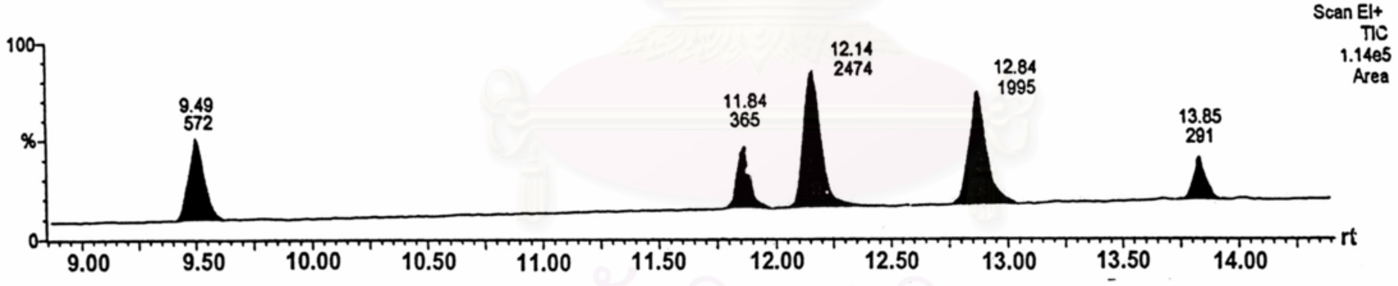

Figure C30 The gas chromatogram of hydrogenated soybean oil methyl ester using CW I catalyst. At condition: 150 °C, 150 psig, and 120 min.

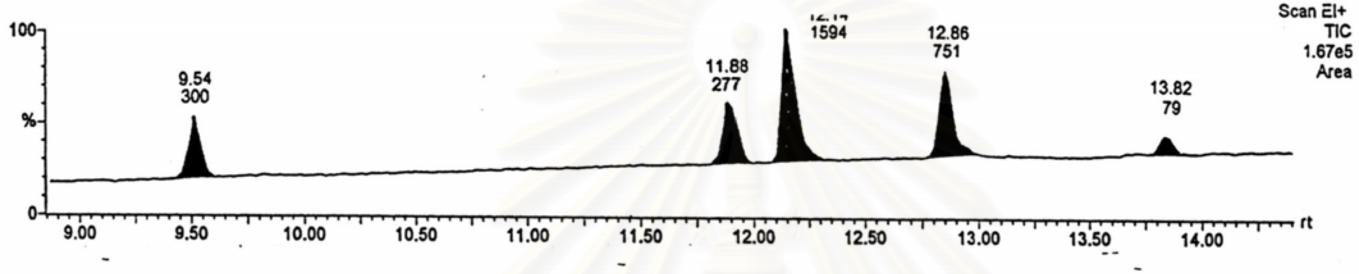

Figure C31 The gas chromatogram of hydrogenated soybean oil methyl ester using CW II catalyst. At condition: 150 °C, 150 psig, and 120 min.

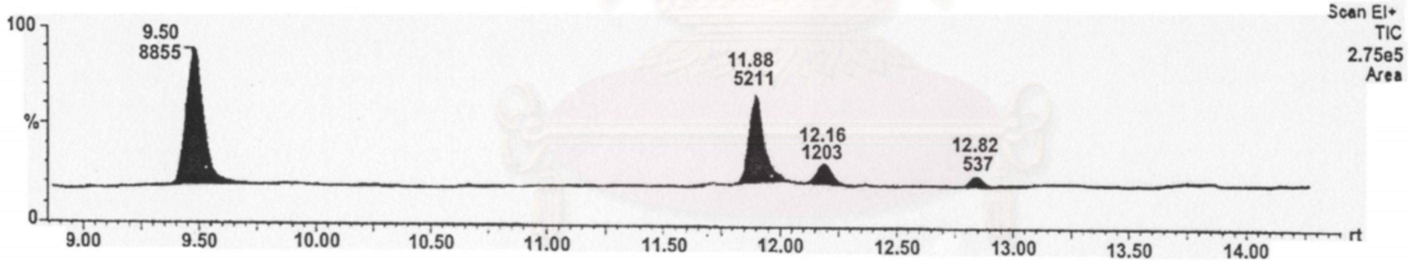

Figure C32 The gas chromatogram of separation between saturated and unsaturated soybean oil methyl ester (part I)

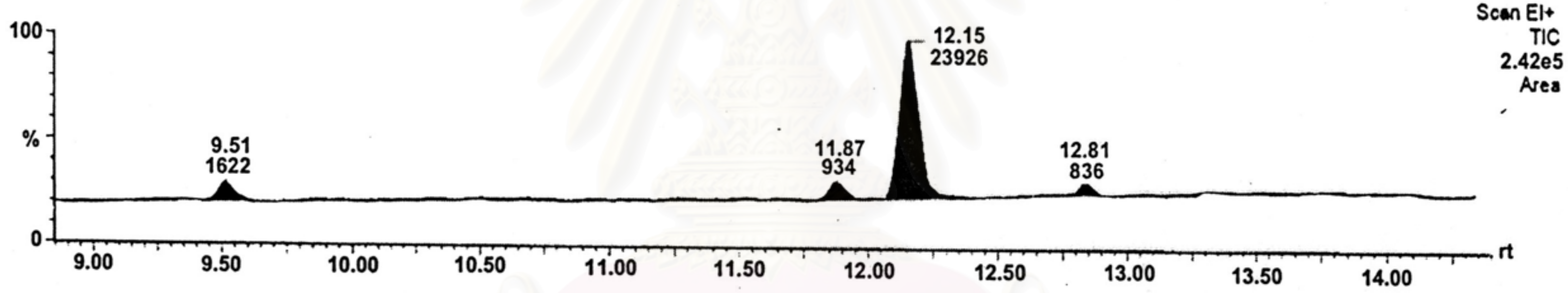

Figure C33 The gas chromatogram of separation between saturated and unsaturated soybean oil methyl ester (part II)

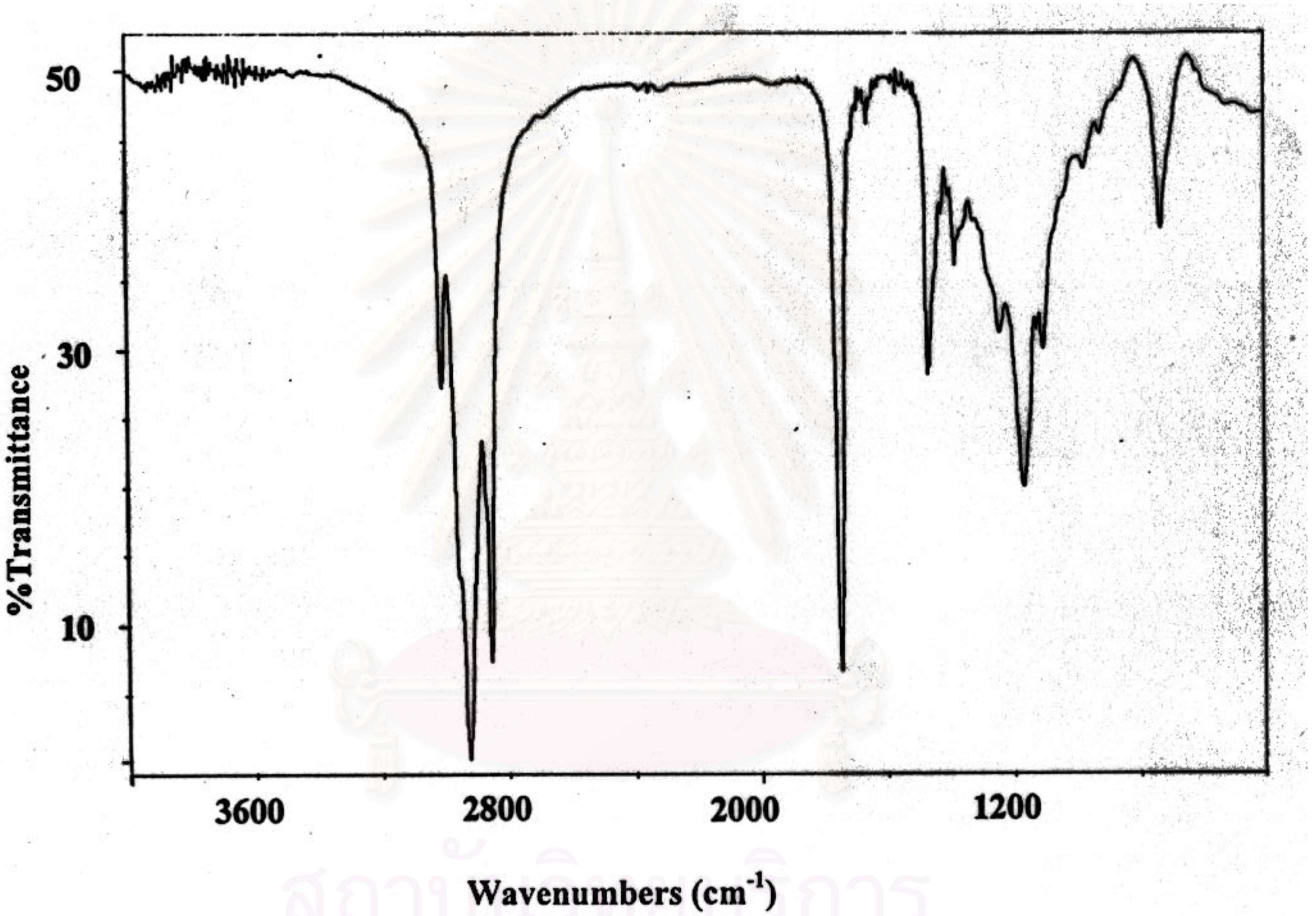

Figure D1 The infrared spectrum of original soybean oil.

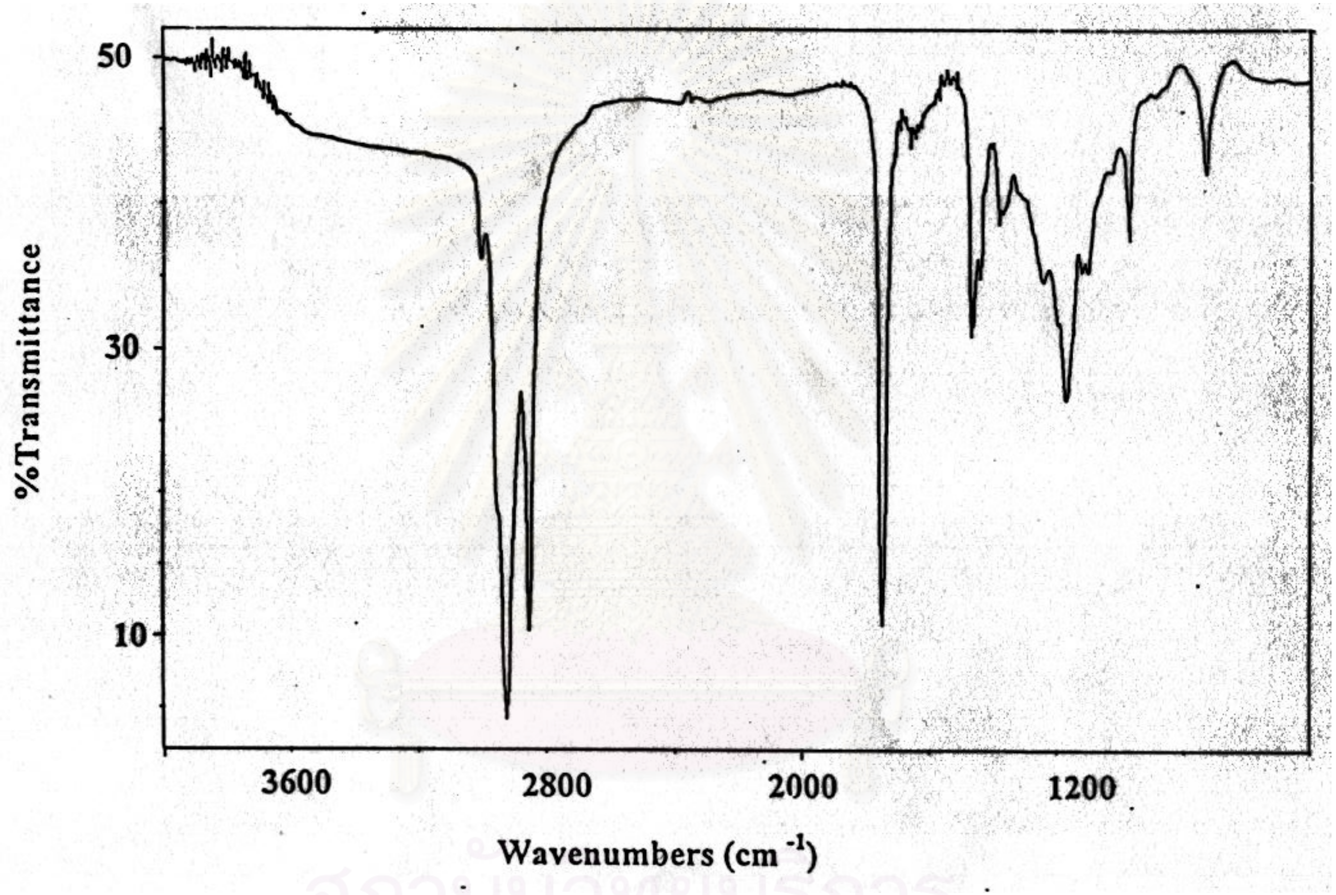

Figure D2 The infrared spectrum of soybean oil methyl ester.

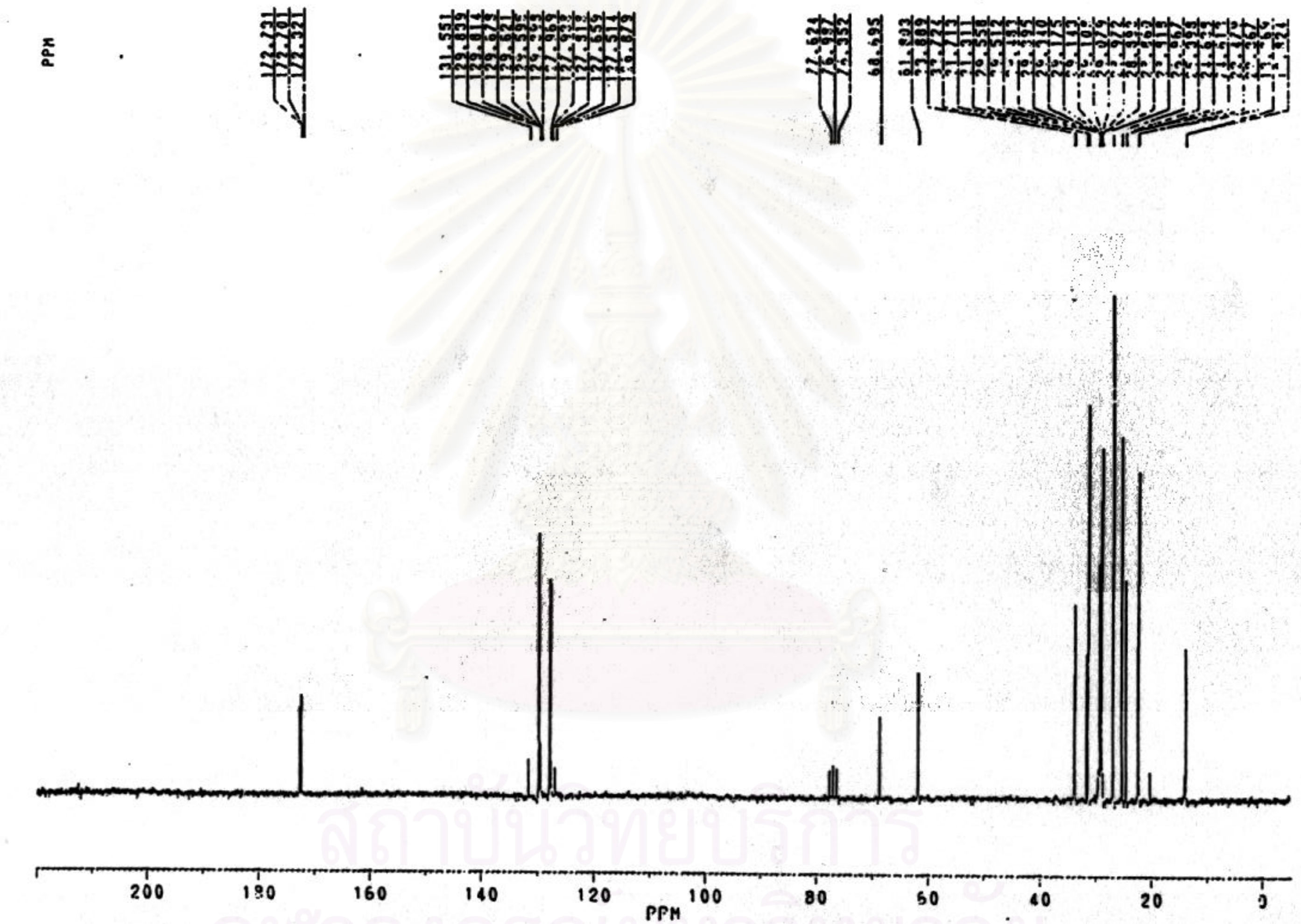

Figure D3 ^{13}C-NMR Spectrum of original soybean oil.

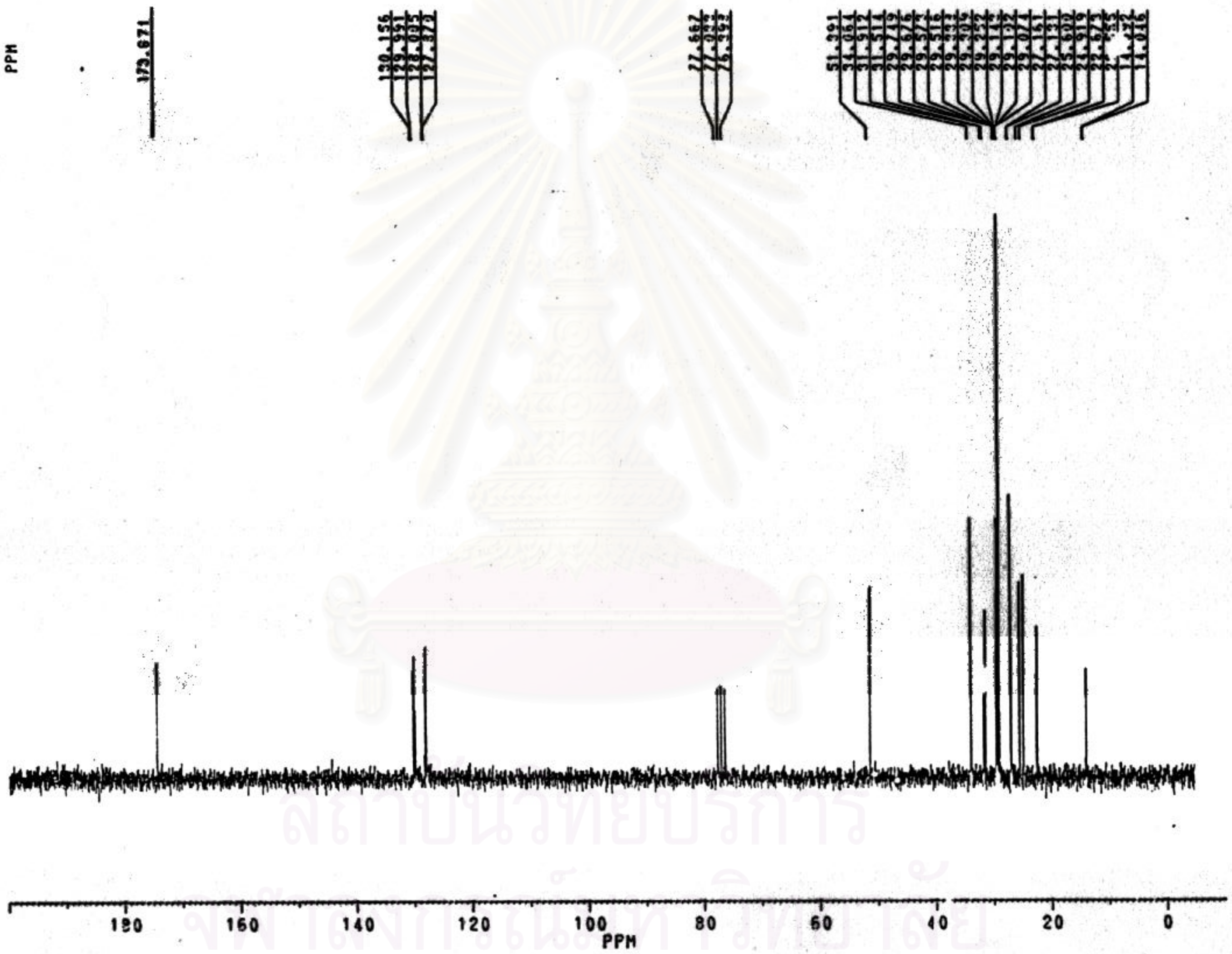

Figure D4 ^{13}C-NMR Spectrum of soybean oil fatty acid methyl ester.

Appendix E

Table E1: Data on the characterization of original soybean oil.

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	131	132	133	132	0.82
% Fatty acid composition					
C16:0 palmitic acid	9.81	10.46	8.67	9.65	0.74
C18:0 stearic acid	5.57	6.55	5.48	5.80	0.39
C18:1 oleic acid	27.00	27.16	27.5	27.22	0.21
C18:2 linoleic acid	51.68	52.08	50.88	51.55	0.50
C18:3 linolenic acid	5.94	3.95	7.47	5.79	1.44

Table E2: Data on the characterization of hydrogenated soybean oil.

(NW I; 200 °C, 200 psig, and 180 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	98	98	98	98	0.00
% Fatty acid composition					
C16:0 palmitic acid	10.41	9.84	10.81	10.26	0.40
C18:0 stearic acid	11.77	11.84	11.31	11.64	0.24
C18:1 oleic acid	49.70	49.61	50.56	49.99	0.43
C18:2 linoleic acid	25.47	25.32	24.32	25.04	0.51
C18:3 linolenic acid	2.65	3.39	3.30	3.11	0.33

Table E3: Data on the characterization of hydrogenated soybean oil.
(NW II; 200 °C, 200 psig, and 180 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	77	76	75	76	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.53	10.51	10.67	10.57	0.07
C18:0 stearic acid	88.12	87.95	86.84	87.64	0.57
C18:1 oleic acid	1.35	1.54	2.49	1.79	0.50
C18:2 linoleic acid	0.00	0.00	0.00	0.00	0.00
C18:3 linolenic acid	0.00	0.00	0.00	0.00	0.00

Table E4: Data on the characterization of hydrogenated soybean oil.
(CW I; 200 °C, 200 psig, and 180 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	101	101	101	101	0.00
% Fatty acid composition					
C16:0 palmitic acid	10.25	10.76	11.09	10.70	0.35
C18:0 stearic acid	10.34	10.15	9.87	10.11	0.19
C18:1 oleic acid	48.23	49.54	48.13	48.63	0.64
C18:2 linoleic acid	27.77	27.51	26.47	27.25	0.56
C18:3 linolenic acid	3.41	2.04	4.44	3.30	0.98

Table E5: Data on the characterization of hydrogenated soybean oil.

(CW II; 200 °C, 200 psig, and 180 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	88	86	87	87	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.11	10.76	9.89	10.24	0.37
C18:0 stearic acid	11.15	11.07	10.88	11.03	0.12
C18:1 oleic acid	51.23	49.72	50.65	50.53	0.62
C18:2 linoleic acid	26.34	26.54	27.12	26.67	0.33
C18:3 linolenic acid	1.17	1.91	1.46	1.51	0.31

Table E6: Data on the characterization of hydrogenated soybean oil.

(NW II; 100 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	125	124	120	123	2.16
% Fatty acid composition					
C16:0 palmitic acid	12.10	13.25	11.99	12.45	0.57
C18:0 stearic acid	5.41	5.94	5.95	5.77	0.25
C18:1 oleic acid	27.73	26.88	21.50	27.37	2.76
C18:2 linoleic acid	49.30	48.13	47.77	48.40	0.65
C18:3 linolenic acid	5.55	5.80	6.79	6.04	0.54

Table E7: Data on the characterization of hydrogenated soybean oil.

(NW II; 120 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	122	119	119	120	1.41
% Fatty acid composition					
C16:0 palmitic acid	10.68	13.48	12.11	12.09	1.14
C18:0 stearic acid	5.81	5.55	5.47	5.61	0.14
C18:1 oleic acid	29.20	27.12	27.65	27.99	0.88
C18:2 linoleic acid	49.01	48.51	49.21	48.91	0.29
C18:3 linolenic acid	5.20	5.34	5.56	5.40	0.15

Table E8: Data on the characterization of hydrogenated soybean oil.

(NW II; 150 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	97	97	97	97	0.00
% Fatty acid composition					
C16:0 palmitic acid	9.43	10.48	7.13	9.01	1.40
C18:0 stearic acid	8.41	7.51	8.86	8.26	0.56
C18:1 oleic acid	54.69	55.76	54.02	54.82	0.72
C18:2 linoleic acid	25.36	25.54	26.45	25.78	0.48
C18:3 linolenic acid	2.11	0.71	3.54	2.12	1.55

Table E9: Data on the characterization of hydrogenated soybean oil.

(NW II; 200 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	100	99	98	99	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.39	11.11	11.20	11.20	0.36
C18:0 stearic acid	8.11	8.50	7.69	7.69	0.33
C18:1 oleic acid	54.85	53.99	53.64	53.64	0.51
C18:2 linoleic acid	25.49	26.16	25.15	25.15	0.42
C18:3 linolenic acid	1.16	0.24	2.32	2.32	0.85

Table E10: Data on the characterization of hydrogenated soybean oil.

(CW II; 100 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	125	125	125	125	0.00
% Fatty acid composition					
C16:0 palmitic acid	10.73	10.99	9.81	10.51	0.51
C18:0 stearic acid	5.22	4.84	5.12	5.06	0.16
C18:1 oleic acid	29.58	30.00	29.09	29.56	0.37
C18:2 linoleic acid	48.80	47.87	48.88	48.52	0.46
C18:3 linolenic acid	5.67	6.30	7.10	6.36	0.58

Table E11: Data on the characterization of hydrogenated soybean oil.
(CW II; 120 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	126	125	124	125	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.87	9.26	9.16	9.76	0.79
C18:0 stearic acid	8.47	5.63	5.98	5.69	0.21
C18:1 oleic acid	32.07	31.03	32.31	31.80	0.55
C18:2 linoleic acid	47.59	48.66	43.87	46.71	2.06
C18:3 linolenic acid	4.00	5.42	8.68	6.03	1.96

Table E12: Data on the characterization of hydrogenated soybean oil.
(CW II; 150 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	109	109	112	110	1.41
% Fatty acid composition					
C16:0 palmitic acid	10.17	9.65	10.72	10.18	0.44
C18:0 stearic acid	6.48	7.22	4.93	6.21	0.95
C18:1 oleic acid	41.02	41.09	38.67	40.26	1.13
C18:2 linoleic acid	37.76	37.50	39.49	38.25	0.88
C18:3 linolenic acid	4.60	4.54	6.19	5.11	0.76

Table E13: Data on the characterization of hydrogenated soybean oil.

(CW II; 200 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	108	108	108	108	0.00
% Fatty acid composition					
C16:0 palmitic acid	10.18	10.56	10.21	10.32	0.17
C18:0 stearic acid	7.04	7.43	8.64	7.70	0.68
C18:1 oleic acid	52.99	51.77	51.98	52.25	0.53
C18:2 linoleic acid	25.48	26.45	26.77	26.23	0.55
C18:3 linolenic acid	4.31	3.79	2.40	3.50	0.81

Table E14: Data on the characterization of hydrogenated soybean oil.

(NW II; 150 °C, 100 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	119	120	121	120	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.49	11.00	10.61	10.70	0.22
C18:0 stearic acid	5.46	5.14	4.98	5.19	0.20
C18:1 oleic acid	27.43	27.12	26.95	27.17	0.20
C18:2 linoleic acid	50.97	51.18	50.99	51.05	0.09
C18:3 linolenic acid	5.65	5.56	6.47	5.89	0.41

Table E15: Data on the characterization of hydrogenated soybean oil.
(NW II; 150 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	97	97	97	97	0.00
% Fatty acid composition					
C16:0 palmitic acid	9.43	10.48	7.13	9.01	1.40
C18:0 stearic acid	8.41	7.51	8.86	8.26	0.56
C18:1 oleic acid	54.69	55.76	54.02	54.82	0.72
C18:2 linoleic acid	25.36	25.54	26.45	25.78	0.48
C18:3 linolenic acid	2.11	0.71	3.54	2.12	1.55

Table E16: Data on the characterization of hydrogenated soybean oil.
(NW II; 150 °C, 200 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	91	92	93	92	0.82
% Fatty acid composition					
C16:0 palmitic acid	11.48	9.50	9.79	10.26	0.87
C18:0 stearic acid	12.15	13.34	9.99	11.83	1.39
C18:1 oleic acid	51.16	50.68	50.00	50.61	0.47
C18:2 linoleic acid	22.07	24.42	27.46	24.65	2.21
C18:3 linolenic acid	3.14	2.06	2.76	2.65	0.44

Table E17: Data on the characterization of hydrogenated soybean oil.
(CW II; 150 °C, 100 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	130	128	129	129	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.25	11.01	10.00	10.42	0.43
C18:0 stearic acid	5.20	5.65	4.78	5.21	0.35
C18:1 oleic acid	28.26	29.01	26.88	28.05	0.88
C18:2 linoleic acid	50.84	49.77	52.39	51.00	1.07
C18:3 linolenic acid	5.45	4.56	5.95	5.32	0.58

Table E18: Data on the characterization of hydrogenated soybean oil.
(CW II; 150 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	109	109	112	110	1.41
% Fatty acid composition					
C16:0 palmitic acid	10.17	9.65	10.72	10.18	0.44
C18:0 stearic acid	6.48	7.22	4.93	6.21	0.95
C18:1 oleic acid	41.02	41.09	38.67	40.26	1.13
C18:2 linoleic acid	37.76	37.50	39.49	38.25	0.88
C18:3 linolenic acid	4.60	4.54	6.19	5.11	0.76

Table E19: Data on the characterization of hydrogenated soybean oil.
(CW II; 150 °C, 200 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	107	107	107	107	0.00
% Fatty acid composition					
C16:0 palmitic acid	7.53	9.18	12.63	9.78	2.12
C18:0 stearic acid	7.99	9.16	7.44	8.19	0.72
C18:1 oleic acid	40.56	41.20	40.70	40.82	0.28
C18:2 linoleic acid	37.83	35.50	35.01	36.12	1.23
C18:3 linolenic acid	6.09	4.96	4.22	5.09	0.77

Table E20: Data on the characterization of hydrogenated soybean oil.
(NW II; 150 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	97	97	97	97	0.00
% Fatty acid composition					
C16:0 palmitic acid	9.43	10.48	7.13	9.01	1.40
C18:0 stearic acid	8.41	7.51	8.86	8.26	0.56
C18:1 oleic acid	54.69	55.76	54.02	54.82	0.72
C18:2 linoleic acid	25.36	25.54	26.45	25.78	0.48
C18:3 linolenic acid	2.11	0.71	3.54	2.12	1.55

Table E21: Data on the characterization of hydrogenated soybean oil.

(NW II; 150 °C, 150 psig, and 100 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	94	95	96	95	0.00
% Fatty acid composition					
C16:0 palmitic acid	10.03	9.94	9.16	9.71	0.39
C18:0 stearic acid	8095	9.32	9.66	9.31	0.29
C18:1 oleic acid	61.73	60.58	59.88	60.73	0.76
C18:2 linoleic acid	19.19	20.09	21.23	20.17	0.84
C18:3 linolenic acid	0.10	0.07	0.07	0.08	0.01

Table E22: Data on the characterization of hydrogenated soybean oil.

(NW II; 150 °C, 150 psig, and 120 min)

Properties	Sample Number			Average	SD.
	I	II	III		
Iodine Value (I.V.)	90	90	90	90	0.00
% Fatty acid composition					
C16:0 palmitic acid	9.81	9.87	7.59	9.09	1.06
C18:0 stearic acid	9.88	10.12	9.73	9.91	0.16
C18:1 oleic acid	71.66	72.09	73.99	72.58	1.01
C18:2 linoleic acid	8.65	7.92	8.69	8.42	0.35
C18:3 linolenic acid	0.00	0.00	0.00	0.00	0.00

Table E23: Data on the characterization of hydrogenated soybean oil.
(NW II; 150 °C, 150 psig, and 140 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	86	87	88	87	0.82
% Fatty acid composition					
C16:0 palmitic acid	10.52	9.43	7.05	9.00	1.45
C18:0 stearic acid	14.11	15.12	17.78	15.67	1.55
C18:1 oleic acid	67.12	66.04	67.12	66.76	0.51
C18:2 linoleic acid	8.25	9.41	8.05	8.57	0.60
C18:3 linolenic acid	0.00	0.00	0.00	0.00	0.00

Table E24: Data on the characterization of hydrogenated soybean oil.
(CW II; 150 °C, 150 psig, and 60 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	109	109	112	110	1.41
% Fatty acid composition					
C16:0 palmitic acid	10.17	9.65	10.72	10.18	0.44
C18:0 stearic acid	6.48	7.22	4.93	6.21	0.95
C18:1 oleic acid	41.02	41.09	38.67	40.26	1.13
C18:2 linoleic acid	37.76	37.50	39.49	38.25	0.88
C18:3 linolenic acid	4.60	4.54	6.19	5.11	0.76

Table E25: Data on the characterization of hydrogenated soybean oil.

(CW II; 150 °C, 150 psig, and 100 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	100	100	100	100	0.00
% Fatty acid composition					
C16:0 palmitic acid	11.08	10.35	8.10	9.84	1.27
C18:0 stearic acid	9.67	10.06	7.45	9.06	1.15
C18:1 oleic acid	42.53	41.83	42.60	42.32	0.35
C18:2 linoleic acid	32.60	34.4	37.69	34.90	2.11
C18:3 linolenic acid	4.12	3.36	4.16	3.88	0.37

Table E26: Data on the characterization of hydrogenated soybean oil.

(CW II; 150 °C, 150 psig, and 120 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	98	97	99	98	0.82
% Fatty acid composition					
C16:0 palmitic acid	8.5	9.19	12.28	9.99	1.65
C18:0 stearic acid	9.11	10.01	8.60	9.24	0.58
C18:1 oleic acid	52.65	52.12	54.59	53.12	1.06
C18:2 linoleic acid	26.79	26.16	22.08	25.01	2.09
C18:3 linolenic acid	2.95	2.52	2.45	2.64	0.22

Table E27: Data on the characterization of hydrogenated soybean oil.

(CW II; 150 °C, 150 psig, and 140 min)

Properties	Sample Number			Average	SD
	I	II	III		
Iodine Value (I.V.)	90	90	90	90	0.00
% Fatty acid composition					
C16:0 palmitic acid	9.53	10.72	8.88	9.71	0.76
C18:0 stearic acid	10.98	11.21	11.80	11.33	0.35
C18:1 oleic acid	60.21	60.96	60.45	60.54	0.31
C18:2 linoleic acid	18.21	17.03	16.75	17.33	0.64
C18:3 linolenic acid	1.07	0.08	2.12	1.09	0.83

Table E28: Data on the characterization of hydrogenated soybean oil.

(NW I; 150 °C, 150 psig, and 120 min)

Properties	Sample Number			Average	SD.
	I	II	III		
Iodine Value (I.V.)	120	121	122	121	0.82
% Fatty acid composition					
C16:0 palmitic acid	7.61	9.98	11.33	9.64	1.54
C18:0 stearic acid	8.05	7.12	7.27	7.48	0.41
C18:1 oleic acid	48.12	48.88	49.31	48.77	0.49
C18:2 linoleic acid	31.11	30.07	29.00	30.06	0.86
C18:3 linolenic acid	5.11	3.95	3.09	4.05	0.83

Table E29: Data on the characterization of hydrogenated soybean oil.
(NW II; 150 °C, 150 psig, and 120 min)

Properties	Sample Number			Average	SD.
	I	II	III		
Iodine Value (I.V.)	90	90	90	90	0.00
% Fatty acid composition					
C16:0 palmitic acid	9.81	9.87	7.59	9.09	1.06
C18:0 stearic acid	9.88	10.12	9.73	9.91	0.16
C18:1 oleic acid	71.66	72.09	73.99	72.58	1.01
C18:2 linoleic acid	8.65	7.92	8.69	8.42	0.35
C18:3 linolenic acid	0.00	0.00	0.00	0.00	0.00

Table E30: Data on the characterization of hydrogenated soybean oil.
(CW I; 150 °C, 150 psig, and 120 min)

Properties	Sample Number			Average	SD.
	I	II	III		
Iodine Value (I.V.)	123	122	124	123	0.82
% Fatty acid composition					
C16:0 palmitic acid	9.41	9.30	10.03	9.58	0.32
C18:0 stearic acid	6.67	6.21	5.45	6.11	0.50
C18:1 oleic acid	46.12	45.95	45.99	46.02	0.08
C18:2 linoleic acid	32.95	33.45	33.83	33.41	0.36
C18:3 linolenic acid	4.35	5.09	4.70	4.88	0.30

Table E31: Data on the characterization of hydrogenated soybean oil.

(CW II; 150 °C, 150 psig, and 120 min)

Properties	**Sample Number**			**Average**	**SD.**
	I	**II**	**III**		
Iodine Value (I.V.)	98	97	99	98	0.82
% Fatty acid composition					
C16:0 palmitic acid	8.5	9.19	12.28	9.99	1.65
C18:0 stearic acid	9.11	10.01	8.60	9.24	0.58
C18:1 oleic acid	52.65	52.12	54.59	53.12	1.06
C18:2 linoleic acid	26.79	26.16	22.08	25.01	2.09
C18:3 linolenic acid	2.95	2.52	2.45	2.64	0.22

Table E32: Data on the characterization of saturated fraction.

Acid component	**Sample Number**			**Average**	**SD**
	I	**II**	**III**		
Saturated					
C16:0 palmitic acid	55.98	56.45	55.63	56.02	0.33
C18:0 stearic acid	33.12	32.43	33.36	32.97	0.39
Unsaturated					
C18:1 oleic acid	7.59	8.02	7.22	7.61	0.33
C18:2 linoleic acid	3.31	3.10	3.79	3.40	0.29
C18:3 linolenic acid	0.00	0.00	0.00	0.00	0.00

Table E33: Data on the characterization of unsaturated fraction.

Acid component	Sample Number			Average	SD
	I	II	III		
Saturated					
C16:0 palmitic acid	6.12	5.12	6.58	5.94	0.61
C18:0 stearic acid	2.76	4.59	2.91	3.42	0.83
Unsaturated					
C18:1 oleic acid	88.32	86.52	87.90	87.58	0.77
C18:2 linoleic acid	2.80	3.77	2.61	3.06	0.51
C18:3 linolenic acid	0.00	0.00	0.00	0.00	0.00

VITA

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