การเตรียมลิกโนซัลโฟเนตจากลิกนินในน้ำดำของกระบวนการผลิตเยื่อกระดาษแบบคราฟต์จากไม้ยูคาลิปตัส

นายศุภเจตน์ ผ่องใส

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2547

ISBN 974-17-6770-6

PREPARATION OF LIGNOSULFONATE FROM LIGNIN IN BLACK LIQUOR FROM EUCALYPTUS KRAFT PULPING

Mr. Supachet Pongsai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic year 2004

ISBN 974-17-6770-6

Thesis Title	Preparation of lignosulfonate from lignin in black liquor from eucalyptus kraft pulping
By	Mr. Supachet Pongsai
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Professor Sophon Reongsumran, Ph.D.

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

.... Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

Thesis Committee

.... Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

.... Thesis Advisor
(Professor Sophon Roengsumran, Ph.D.)

.... Member
(Associate Professor Amorn Petsom, Ph.D.)

.... Member
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

.... Member
(Assistant Professor Thumnoon Nhujak, Ph.D.)

ศุภเจตน์ ผ่องใส: การเตรียมลิกโนซัลโฟเนตจากลิกนินในน้ำดำของกระบวนการผลิตเยื่อกระดาษแบบคราฟต์จากไม้ยูคาลิปตัส (PREPARATION OF LIGNOSULFONATE FROM LIGNIN IN BLACK LIQUOR FROM EUCALYPTUS KRAFT PULPING) อ. ที่ปรึกษา: ศาสตราจารย์ ดร.โสภณ เริงสำราญ, 96 หน้า, ISBN 974-17-6770-6

การแยกลิกนินออกจากน้ำดำของกระบวนการผลิตเยื่อกระดาษแบบคราฟต์จากไม้ยูคาลิปตัส ใช้ภาวะที่เหมาะสมในการแยกคือตกตะกอนด้วยกรดที่ pH 3 และล้างด้วยน้ำร้อน โดยลิกนินที่แยกได้นี้ถูกนำมาทำปฏิกิริยาแบบซัลโฟเนชัน และซัลโฟเมทิลเลชันเพื่อใช้ในการเตรียม ลิกโนซัลโฟเนต ภาวะที่เหมาะสมสำหรับใช้ในการเตรียมลิกโนซัลโฟเนตจากลิกนินที่แยกได้คือ ภาวะการเกิดปฏิกิริยาแบบซัลโฟเมทิลเลชันที่อุณหภูมิ 130 องศาเซลเซียส โดยใช้อัตราส่วนของโซเดียมซัลไฟต์ต่อฟอร์มาลดีไฮด์ต่อลิกนินเป็น 0.5 ต่อ 0.119 ต่อ 1 โดยน้ำหนัก เป็นเวลา 2 ชั่วโมง เนื่องจากที่ภาวะดังกล่าวสามารถได้รับปริมาณของลิกโนซัลโฟเนตในจำนวนที่สูงสุด คือ 12.66 กรัมต่อ 10 กรัมลิกนิน รวมทั้งสมบัติของลิกโนซัลโฟเนตที่เตรียมได้นี้มีสมบัติที่ใกล้เคียงกันกับสมบัติของลิกโนซัลโฟเนตที่เชิงการค้า

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.. ลายมือชื่อนิสิต...
ปีการศึกษา......2547...... ลายมือชื่ออาจารย์ที่ปรึกษา...........................

4572517623: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: LIGNOSULFONATE / LIGNIN / BLACK LIQUOR / SULFONATION / SULFOMETHYLATION

SUPACHET PONGSAI: PREPARATION OF LIGNOSULFONATE FROM LIGNIN IN BLACK LIQUOR FROM EUCALYPTUS KRAFT PULPING. THESIS ADVISOR: PROF. SOPHON ROENGSUMRAN, Ph.D. 96 pp. ISBN 974-17-6770-6.

The lignin was isolated from black liquor from eucalyptus kraft pulping by precipitating with an acid solution at pH 3 and then washing with hot water. The isolated lignin was used as the starting material for preparation of lignosulfonate by sulfonation and sulfomethylation reactions. The sulfomethylation was the optimum reaction for preparation of a lignosulfonate. The reaction was performed using 130 ^{o}C with the 0.5: 0.119: 1 by weight ratio of sodium sulfite: formaldehyde: lignin, for 2 hours, giving lignosulfonate 12.66 g/ 10 g of isolated lignin. In addition, the physical properties of synthesized lignosulfonate from this optimum condition were similar to those of commercial lignosulfonate.

Field of study..Petrochemistry and Polymer Science. Student’s signature………………….
Academic year……2004…… Advisor’s signature………………...

ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to his advisor, Professor Sophon Roengsumran, Ph.D., for his encouraging guidance, supervision and helpful suggestions throughout the course of this work. In addition, he is also grateful to Associate Professor Amorn Petsom, Ph.D., for his valuable criticism and helpfulness. He would like to thank Professor Pattarapan Prasassarakich, Ph.D., Assistant Professor Warinthorn Chavasiri, Ph.D., and Assistant Professor Thumnoon Nhujak, Ph.D., for their valuable suggestion, discussions and comments.

He also thanks the Chemistry Department, Chulalongkorn University for their help in permitting the author to use some equipment and their support during this work.

The author would like to thank his friends in the Program of Petrochemistry and Polymer Science for their assistance throughout the research.

Finally, the author would like to express his greatest appreciation to his family for their support throughout his entire education.

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ABBREVIATIONS

^{o}C = Celcius degree

ml = milliliter

l = liter

g = gram

M = molar

Nm = newtonmeter

ppm = part per million

% = percent

cm^{-1} = wavenumber unit

FT-IR = Fourier transform-infrared spectroscopy

^{1}H NMR = Proton nuclear magnetic resonance

^{13}C NMR = Carbon nuclear magnetic resonance

XRF = X-ray fluorescence

GPC = Gel permeation chromatography

CHAPTER I

INTRODUCTION

1.1 GENERAL

The current annual Thailand economic is growing dramatically. This is leading parallely to an increasing of paper demand. In the same way, eucalyptus trees are cultivated increasingly to supply raw materials in this paper-making industry. Thus this eucalyptus woods also are delivered on a pulping process. Then pulping process changes eucalyptus wood to be a pulp, which is continued into other process.

Kraft pulping process is used generally in Thailand paper-making industry because this kraft pulping gives a strong pulp and also can recycle chemical reagents. In addition to this kraft pulping also gives a waste to form the black liquor. This black liquor normally consists of sodium, sulfur, carbohydrate and lignin. This black liquor was delivered into the step of water evaporation to concentrate the quantities of lignin. After water evaporation, the concentrated black liquor just was applied as a source of fuel by sending into burning system for using in a next pulping process. However, if there are too much quantities of black liquor that was generated from kraft pulping, this black liquor could not used all of this quantities are fuel. So it was released to water treatment system. However, this treatment can not treat all of lignin in liquor. So black liquor has affected for environment.

Lignin was an important component in black liquor. If this component was separated to a single lignin component, this lignin component also can be used in variety application such as for a starting material of dispersant [1], coating material [2] and also for the lignosulfonate synthesis [3]. Expectively, the lignosulfonate can be applied in many fields for example as binder [4], dispersant [5] and emulsifier [6]. However, This lignosulfonate still has to be imported considerably in any year. Therefore this research is directed to synthesize lignosulfonate from separated lignin in order to reduce quantities of imported lignosulfonate and also solve environment problem from releasing black liquor onto surrounding area.

1.2 Objectives

1. To modify method for lignin isolation from eucalyptus kraft pulping black liquor.
2. To modify method for sulfonation of isolated lignin.
3. To compare the properties of synthesized lignosulfonates with commercial available lignosulfonate.

1.3 Scope of investigation

The scope of this research intend to prepare lignosulfonate from lignin isolated from black liquor by treatment of isolated lignin with the sulfonating agents such as sulfur trioxide, fuming sulfuric acid, sodium sulfite or sulfomethylating agent. In this way, many different parameters will be varied such as reagent quantity, reaction time and reaction temperature. These parameters will be determined to result in a desired yield. Finally, the physical properties of this synthesized lignosulfonate also are determined to compare with commercial lignosulfonate.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Lignin

In the past, lignin was called chemical substances of wood. After that, it was called only part of noncellulose in wood. In the present, part of noncellulose can be isolated many types of chemical substances such as carbohydrate, tannins, rosins and lignin etc. Then these chemical substances were investigated widely in many fields.

Lignin is the second of most abundant renewable organic matter on earth, immediately after cellulose, which it accompanies in wood, straw and other plant tissues. The amount of lignin in plants varies widely and is normally in range of 20-30 % by weight. In admixture with hemicellulose, it forms the cementing material for cellulose fibrils and imparts strength to the structural elements of the plants. In chemical structure, researchers were unclear about the nature of this very abundant material. Although it had a higher carbon content than the carbohydrate, its chemical nature remained obscure for a long time. Until in 1954 Lange, who applied UV microscopy at various wavelengths directly on thin wood section, obtaining the lignin spectrum. This lignin spectrum indicated typical of aromatic compounds. So the mail structure of lignin was aromatic compounds [7]. However, it was a amorphous polymer which be complex to discover a true structure.

Beside aromatic structure, other lignin structure also consisted of hydroxyl, methoxyl and carbonyl groups. So differential types of lignin also differ in these functional groups. Moreover, differentces of lignin structure depended on many factors such as source and extraction cause of its differences. Therefore lignin has many types and also can be nomenclatured by source such as wheat straw lignin, softwood lignin and hardwood lignin. In a same way, It can be called by extraction method such as native lignin (protolignin), milled wood lignin (MWL), sulfite lignin and kraft lignin etc [7].

Even lignin was applied in many products all around the world, it was used few percents to compare with million tons of wood because lignin production used investment higher than petrochemical production in the same application. However petrochemical raw materials decrease continuously, especially have high cost in present. Therefore lignin become important material again.

2.1.1 General properties of lignin

Lignin is a brown solid powder. Its density is 1.3-1.4 g/cm^3. Refractive index is 1.6. In nature of lignin, it insolubles water and strong mineral acids. Therefore 72% sulfuric acid can separate lignin in wood carbohydrate. Almost lignin solubles alkaline solution. A little lignin solubles oxygenerated organic compound and amine. X-ray diffraction indicated lignin to be amorphous polymer. In addition, its low specific viscosity shows that lignin is a branch polymer. Finally, heat of combustion is about 29.5 MJ/kg [8].

2.1.2 Component and structure

Chemical component analysis of lignin was shown in Table 2.1.

Table 2.1 Chemical components of lignin in wood [8]

Species	%C	%H	%O	%OCH_3
Coniferous	63.8	6.3	29.9	15.8
Deciduous	59.8	6.4	33.7	21.4

Lignin is a phenolic polymer, which is built up by oxidative coupling of three major C_6-C_3 (phenylpropane) unit was shown in Figure 2.1, namely, syringyl alcohol (S), guaiacyl alcohol (G) and ρ-hydroxyl alcohol (H) were shown in Figure 2.2, which form a randomized structure in a tridimensional network inside the cell wall. Differential lignin had also difference of S,G,H unit composition [9].

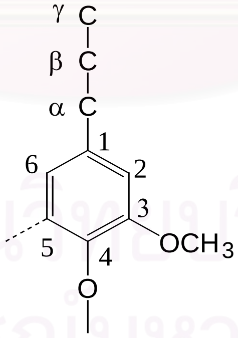


Figure 2.1 Nomenclature of phenylpropane unit

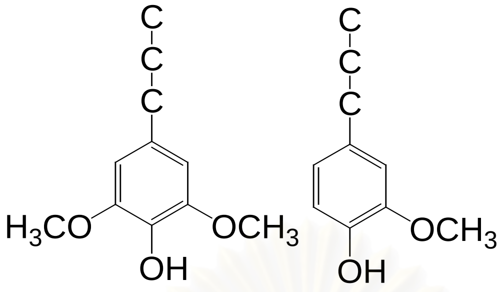


Figure 2.2 Syringyl (S), Guaiacyl (G) and ρ-hydroxyl alcohol (H)

The major interunit linkage of lignin structure is an aryl-aryl ether types such as β-5, β-O-4, 5-5, β-β, α-O-4 and 4-O-5 , shown in Figure 2.3.

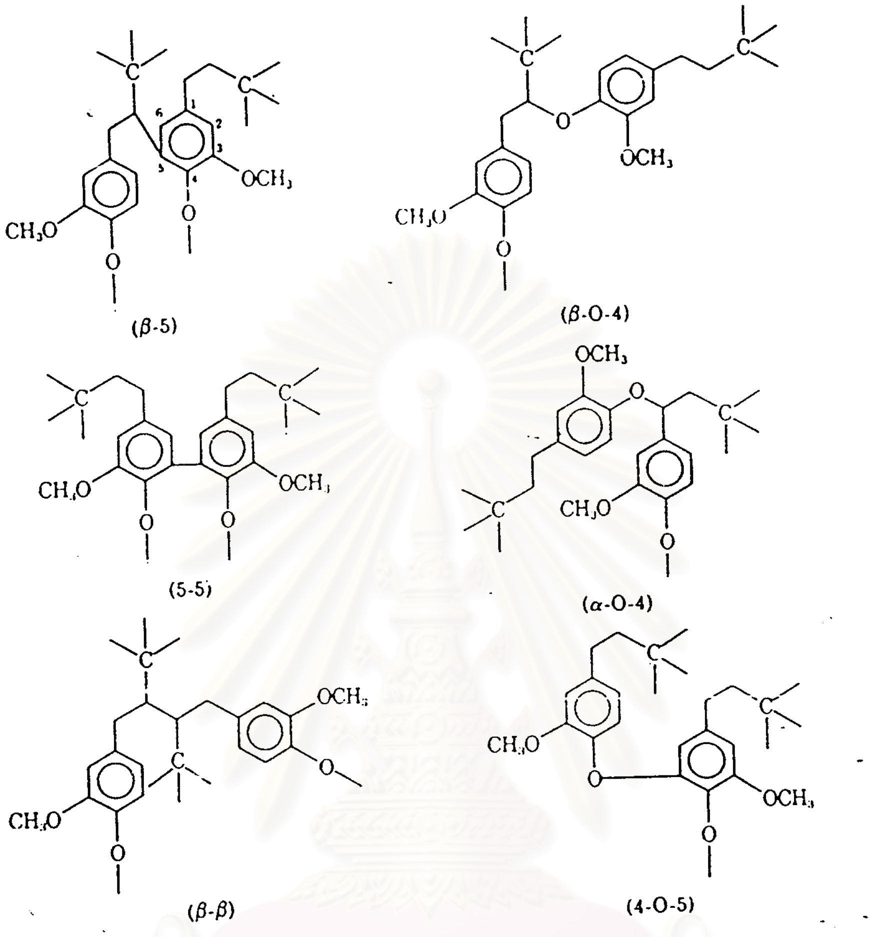


Figure 2.3 Examples of interunit linkage of lignin structure [9]

Besides the some 20 different types of bonds present within the lignin itself, lignin seems to be particularly associated with the hemicellulosic polysaccharides. Therefore, the lignin structure is a complex crosslinking polymers as shown in Figure 2.4.

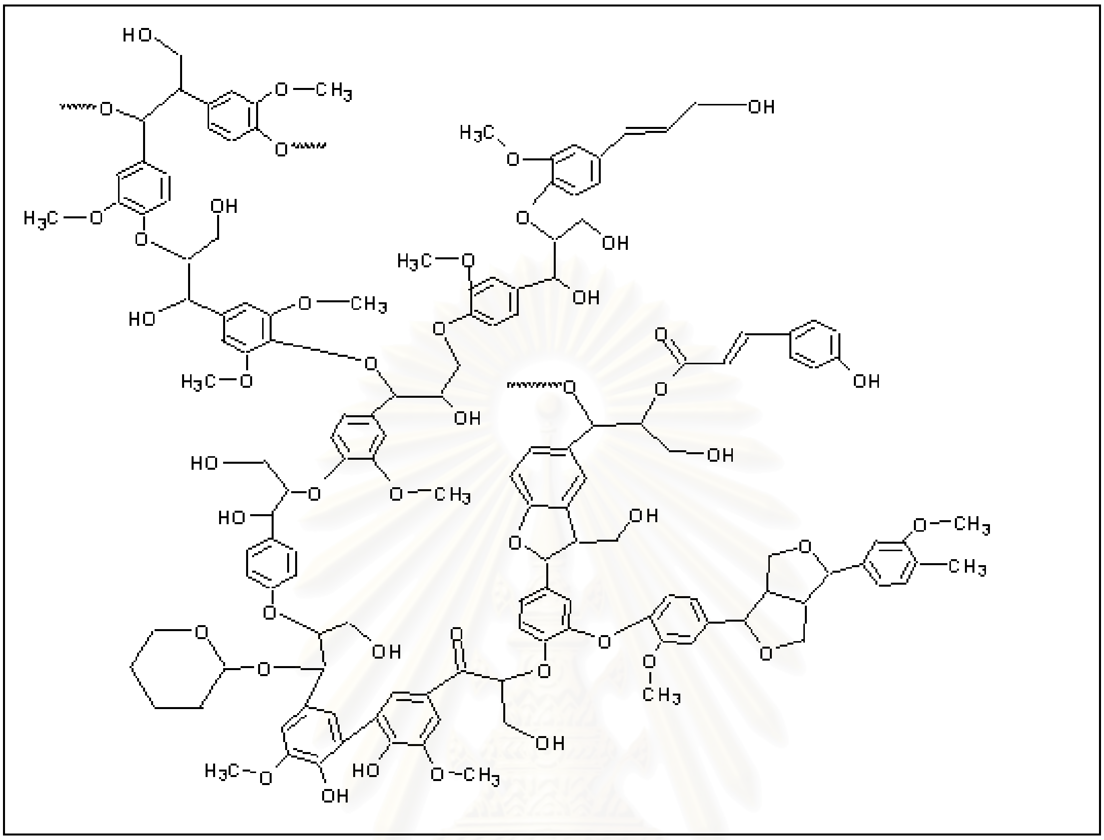


Figure 2.4 Lignin structure

2.1.3 Source of lignin

Source of lignin is wood. Normally, it is insoluble water, unless it is degraded by physical or chemical treatments. Therefore, these treatments can isolate lignin in wood.

From treatment in past, it gave detail of lignin quantity in wood, which differential wood types get differentially a range of quantity. Table 2.2 shows lignin quantity in wood.

Table 2.2 Lignin contents of various woods [8]

Wood	Lignin content (%)
Douglas fir	27.2
Noble fir	29.3
Engelmann	26.3
Jack pine	26.7
Slash pine	28.0
Western hemlock	27.8
Beech	21.0
Trembling aspen	19.3
White birch	20.0
Yellow birch	22.7
Chestnut oak	24.3
Red maple	22.3

Wood grow a compression condition has lignin contents difference from normal condition. Beside lignin contents depend on main factor such as age, temperature and season etc, which is shown in Table 2.3

Table 2.3 Lignin contents of various conditions [8, 10]

Source of lignin	Lignin content (%)
Spruce wood	
Normal	26.0
Compression	38.0
Eucalyptus	
Normal	29.5
Tension	13.8
Red pine (Tracheids)	
Normal	28
Compression	40
Loblolly pine	
Early sapwood	28.1
Late sapwood	26.8
Early heartwood	26.8
Late heartwood	24.2

Although lignin comes from many types of source, any source does not bring a useful such as wood and bark from saw industry, agriculture and pulping factory. Especially pulping industry has potential sufficiently to recycle lignin.

2.1.4 Division of lignin

It can be divided in many ways such as

-Source (woody plant) of the lignin

-Methods used to remove lignin from the plant.

-Methods used to purify the lignin.

-Nature of the chemical modification of the lignin after isolation

For division with woody plant, this can divide mainly 3 types: softwood lignin, hardwood lignin and non-wood lignin (straw, grass). Lignin of differential botanical origin differs in the composition of phenylpropane unit (S, G and H). The composition may vary from species to species, and also vary within the differential parts of the same plant. Table 2.4 shows the approximate compositions of some representative classes of lignins.

Table 2.4 The approximate compositions of some representative classes of lignins [9].

	%S	%G	%H
Softwood lignin	1	95	4
Hardwood lignin	50	50	2
Grass lignin	25	70	5
Compression wood lignin	0	70	30

1.) Softwood lignin such as pine, is used generally for producing a long fiber, which increase strength of paper. This lignin consists of the prominent condensed unit, where the aromatic rings are linked to other units with carbon or oxygen bonds [9], are shown in Figure 2.5.

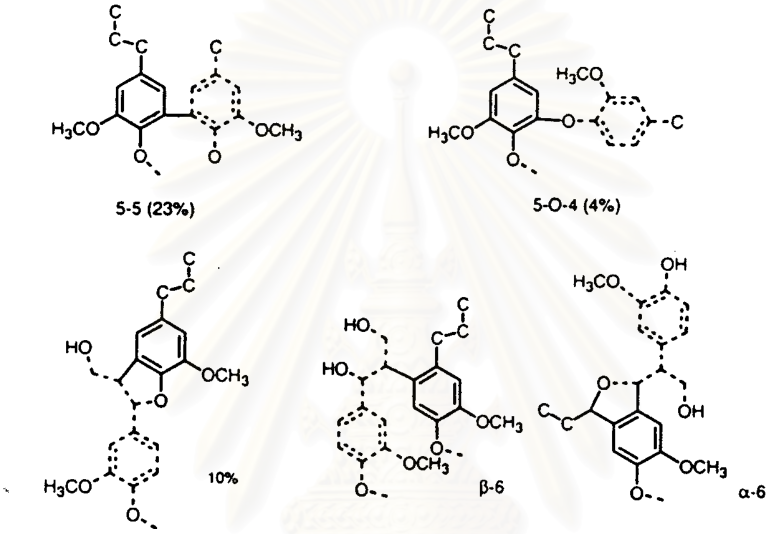


Figure 2.5 Structures and approximate abundancies of condensed units in lignin

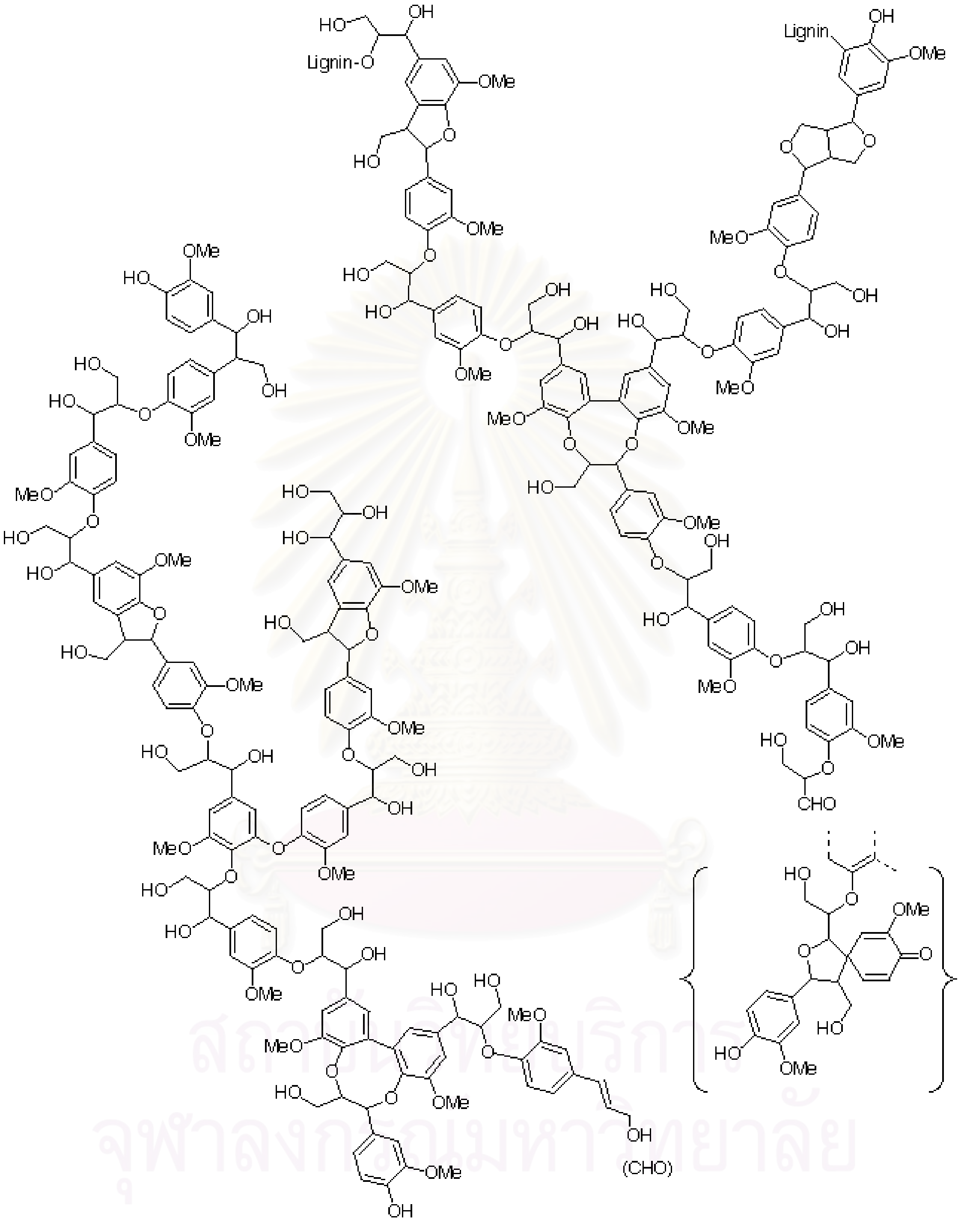


Figure 2.6 Softwood lignin structure

2.) Hardwood lignin such as eucalyptus and oak, is used to produce a shot fiber, which increase density of paper. Hardwood lignins differ from softwood lignins mainly in the inclusion of syringyl units (see Table 2.4), with concomitant reduction in the occurrence of condensed units. A larger proportion of β-O-4 structural units, β-1 and resinol (β-β) units (see Figure 2.3) is also typical features of hardwood lignins [9].

3.) Non-wood lignin (straw, grass) such as cotton, bamboo. Lignins in grasses are composed of a lignin core composed of guaiacyl and syringyl units with peripheral groups that include ρ-hydroxycinnamic acid and ferulic acid units, the former being the major component. These units are chemically bound to lignin core, mostly as esters. Some ρ-hydroxyphenylpropane unit are also incorporated in the lignin but the amounts are of the same order of magnitude as in softwood lignin (see in Table 2.4) [3].

For division of lignin with method, which used to remove lignin from the plant [11], this can be divided many methods:

Brauns Lignin

It is obtained by the solvent extraction of wood meal. Lignin yield in this procedure is very low (2-3%). Often referred to in early publications as Native Lignin.

Cellulolytic Enzyme Lignin

A Lignin preparation was isolated by cellulolytic enzyme treatment of finely ground wood meal followed by solvent extraction. Although a tedious procedure, relatively high yields of lignin are obtained.

Dioxane Acidolysis Lignin

A lignin preparation isolated by the treatment of woody material with dioxane/dilute HCl. Certain linkages are cleaved by this procedure thus altering the lignin structure.

Milled Wood Lignin

It is isolated by solvent extraction and purification of finely ground wood meal. Yield is ~ 25% of the total lignin. Of the lignin preparations available, this is thought to best represent lignin found in wood. Also known as Bjorkman Lignin.

Klason Lignin

Lignin preparation isolated through the strong acid degradation of woody materials. This procedure is used to quantify the amount of lignin in woody materials. The lignin structure is markedly changed by the drastic conditions used in this treatment.

Periodate Lignin

It is lignin isolated through successive treatments of woody material with sodium periodate followed by boiling water. This removes carbohydrates leaving lignin. Some degradation of the lignin occurs with this method.

Organosolv Lignin

Lignin products produced from a number of different organic solvent-based systems are referred to as organosolv lignins. The water insoluble products produced in these systems are usually purified and contain a very high percentage of lignin. Many different modified lignin products have been developed from organosolv lignins including water-soluble sulfonated materials. These lignin products are currently not marketed because of unfavorable economics associated with the production of pulp using these systems. The following are the four major organosolv processes:

Alcell: Ethanol/water pulping.

ASAM: Alkaline sulfite anthraquinone methanol pulping.

Organocell: Methanol pulping followed by methanol, NaOH, and anthraquinone pulping.

Acetosolv: Acetic acid/HCl pulping.

Steam Explosion Lignin

Woody material is separated into fibers through high temperature/high pressure treatment with steam. The lignin material that is obtained contains low level of carbohydrate and wood extractive impurities. The water insoluble lignin itself has somewhat reduced molecular weight caused by acid hydrolysis reactions. This type of system is often used along with enzymatic hydrolysis to produce sugars for fermentation.

2.1.5 Application of lignin

Lignin was applied and was modified in many fields for example:

- Binder in concrete [12], polymer [13], fiber [14], plywood [15], fertilizer [2], animal feed [16], veneer [17], linerborad [18]
- Additive in ink , vanish, paint [19], electrode [20], thermosetting plastic [21], household cleaning, laudry detergent [22], synthetic rubber [23]
- Chelating agent in bleaching process [24]
- Antioxidant in polypropylene [25], edible oil [26]
- Anti-carcinogen [27]
- Dispersant in bitumen [1]
- Preparation of activated carbon [28]
- Emulsion in asphalt [29]
- Absorber in water aqueous liquid [30]
- Precursor in vanillin and phenol compound synthesis [31].

2.2 Pulp-making process

2.2.1 Raw materials for pulping process

Fibers, which are in woods, are raw materials for this process. However only some woods can get a good fiber to suitable for pulping process. Moreover wood cost is also considered to select a suitable type of wood for budget reducing.

Wood as raw material in pulping process can divide 2 classes:

1.) *Wood* can separate 2 classes:

1.1) *Softwood*, such as pine spruce, grows in high and cool area. It grows slowly. Its leafs are long and small. Fibers are called long fibers, which are rough and strong. This fiber long about 3 mm and wide about 0.02-0.04 mm.

1.2) *Hardwood*, such as eucalyptus, acacia, birch and aspen. It grows quickly in tropical area. Its leafs are wide. Fibers are called shot fibers. These fiber characteristics are shot, fine and low strong fiber. Its lengths are 0.01-0.02 mm.

2.) *Non-wood*, such as cotton, bamboo, gives fiber to suitable for paper making. Beside straw and sugar cane, which are residues in agriculture also give good fibers. However these fiber lengths are not fix. Its length may be less 0.1 mm to more 1 cm.

Long fiber gets a pulp to differ from shot fiber. Long fiber, which is strong fiber, use for a high impact paper such as paper for packaging, paper bag and corrugative box etc. For shot fiber, owing to it is a fined fiber which get a smooth paper. Therefore it suitable to produce printing and writing paper. In paper making from non-wood, It has a many problems for paper making because of it needs a high volume warehouse for storage. Especially these plants can not feed raw material fibers all season, only in harvest period such as rice straw. Therefore it does not suitable for paper industry.

2.2.2 pulping process

The objective of pulping is to solubilize and remove the lignin portion of wood leaving the industrial fiber composed essentially of pure carbohydrate material. While many variations are used throughout the world, the most convenient classification of pulping method is by whether they are acidic or alkaline. Each has its own specific advantages and disadvantages. All processes use aqueous systems under heat and pressure.

1.) Sulfite process (acidic process) [32]

Lignin will react with the bisulfite ion (HSO_3) under acidic conditions to form lignosulfonates (LS) that are soluble in water. For many years, This was the preferred process since it produced pulps of light color that could easily be bleached, used cheap chemicals in fairly limited amounts so that no recovery was necessary, and was a relatively simple process to operate.

Spruce and fir are the preferred species for sulfite process since they produce relatively strong, light-colored pulps. About 20 percent of newsprint consist of this type of pulp that has not been bleached. Thus the sulfite industry is concentrated in Canada, northern United States and the pacific coast where the supplies of spruce and fir are greatest and the largest quantities of newsprint are produced.

2.) Kraft process (sulfate process or alkaline process) [32]

Any kind of wood can be pulped practically by the kraft process since it produces the strongest pulps with good economics. Thus it has grown to be the dominant process in the world. This process uses a mixture of sodium hydroxide and sodium sulfide as the active chemical. It has pulping conditions which was shown in Table 2.5.

Table 2.5 Typical kraft pulping conditions [32]

Pressure	100-110 psig
Temperature	170-175 °C
Time	2-3 hrs.
Alkaline charge	15-25% of weight of wood (5:2 $NaOH:Na_2S$)
Liquor to wood ratio	4:1 (by weight)

Due to the high alkali charge, the chemicals must be recovered and reused. This also alleviates pollution problems since the yield of pulp is only about 45 percent of the original wood weight and these organic residues must be eliminated. After being cooked in the digester, the pulp is washed in a countercurrent rotary vacuum washer system using three or four stages. The pulp is then ready for bleaching or for use in papers such as grocery bags.

The separated liquor is very dark and is known as black liquor. It is concentrated in multieffect evaporators to 60-65 percent solids. At this concentration the quantity of dissolved organic compounds from the wood (lignin and carbohydrate) is sufficient to allow the liquor to be burned in recovery furnace. After burning, the inorganics collect on the bottom of furnace as a molten smelt of Na_2CO_3 and Na_2S. Sodium sulfate is added to the liquor as make-up and is reduced to Na_2S by carbon. After dissolving in water, this mixture (called green liquor) is reacted with slaked lime.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

Since The Na_2S does not react with the lime the resultant mixture of NaOH and Na_2S (called white liquor) can be reuse to pulp other wood. Chemical system is a closed one as shown in Figure 2.7

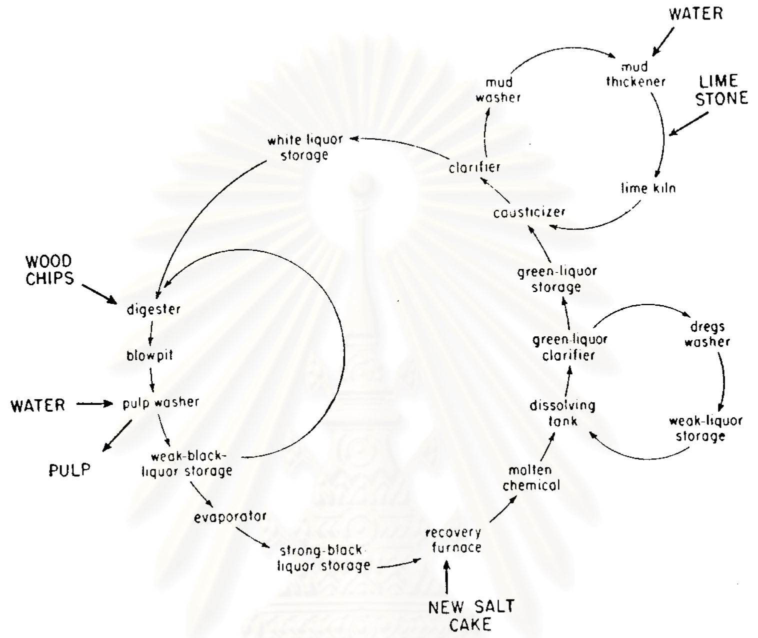


Figure 2.7 Diagram shows cyclic nature of the kraft recovery process [32]

2.2.3 Black liquor from kraft pulping

Black liquor had solid contents in range 25-30%. These solids consisted of lignin in range 25-45 % by solid weight [7, 33, 34]. The solid components in black liquor are shown in Table 2.6

Table 2.6 Black liquor components [31, 33, 34]

Component	Content (% by solid weight)
Organic compounds	
Lignin	25-45%
Aliphatic carboxylic acids	25-35%
Others compound	3-5%
Inorganic compounds	
Sodium	17-20%
Sulfur	3-5%

The black liquor is burned in order to recycle these chemicals and contribute the production of energy for next pulping. Then lignin in black liquor also is burned to get energy. However, this lignin should be applied in many fields more than burning for examples dispersant, coating, vanillin synthesis and lignosulfonate synthesis.

2.3 Chemical reaction during kraft pulping process

As in sulfite pulping, fragmentation of lignin depends on the cleavage of ether linkages, whereas the carbon-to-carbonlinkages are essentially stable. The presence of hydrosulfide ions greatly facilitates delignification because of their strong nucleophilicity in comparison with hydroxyl ions, which, instead, are strongly basic. Cleavage of ether linkages, promoted both by hydroxyl and hydrosulfide ions, results also in increasing hydrophilicity of lignin because of the liberation of phenolic hydroxyl groups. The degraded lignin is dissolved in the cooking liquor as sodium phenolates. Studies with model substances representing various structural unit in lignin have largely clarified the delignification reaction in kraft pulping [7].

Etherified phenolic structure containing β-aryl ether bonds In etherified *p*-phenolic structure the β-aryl ether linkage is cleaved by hydroxide ions according to the mechanism shown in Figure 2.8.

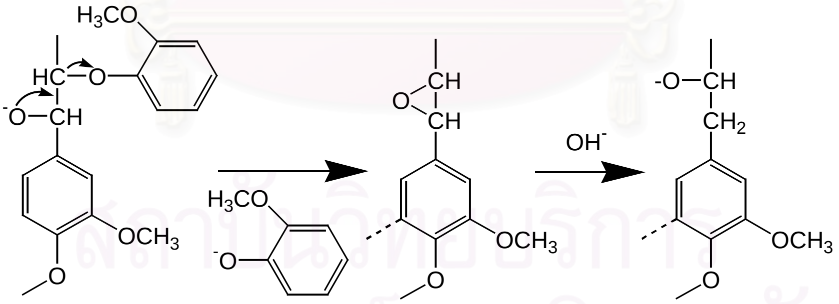


Figure 2.8 Cleavage of β-aryl ether bonds in nonphenolic phenylpropane units by hydroxide ions [7]

Free phenolic structure containing β-aryl ether bonds In kraft pulping, hydrosulfide ions are present (strong nucleophiles). They react with the phenylpropane unit to convert the structure with clevage of β-aryl ether bond (shown in Figure 2.9).

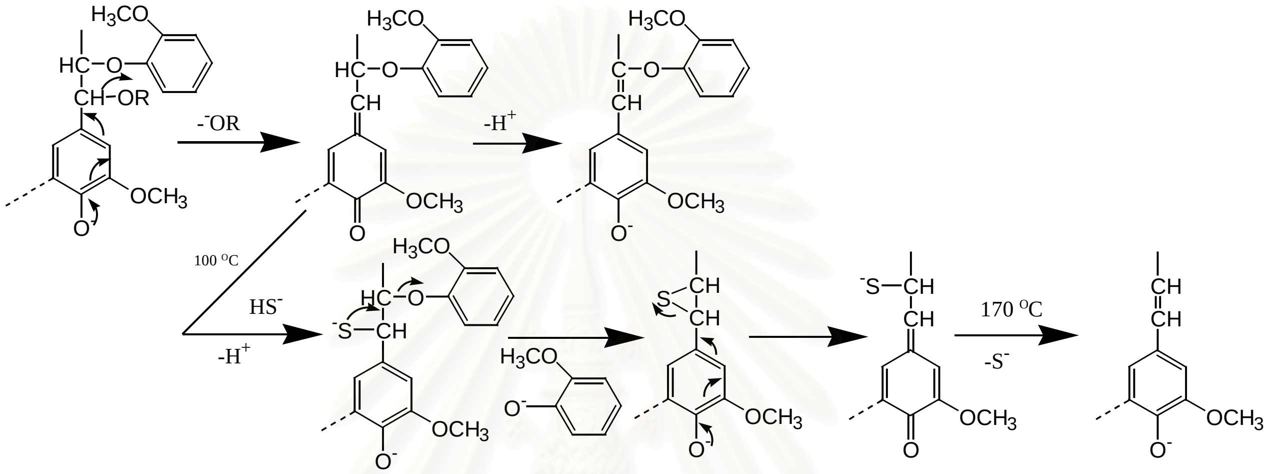


Figure 2.9 Main reaction of the phenolic β-aryl ether structures during kraft pulping [7]

2.4 Pulping process of Advance Agro (Thailand) Co. Ltd. [35]

Advance Agro grows *Camadulensis* eucalyptus as raw material for pulping. Paper make form eucalyptus wood has a lot of advantage such as

-Good formation of paper

-High bulk

-Good opacity produces thick paper with high opaque rate

-Smooth paper

-High brightness

Company uses kraft process for pulping. Procedure is shown in Figure 2.9

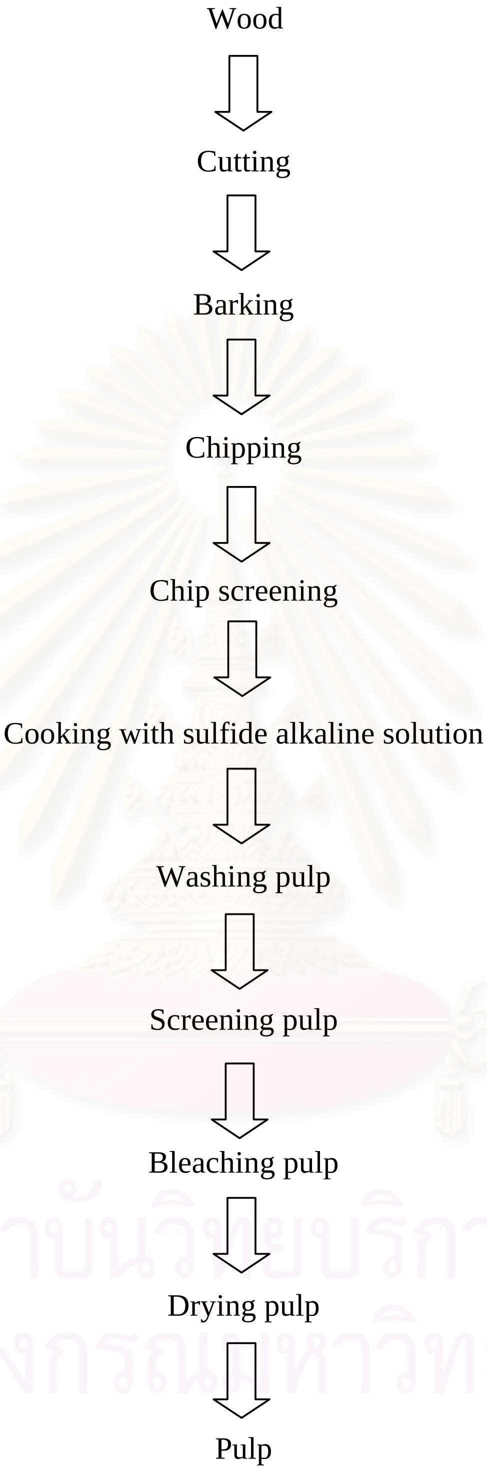


Figure 2.10 Procedure of Advance Agro pulping process

2.5 Lignosulfonate

Lignin, which has sulfonated group in structure, is called lignosulfonate (LS). Almost lignosulfonate come from sulfite process. It soluble water. Therefore it is applied in many fields such as

Lignosulfonate as a binder

Lignosulfonates are a very effective and economical adhesive, acting as a binding agent or "glue" in pellets or compressed materials. Lignosulfonates used on unpaved roads reduce environmental concerns from airborne dust particles and stabilize the road surface. This binding ability makes it a useful component of:

- coal briquettes *[36]*
- polyurethane foam [37]
- carbon black [39]
- fertilizers & herbicides [40]
- *p*lywood & particle board [4]
- *a*nimal feed pellets [38]
- dust suppressants [40]

Lignosulfonate as a dispersant

Lignosulfonate prevents the clumping and settling of undissolved particles in suspensions. By attaching to the particle surface, it keeps the particle from being attracted to other particles and reduces the amount of water needed to use the product effectively. The dispersing property makes lignosulfonate useful in:

- cement mixes [5]
- gypsum board [42]
- dyes & pigments [41]

Lignosulfonate as an Emulsifier

Lignosulfonate stabilizes emulsions of immiscible liquids, such as oil and water, making them highly resistant to breaking. Lignosulfonates are at work as emulsifiers in:

- asphalt emulsions [6]
- wax emulsions [6]

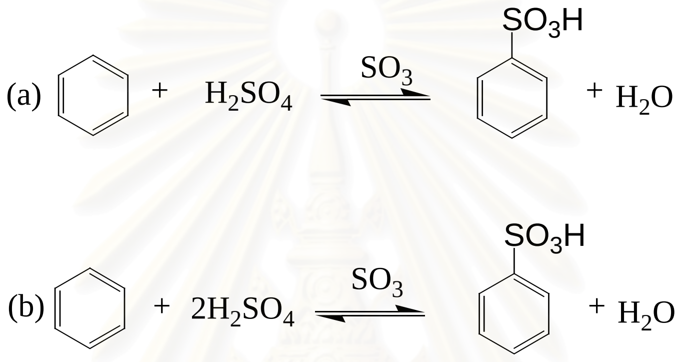
Lignosulfonate as a Sequestrant

Lignosulfonates can tie up metal ions, preventing them from reacting with other compounds and becoming insoluble. Metal ions sequestered with lignosulfonates stay dissolved in solution, keeping them available to plants and preventing scaly deposits in water systems. As a result, they are used in:

- micronutrient systems [11]
- cleaning compounds [11]
- water treatments for boilers and cooling systems [11]

2.6 Sulfonation

The sulfonation can be handled with oleum, sulfuric acid, gaseous sulfur trioxide or sulfite. The sulfonating group is introduced into structure by electrophilic substitution. It accomplishes this by the use of sulfur trioxide in the presence of sulfuric acid (Figure 2.10-a) [43, 44].



$$SO_3 + H_2O \dashrightarrow H_2SO_4$$

Figure 2.11 Reaction of sulfonation

Sulfur trioxide gas is dissolved into concentrated sulfuric acid at 20% to give what is called “fuming sulfuric acid” which earns its name by billowing out white plumes of smokey SO_3 fumes when the bottle is opened. The sulfur trioxide (SO_3) Serves two purposes. It acts first as the sulfonating agent and it prevents the unfavorable reversible of this equilibrium by reacting with and effectively removing the water product thus driving this equilibrium to the right.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The sulfonation can be accomplished without the sulfur trioxide by using excess sulfuric acid (Figure 2.10-b) [43, 44]. The extra sulfuric acid will act as a dehydrating agent absorbing the water and preventing the reversal of the equilibrium. This is not as efficient as the sulfur trioxide so the reaction is much slower.

The reaction mechanism in the presence of the sulfur trioxide differs by that of excess concentrated sulfuric acid in that step 1 in the mechanism shown in Figure 2.11 below is not necessary, and the mechanism begins essentially with step 2. In both environment the SO_3 is apparently the sulfonating agent (step 2 in Figure 2.11) [43, 44].

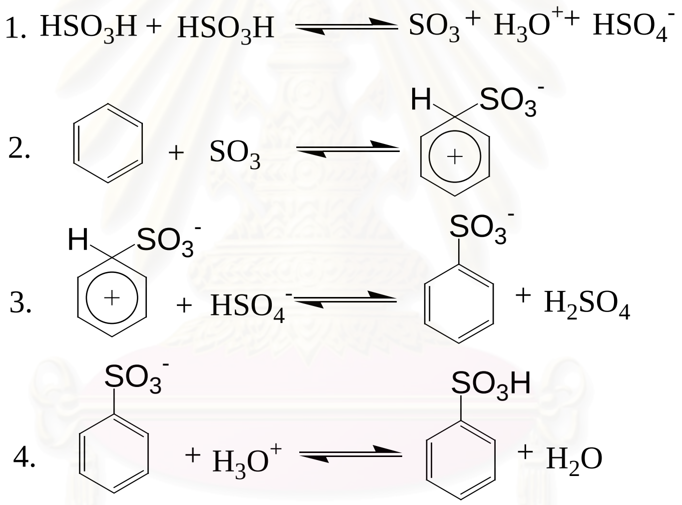


Figure 2.12 The reaction mechanism of sulfonation

2.7 sulfomethylation

The sulfomethylation can be handled with formaldehyde and sulfite to form hydroxy methane sulfonate intermediate. This intermediate turns to undergo reaction with reactant to form methylsulfonate in structure (shown in Figure 2.12) [45].

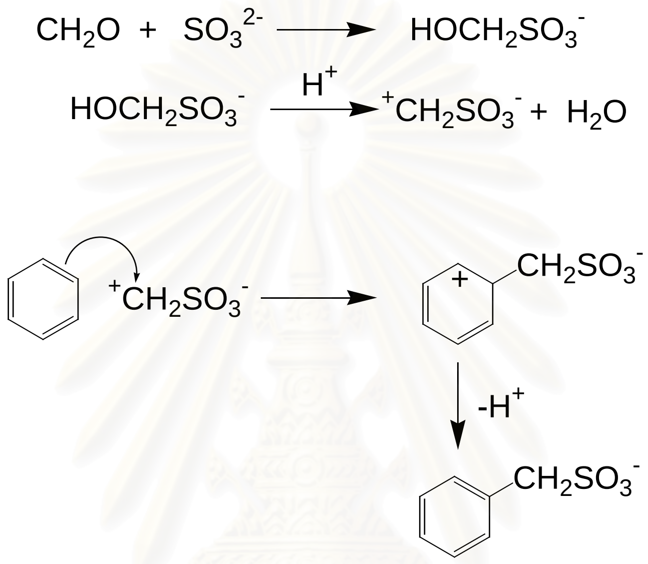


Figure 2.13 The reaction mechanism of sulfomethylation

2.8 Literature reviews

In the past, isolation of lignin was studied in field of:

McCoy B.J. [46] extracted lignin from samples of white fir sapwood with supercritical t-butanol and isopropanol. Experiments were carried out with a continuos flow system to study the effect of temperature and pressure on the dynamic response of extraction process. Increasing the temperature dramatically increased the fraction of lignin extracted. Increased pressure also showed increased yields. Additional analysis examined changes in porosity of wood residues extracted with supercritical isopropanol and t-butanol.

Sun R. [47] treated Caligonum monogoliacum and Tamarix spp. with ethanol-water (60/40,v/v) under acid catalyst (0.2 N HCl) at 70 ^{o}C for 4 h and then post-treatment with 2% hydrogen peroxide at pH 11.5 for 16 h at 45 ^{o}C, respectively. Alkaline peroxide post-treatment released a higher amount of lignin (10.6% from Caligonum monogoliacum and 6.4% from Tamarix spp.).

Halkar U.P. [48] extracted lignin from walnut (Juglans regia) shell oil by roasting at 250-300 ^{o}C. The lignin breakdown compounds of the oil were then isolated by solvent extraction using petroleum-ether (60-80 fraction), separated by preparative TLC and were fully characterized. The major compounds arising from lignin breakdown are thus identified guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, syringol, 4-methylsyringol, 4-ethylsyringol and 4-propylsyringol.

Sun R. [49] extracted lignin from fast-growing poplar wood with 5, 7.5, and 10% sodium hydroxide at 50 ^{o}C for 4-12 h . The pure lignin (PL) show relatively free of associated polysaccharides and are composed of large amount of syringyl units together with noticeable quantities of guaiacyl and fewer p-hydroxyphenyl units. The lignin fraction, extracted with 5% sodium hydroxide at 50 ^{o}C for 12 h from the dewaxed fast-growing poplar wood, is composed mainly of β-O-4 ether bonds together with small amounts of β-β and β-5 carbon-carbon linkages between the lignin structural units.

Sun R. [50] treated the dewaxed wheat straw with 0.5 M potassium hydroxide at 35 ^{o}C for 2.5 h without ultrasonic irradiation and with ultrasound assistance for 5, 10, 15, 20, 25, 30 and 35 min results in a dissolution of the original lignin. The lignin preparation isolated by alkali with ultrasound gives the high yield of lignin more than without ultrasound and also slightly higher molecular weight and thermal stability than without ultrasound.

Tanistra I. [51] prepared high-purified lignin from black liquor by using ultrafiltration polyacrylonitrile membranes. As a result, concentrates enriched with macromolecular lignin were obtained. Raising the transmembrane pressure, the lignin concentrates of high purity level were obtained (purity level higher than 80%).

Jonsson A.S. [52] separated lignin from the cellulose during kraft pulping by ultrafiltration and dialfiltration. The result shows the lignin purity to be 36% in the original kraft black liquor that was separated by ultrafiltration and 78% the perity lignin was given after semi-continuous dialfiltration.

Rohella R.S. [53] separated lignin from kraft black liquor with acid precipitating at pH 3 and then extracted with solvent and also treated with 72% sulfuric acid. This isolated lignin was high-purified lignin that had activation energy 29.87 kJ/mol.

Nada A.A [54] separated lignin from black liquor in 5 pulping processes: soda pulping, kraft pulping, sulfite pulping, butanol-water pulping and peroxyformic pulping.

As a result, lignin could be precipitated from soda and kraft black liquor by using 5% sulfuric acid at pH 2-3. Lignin was precipitated from sulfite black liquor by using methyl alcohol to isolate lignosulfonate. Lignin was precipitated from butanol black liquor by using benzene. Lignin was precipitated from peroxyacid by using water.

Perissotto D.O. [55] separated lignin from eucalyptus kraft pulping by using of acetone:water and dioxane:HCl 0.1 M. A detailed structural characterization of the kraft pulp extracts by FTIR and NMR showed that these brown extractives was the lignin structure.

Lachenal D. [56] extracted lignin in kraft pulp by enzymatic hydrolysis of carbohydrate, acidolysis with dioxne-water-HCl (conventional method) and acidolysis with acetic acid-water-$ZnCl_2$. The latter method was shown to extract lignin with a better yield than for conventional acidolysis and with a much lower content in impurities than for enzymatic hydrolysis.

In the past, preparation of lignosulfonate form lignin was studied in field of

Sulfite pulping proces This process changes lignin to form lignosulfonate by using sulfite compound in various condition. The sulfite compound reacts with lignin to cleave α-hydroxyl and α-ether groups in lignin structure (shown in Figure 2.14) [7].

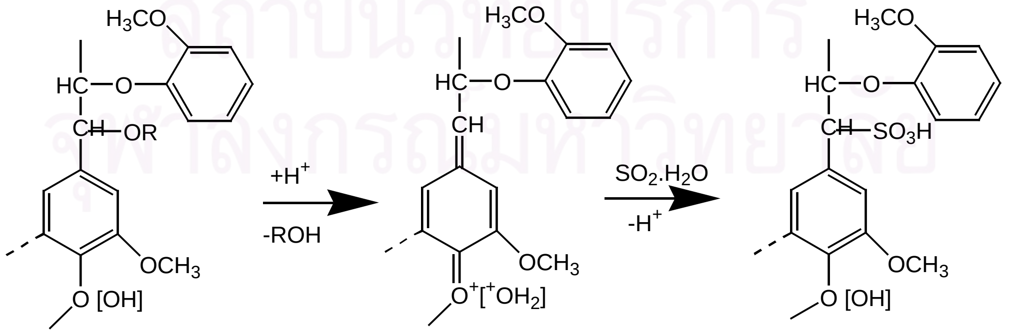


Figure 2.14 Behavior of α-ether structure during sulfite pulping

Dilling P. [3] sulfonated the pine lignin with sulfuric acid having a concentration of at least about 95%, while maintaining the temperature of the reaction below 40 ^{o}C for a sufficient time in sulfonation. Sulfonation of lignin with sulfuric acid increase the sulfuric acid quantity onto the structure of lignin at least about 1.7 moles sulfonic acid per mole of lignin, while providing water-solubility of the product at a wide range of pH levels.

Dilling P. [57] sulfonated the pine lignin with fuming sulfuric acid. The result was appeared form sulfonation with fuming sulfuric acid to provide an increases the sulfonic acid quantity onto the lignin structure at least about 4.2 moles sulfonic acid per mole lignin, while providing essentially complete water solubility of the product at all pH levels.

Chaabouni M. [58] investigated preparation of a sulfonated esparto grass lignin (SEL) and its behavior as a plasticizing-water-reducing agent for cement-water systems. SEL is prepared by extracting the lignin from the black liquor of a soda esparto grass pulping process and then sulfonating it with a mixture of sodium sulfite and formaldehyde. Analysis results show that both the molecular weight average and the combined sulfur content are relatively high. On the other hand, SEL could reduce the water content, improve the workability and compressive strength of mortars. SEL also permits a very low rate of slump loss of cements without excessive extension of the final set time.

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Black liquor: waste from kraft process of Advance Agro (Thailand) Co. Ltd.
2. 96% Sulfuric acid: Merck
3. 65% Fuming sulfuric acid: Merck
4. Sodium sulfite: Fulka
5. 35% Formaldehyde solution: Merck
6. Sodium hydroxide: Fulka
7. Sodium chloride: commercial grade
8. Methanol: commercial grade
9. Sodium lignosulfonate: commercial grade

3.2 Apparatus

1. Fourier transform infrared spectrophotometer (FT-IR):

   Model 1760x; Perkin Elmer

2. Nuclear magnetic resonance spectroscopy (NMR):

   Model 1760 AC-F 200 (200MHz); Bruker Spectrospin

3. Gel permeation chromatography (GPC):

   Model PL-GPC 110

The condition obtained GPC chromatogram was the following.

Eluent: 0.01 M NaOH

Flow rate: 0.6 ml/min

Injection volume: 20 µl

Temperature: 30 °C

Column set: Ultralinear hydrogel 1 column

Polymer standard: Polysaccharide standard kits

Calibration method: Polysaccharide standard calibration

Detector: Refractive index detector

4. X-ray fluorescence spectrometer:

   Model: PW-2400

5. Contact angle

   Model: Kruss/DSA 10

3.3 Procedures

3.3.1 Isolation of lignin from black liquor

The lignin was separated from black liquor by adding 25% sulfuric acid to result the lignin precipitate at pH 3. Then lignin precipitate was filtered to give solid lignin. The solid lignin was then washed with hot water many times until water was clear. Finally the washed lignin precipitate was dried in vacuum oven to give a purified lignin in 188.13 g/ 1000 ml of black liquor. The purified lignin was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, GPC and XRF.

3.3.2 Sulfonation of isolated lignin with 96% sulfuric acid

The solution of lignin (10 g) in methanol (50 ml) was placed in a 250 ml round bottom flask. 96% sulfuric acid (10 g) was added to the solution by dropwise for 1 hour. During dropping acid, the reaction mixture was stirred to below 30 ^{o}C. After finishing dropping, the mixture was held at room temperature for 30 minutes. Then mixture was evaporated by rotary evaporator to remove methanol. After that mixture was washed with cool saturated sodium chloride solution to remove excess sulfuric acid. The solid was neutralized with 5 M sodium hydroxide solution. The neutralized mixture was evaporated by rotary evaporator to remove water. Then the mixture was extracted with methanol. After that methanol extractive portion was evaporated by rotary evaporator to result the solid mixture of sodium lignosulfonate and unreacted lignin. Then the water was added into the solid mixture to dissolve sodium lignosulfonate. The solid mixture was filtered to give the filtrate of sodium lignosulfonate. Finally this filtrate was dried to give sodium lignosulfonate 0.34 g/ 10 g of isolated lignin. This synthesized sodium lignosulfonate was characterized by FT-IR and ^{13}C NMR.

3.3.3 Sulfonation of isolated lignin with 65% fuming sulfuric acid

The solution of lignin (10 g) in methanol (50 ml) was placed in a 250 ml round bottom flask. Then 65% fuming sulfuric acid which varied quantities to be 5, 10 and 15 g was added to the solution by dropwise for 1 hour. During dropping acid, the reaction mixture was stirred to below 30 ^{o}C. After finishing dropping, the mixture was held at room temperature for 30 minutes. Then mixture was evaporated by rotary evaporator to remove methanol. After that the mixture was washed with cool saturated sodium chloride solution to remove excess sulfuric acid. The solid was neutralized with 5 M sodium hydroxide solution. The neutralized mixture was evaporated by rotary evaporator to remove water. Then the mixture was extracted with methanol. After that methanol extractive portion was evaporated by rotary evaporator to result the solid mixture of sodium lignosulfonate and unreacted lignin. Then the water was added into the solid mixture to dissolve sodium lignosulfonate. The solid mixture was filtered to give the filtrate of sodium lignosulfonate. Finally this filtrate was dried to give sodium lignosulfonate yield (Table 4.1). This synthesized sodium lignosulfonate was characterized by FT-IR, ^{13}C NMR, GPC and XRF.

3.3.4 Sulfonation of isolated lignin with sodium sulfite

The slurry of lignin (10 g) in water (50 ml) was placed in a 250 ml round bottom flask. 5 M sulfuric acid (0.1 ml) was dropped to be a catalyst. After that, sodium sulfite (5 g) was added. The reaction mixture was stirred at 130 ^{o}C for 2 hours. After stirring, the mixture was filtered to remove unreacted lignin. Then filtrate was evaporated by rotary evaporator to remove water. After that the solid which got after evaporation was extracted with methanol. Finally, the extractive solution was dried to give sodium lignosulfonate 3.87 g/ 10 g of isolated lignin yield. This synthesized sodium lignosulfonate was characterized by FT-IR, ^{13}C NMR, GPC and XRF.

3.3.5 Sulfomethylation of isolated lignin

The slurry of lignin (10 g) in water (50 ml) was placed in a 250 ml round bottom flask Then 5 M sulfuric acid (0.1 ml) was dropped to be a catalyst. After that, sodium sulfite: formaldehyde which varied composition to be 4: 0.95, 5: 1.19 and 10: 2.38 g sodium sulfite: formaldehyde was added. The reaction mixture was stirred by vary temperature at 100 and 130 ^{o}C and vary time 1, 2 and 6 hours. After stirring, the mixture was filtered to remove unreacted lignin. Then filtrate was evaporated by rotary evaporator to remove water. After that solid which got after evaporation was washed with saturated sodium chloride solution to remove an intermediate component and then the washed solid was extracted with methanol. Finally, the extractive solution was dried to give sodium lignosulfonate yield (Table 4.2). This synthesized sodium lignosulfonate was characterized by FT-IR, ^{13}C NMR, GPC and XRF.

Table 3.1 Conditions of lignosulfonate synthesis

Sulfonating reagent	Quantity of reagent required/ isolated lignin (gram ratio)	Temperature (^{o}C)	Time (hour)
96% sulfuric acid	1:1	30	1.5
65% fuming sulfuric acid	0.5:1	30	1.5
	1:1	30	1.5
	1.5:1	30	1.5
Sodium sulfite	0.5:1	130	2
Sodium sulfite: formaldehyde	0.4:0.095:1	130	2
	0.5:0.119:1	130	2
	1:0.238:1	130	2
	0.5:0.119:1	130	1
	0.5:0.119:1	130	6
	0.5:0.119:1	100	2

3.4 Properties testing of synthesized lignosulfonate

3.4.1 Water solubility of synthesized lignosulfonate

Water solubility was used to measure the amounts of lignosulfonate dissolves in a given amounts of deionized water at room temperature. Water solubility was expressed as grams of lignosulfonate per 1000 ml of deionized water.

3.4.2 Surface tension testing of synthesized lignosulfonate

Surface tension from various concentrations of lignosulfonate solution (10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} M) was tested contact angles instrument. Single liquid of lignosulfonate solution was dropped on a solid surface in the gas phase. After that, contact angle of lignosulfonate drop was analyzed to determinate the surface tension of lignosulfonate.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Isolation of lignin from black liquor

Black liquor, which had pH 14, was adjusted to pH 3.0 with 25% sulfuric acid and precipitate was obtained. The precipitate was then filtered to give the brown solid lignin. For the part of filtrate, the main component of filtrate solution was the polysaccharide, which decomposed and dissolved, in acid condition at pH 3.0. Therefore, this polysaccharide was dissolved in the filtrate solution and separated from solid lignin. However after finishing acidic precipitation, the solid lignin precipitate contained impurities. These impurities may be tannin and inorganic compounds such as sodium carbonate, sodium hydroxide, sodium sulfate and sodium sulfide. To remove inorganic compounds and tannins in form of amphur colloid, the solid lignin precipitate was washed with hot water many times until hot water was clear. The washed lignin precipitate was dried in a vacuum oven to give a pure lignin of 188.13 g/1000 ml. The pure lignin structure was characterized by FT-IR, ^{1}H NMR, ^{13}C MNR, XRF and GPC. These characteristic results of isolated lignin are shown in Figures A1, B1, C1, D1 and E1, respectively.

Form Figure A1, the FT-IR spectrum of isolated lignin shows absorption peaks as summarized in Table 4.1

Table 4.1 IR absorption of isolated lignin

Band (cm^{-1})	Assignment
3424	O-H stretching
2941	C-H stretching of methyl or methylene group
2844	C-H vibration of methyl group
1520	Aromatic skeletal vibration
1458	C-H vibration of methyl group
1334	C-O stretching aromatic methoxyl
1225	C-O stretching aromatic phenyl
1112	O-H stretching of alcohol
828	C-H aromatic out of plane

Form Figure B1, ^1H NMR spectrum of isolated lignin showed chemical shift as listed in Table 4.2

Table 4.2 ^1H NMR of isolated lignin

Band (ppm)	Assignment
7.3-6.0	Aromatic H
4.5-3.5	Aliphatic H for CH_x-OH
4.0-3.0	Methoxy H

Form Figure C1, ^{13}C NMR spectrum of isolated lignin showed chemical shift as given in Table 4.3

Table 4.3 ^{13}C NMR of isolated lignin

Band (ppm)	Assignment
150-145	Carbon 3 and 5 of phenolic syringyl Carbon 3 and 4 guaiacyl
140-137	Carbon 4 of etherified syringyl
136-133	Carbon 1 of guaiacyl and syringyl
117-114	Carbon 5 of guaiacyl
108-102	Carbon 2 and 6 of syringyl
57-55	Carbon of methoxy group

The ^{13}C NMR spectrum of isolated lignin was similar to the that of Dmitry' lignin [59], which showed both carbon signals of guaiacyl and syringyl phenylpropane monomer. This indicates that isolated lignin in this work should have both guaiacyl and syringyl phenylpropane as a main phenylpropane monomer in isolated lignin structure.

From Figure D1, elemental analysis data of isolated lignin with XRF indicated a sulfur quantity of 0.42% in the isolated lignin structure. This sulfur quantity possibly come from the reaction of sulfide alkaline solution during krakt pulping process. The sulfide intermediate changed lignin molecules to form monosulfide lignin, which monosulfide lignin was dissolved in black liquor and was removed from pulp [7]. Other factors resulting a little sulfur in isolated lignin may be due to the remaining excess 25% sulfuric acid added in the step of lignin precipitation.

From Figure E1, GPC analysis data of isolated lignin indicated molecular weight (M_w) of lignin of 13,192, M_n of 9,481 and molecular weight distribution (MWD) of 1.391.

4.2 Sulfonation of isolated lignin

4.2.1 Sulfonation of isolated lignin with 96% sulfuric acid

Mechanism of sulfonation of isolated lignin with 96% sulfutric acid can be explained as Figure 4.1

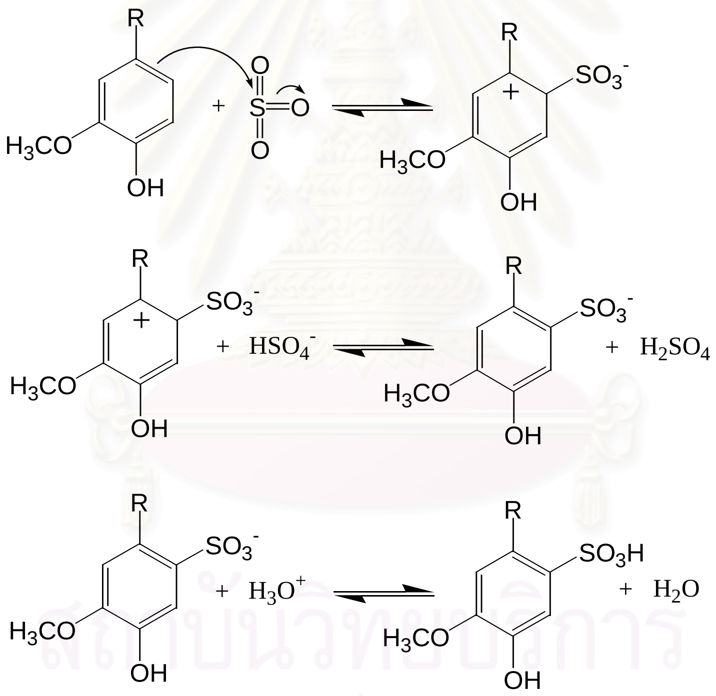


Figure 4.1 Mechanism of sulfonation of isolated lignin with 96% sulfuric acid

The isolated lignin was sulfonated with 96% sulfuric acid to give the lignosulfonic acid. Then lignosulfonic acid was neutralized with 5 M a sodium hydroxide solution to give the sodium lignosulfonate. Sodium lignosulfonate was resulted in a low yield of sodium lignosulfonate (0.34 g/ 10 g isolated lignin). The reason of a low yield of sodium lignosulfonate may be due to the low quantities of sulfur trioxide in 96% sulfuric acid. This sulfur trioxide was used to be a sulfonated reactant which reacted with isolate lignin for synthesis of sodium lignosulfonate. So if sulfur trioxide in 96% sulfuric acid had low quantities, it is not sufficient in treating lignin to be sodium lignosulfonate. Then sulfonation of isolated lignin with 96% sulfuric acid was not suitable for sodium lignosulfonate synthesis. The FT-IR and ^{13}C NMR of sodium lignosulfonate from sulfonation of isolated lignin with 96% sulfuric acid were shown in Figures A2 and C2.

Figure 4.2 compares the FT-IR spectrum of synthesized sodium lignosulfonate with FT-IR spectra of isolated lignin and commercial lignosulfonate (Figure A6).

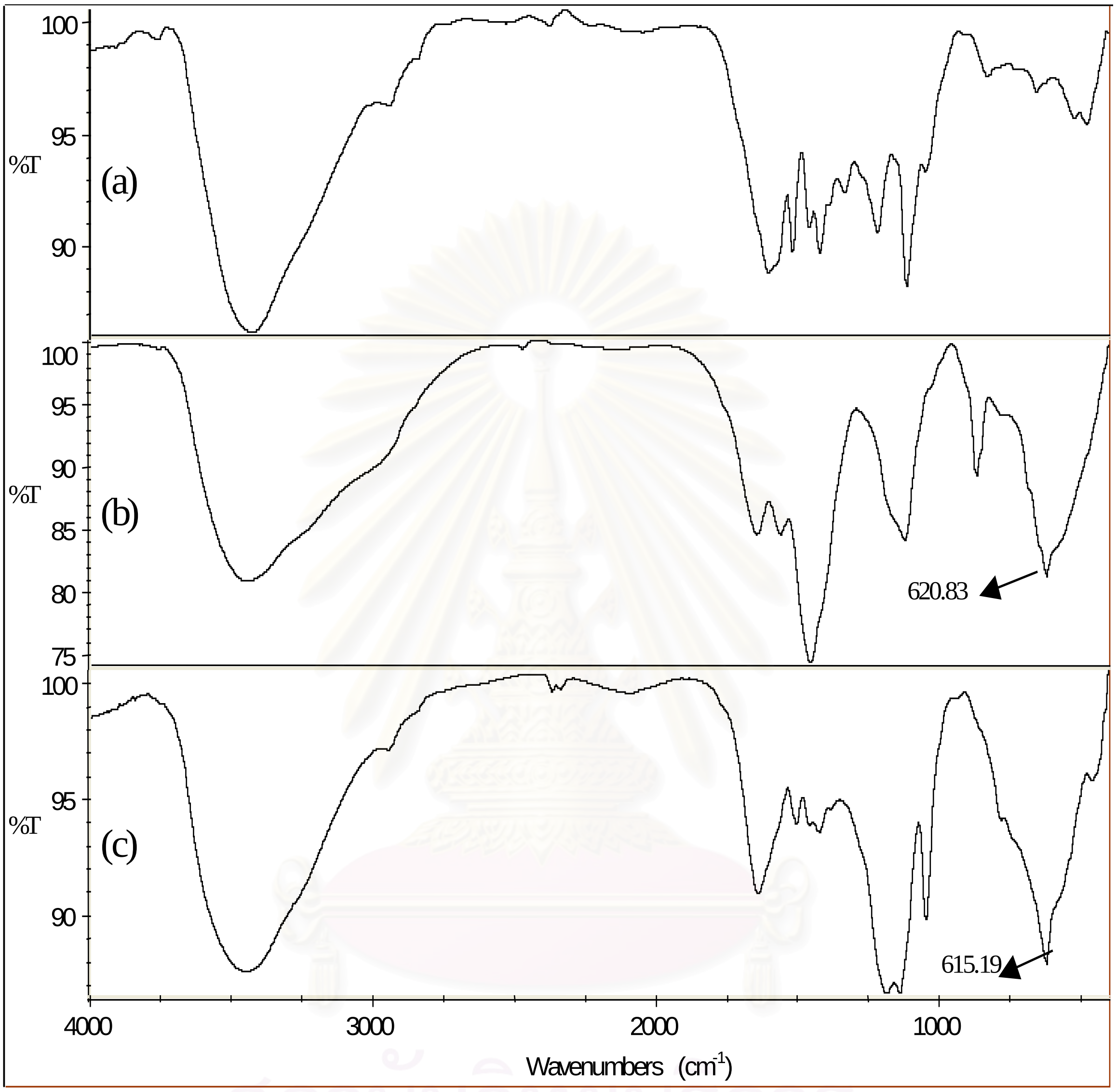


Figure 4.2 FT-IR spectra of (a) isolated lignin, (b) sodium lignosulfonate and (c) commercial lignosulfonate

As seem in Figure 4.2, at a region of 1300-1000 cm^{-1} the FT-IR absorption band of sodium lignosulfonate is similar FT-IR absorption band of commercial lignosulfonate and isolated lignin. In this region 1300-1000 cm^{-1}, this synthesized sodium lignosulfonate appeared the signals of antisymmetric stretching of sulfonate salt appeared at 1180 cm^{-1} and symmetric stretching of sulfonate salt appeared at 1123 cm^{-1} [58]. These both signals of sulfonate salt were appeared the same position with signals of phenol C-O stretching and methoxyl C-O deformation. Therefore only the FT-IR absorption band at region 1300-1000 cm^{-1} could not be used to identify the difference between the characteristic of this synthsized sodium lignosulfonate and isolated lignin. However, the signal at 620 cm^{-1} was assigned to be the C-S vibration of sulfonate salt sulfur which links to carbons of lignin structure. This signal was not observed in unsulfonated lignin. Therefore, this signal may be used for qualitative analysis of the sulfonated product.

From Figure 4.3 shows a comparison of the ^{13}C NMR spectrum of synthesized sodium lignosulfonate (Figure C2), isolated lignin and commercial product (Figure C6).

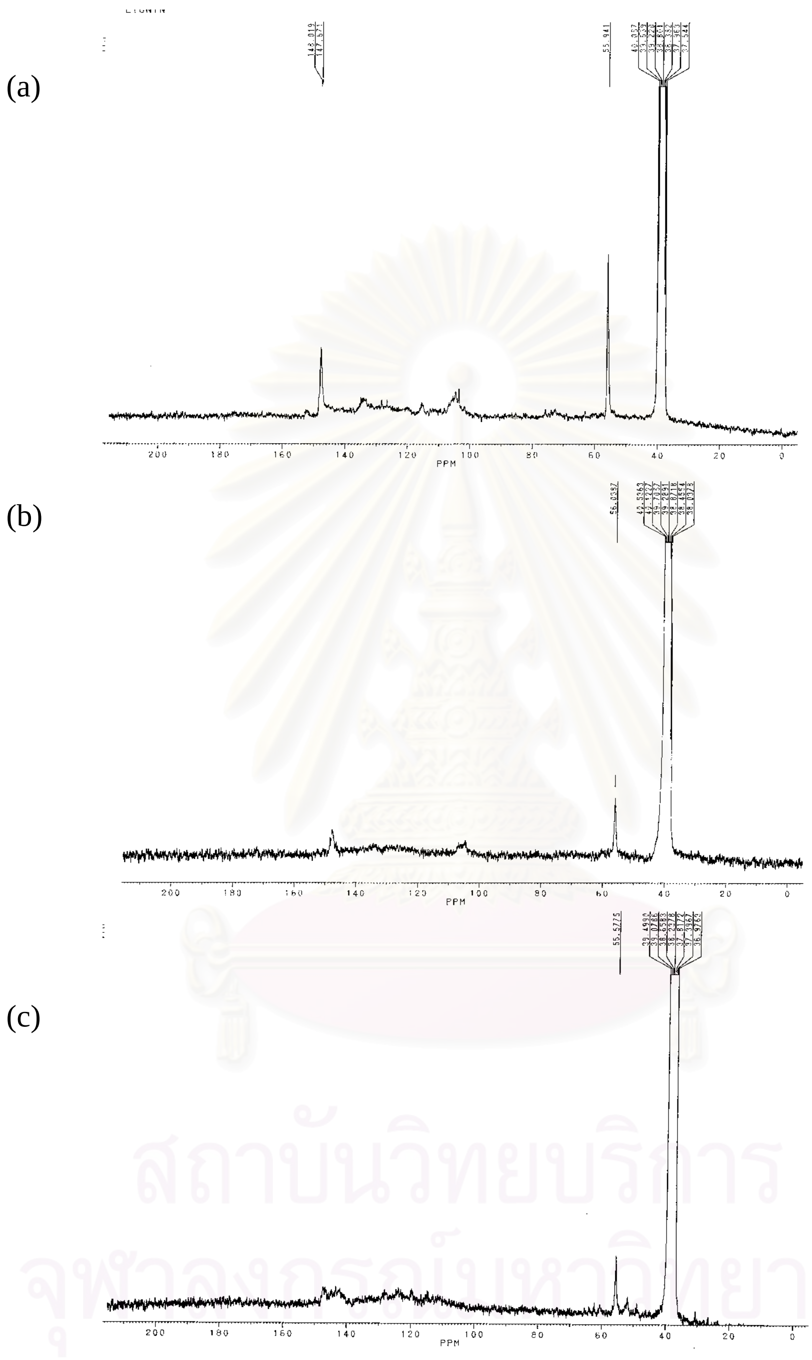


Figure 4.3 ^{13}C NMR spectra of (a) isolated lignin, (b) sodiumlignosulfonate and (c) commercial lignosulfonate

From Figure 4.3, the ^{13}C NMR spectra of synthesized sodium lignosulfonate did not show the signal of the carbon that links to a sulfonate group because this synthesized sodium lignosulfonate had low quantities of this sulfonated carbon in the sodium lignosulfonate structure in comparison with other carbons in the sodium lignosulfonate structure.

4.2.2 Sulfonation of isolated lignin with 65% fuming sulfuric acid

The isolated lignin was sulfonated with 65% fuming sulfuric acid to give the lignosulfonic acid. Then this lignosulfonic acid was neutralized with 5 M sodium hydroxide solution to give the sodium lignosulfonate. Yields of this synthesized sodium lignosulfonate are shown in Table 4.4

Table 4.4 Yields of sodium lignosulfonate from sulfonation of isolated lignin with 65% fuming sulfuric acid

Condition of sulfonation	Quantity of sodium lignosulfonate (g/10 g isolated lignin)
0.5:1 gram ratio of 65% fuming H_2SO_4: isolated lignin	6.01
1:1 gram ratio of 65% fuming H_2SO_4: isolated lignin	8.77
1.5:1 gram ratio of 65% fuming H_2SO_4: isolated lignin	8.81

From Table 4.4, sodium lignosulfonate from conditions 1:1 and 1.5:1 gram ratio of 65% fuming sulfuric acid: isolated lignin got similarly the highest yield. However, sodium lignosulfonate from condition 1:1 gram ratio of 65% fuming sulfuric acid: isolated lignin used 65% fuming sulfuric acid less than the other one. So this 1:1 condition was optimum condition for this synthesis. In addition, sodium lignosulfonate from sulfonation with 65% fuming sulfuric acid gave higher yield than sodium sulfonate from sulfonation with 96% sulfuric acid because of quantities of sulfur trioxide in 65% fuming sulfuric acid which added sulfonic group in isolated lignin structure was higher than sulfur trioxide in 96% sulfuric acid. The FT-IR, ^{13}C NMR, XRF and GPC results of sodium lignosulfonate in condition 1:1 gram ratio of 65% fuming sulfuric acid: isolated lignin are shown in Figure A3, C3, D2 and E3.

From Figure A3, FT-IR spectrum of sodium lignosulfonate from sulfonation with 65% fuming sulfuric acid appeared the signals of antisymmetric stretching of sulfonate salt at 1221 cm^{-1}, symmetric stretching of sulfonate salt at 1118 cm^{-1} and C-S vibration of sulfonate salt at 620 cm^{-1}.

From Figure C3, ^{13}C NMR spectrum of this synthesized sodium lignosulfonate gave detail to similar that of isolated lignin. Therefore its spectrum still could not identify carbon that links to sulfur of a sulfonate salt in sodium lignosulfonate.

From Figure D2, XRF of this sodium lignosulfonate indicated that sodium lignosulfonate structure had quanties of sulfur to be 10.62%. Therefore, this sodium lignosulfonate had the quantity of sulfonate salt in sodium lignosulfonate structure to be equal to the quanntity of sulfur got from XRF. However, its sulfur quantity was lower than sulfur quantity of commercial lignosulfonate (14.26% sulfur, shown in Figure D5).

From Figure E2, GPC of this sodium lignosulfonate shows M_w was 13,490, M_n was 9,322 and MWD was 1.447. However when GPC of this sodium lignosulfonate was compared with GPC of commercial lignosulfonate (Figure E5), M_w, M_n and MWD of sodium lignosulfonate from 65% fuming sulfuric acid sulfonation were lower than M_w, M_n and MWD of commercial sodium lignosulfonate (M_w= 21,602, M_n= 14,354 and MWD= 1.505)

4.2.3 Sulfonation of isolated lignin with sodium sulfite

Mechanism of sulfonation with sodium sulfite was shown in Figure 4.4

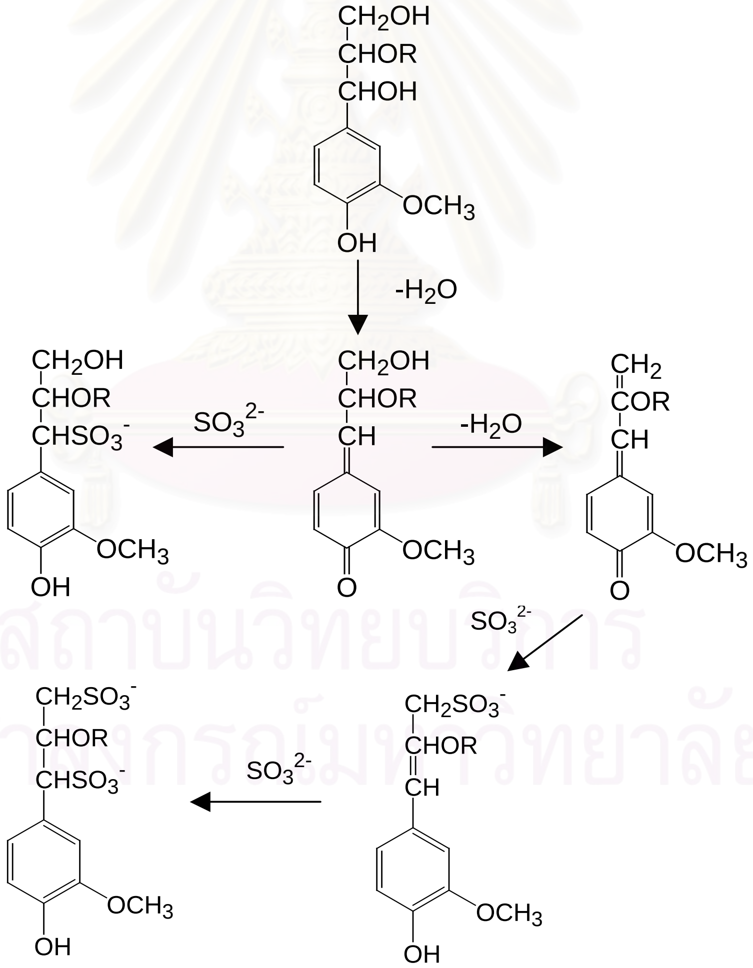


Figure 4.4 Mechanism of sulfonation of isolated lignin with sodium sulfite [60]

After finishing sulfonation of isolated lignin with sodium sulfite, the product was in form of sodium lignosulfonate. This sulfonation gave sodium lignosulfonate in low average yield of 3.87 g,/10 g isolated lignin. The FT-IR, ^{13}C NMR, XRF and GPC results of this sodium lignosulfonate are shown in Figures A4, C4, D3 and E4, respectively.

From Figure A4, FT-IR spectrum of sodium lignosulfonate from sulfonation of isolated lignin with sodium sulfite appeared the signals of antisymmetric stretching of sulfonate salt at 1201 cm^{-1}, symmetric stretching of sulfonate salt at 1118 cm^{-1} and C-S vibration of sulfonate salt at 615 cm^{-1}.

From Figure C3, ^{13}C NMR spectrum of this sodium lignosulfonate also gave detail to similar that of lignin. Therefore its spectra could not identify carbon that links to sulfur of sulfonate salt in sodium lignosulfonate.

From Figure D3, XRF of this sodium lignosulfonate indicated that sodium lignosulfonate structure had quanties of sulfur to be 10.77%. Thus this sodium lignosulfonate had the quantity of sulfonate salt in sodium lignosulfonate structure same the quanntity of sulfur that got from XRF. However, its sulfur quantity was lower than sulfur quantity of commercial lignosulfonate.

From Figure E3, GPC result showed M_w was 13,106, M_n was 9,694 and MWD was 1.352.

4.2.4 Sulfomethylation of isolated lignin

Mechanism of sulfomethylation of isolated lignin is shown in Figure 4.5

$$CH_2O \quad + \quad SO_3^{2-} \longrightarrow HOCH_2SO_3^-$$

$$HOCH_2SO_3^- \xrightarrow{H^+} H_2O^+CH_2SO_3^-$$

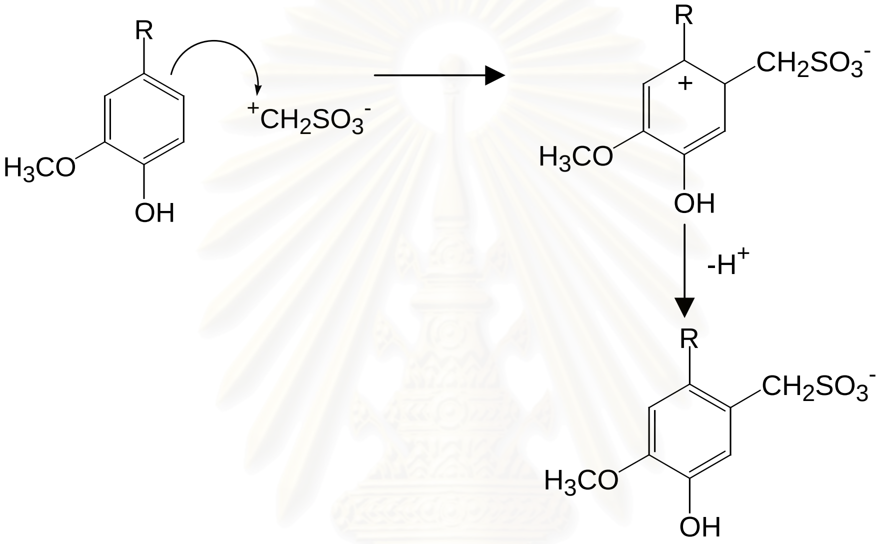


Figure 4.5 Mechanism of sulfomethylation of isolated lignin

After finishing sulfomthylation of isolated lignin with sulfomethylating agent, the product was in form sodium lignosulfonate Yields of sodium lignosulfonate from sulfomethylation in various conditions are shown in Table 4.5

Table 4.5 Yields of sodium lignosulfonate from sulfomethylation of isolated lignin in various conditions

Condition of sulfomethylation	Quantity of sodium lignosulfonate (g/10 g isolated lignin)
0.4:0.1:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 130 °C 2 h	12.06
0.5:0.119:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 130 °C 2 h	12.66
1:0.238:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 130 °C 2 h	12.71
0.5:0.119:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 130 °C 1 h	11.85
0.5:0.119:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 130 °C 6 h	12.58
0.5:0.119:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 100 °C 2 h	12.21

From Table 4.5, conditions of both 0.5:0.119:1 and 1:0.238:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin 130 °C 2 h got the highest yields of sodium lignosulfonate. However, sodium lignosulfonate from condition 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin 130 °C 2 h used reactant less than the other one. Therefore, this 0.5:0.119:1 gram ratio condition was optimum for these sulfomethylations. However, quantities of sodium lignosulfonates, which gave from each conditions, were not much differences in range 11.85-12.71 g. Therefore, although this optimum condition gave the highest sodium lignosulfonate yield, it may not suitable for application in term of industry. The FT-IR, ^{13}C NMR, XRF and GPC results of this synthesized sodium lignosulfonate from condition 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde:isolated lignin 130 °C 2 h are shown in Figures A5, C5a-C5b, D4 and E5.

From Figure A5, FT-IR spectrum of sodium lignosulfonate from sulfomethylation of isolated lignin appeared the signals of antisymmetric stretching of sulfonate salt at 1160 cm^{-1}, symmetric stretching of sulfonate salt at 1129 cm^{-1} and C-S vibration of sulfonate salt at 625 cm^{-1}.

From Figure C5a, ^{13}C NMR spectrum of this synthesized sodium lignosulfonate before washing with saturated sodium chloride solution, showed singlet peak at 74 ppm. This peak was methyl carbon of hydroxymethanesulfonate, which is an intermediate component which occurred during sulfomethylation reaction. Therefore, this component was removed from sodium lignosulfonate by washing with saturated sodium chloride solution. After washing with saturated sodium chloride solution, this intermediate component peak disappeared to show spectrum similar to ^{13}C NMR spectrum of lignin (Figure C5b).

From Figure D4, XRF indicated that sodium lignosulfonate had 15.90% quantities of sulfur, which got sulfur higher than sulfur in commercial lignosulfonate. .

From Figure E4, GPC result showed M_w was 18,118 M_n was 11,932. Its molecular weight is higher than that of isolated lignin and synthesized sodium lignosulfonate form other sulfonations because formaldehyde reactant which unreacted sulfomethylation linked between sodium lignosulfonate molecules together to get high molecular weight of sodium lignosulfonate [61] (Figure 4.6).

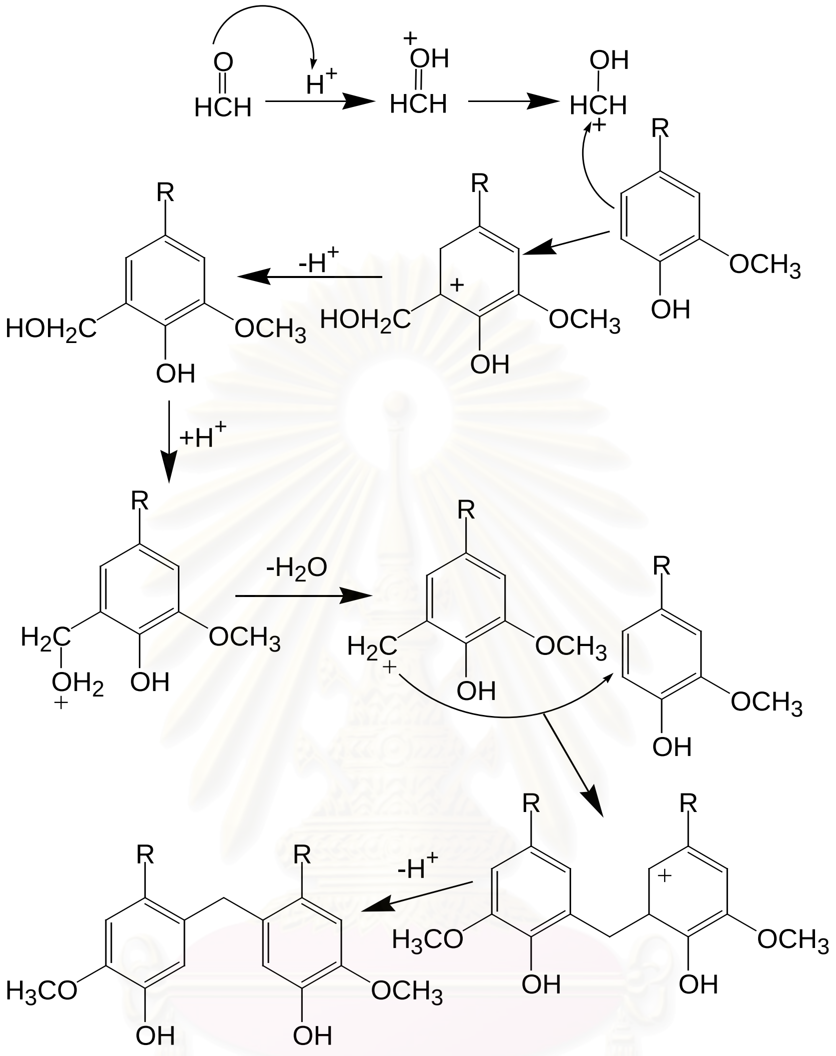


Figure 4.6 Linkation between lignosulfonate molecules with formaldehyde

Formaldehyde reaction also caused of higher molecular weight distribution, which MWD was 1.518.

4.3 Water solubility of synthesized lignosulfonate

From water solubility, their solubility is shown in Table 4.6.

Table 4.6 Solubility of synthesized lignosulfonate

Condition	Water solubility (g/1000ml)
Isolated lignin	-
1:1 gram ratio of 65% fuming H_2SO_4: isolated lignin	170
0.5:1 gram ratio of Na_2SO_3: isolated lignin 130 ^oC 2 h	200
0.5:0.119:1 gram ratio of Na_2SO_3: CH_2O: isolated lignin 130 ^oC 2 h	230
Commercial lignosulfonate	440

From Table 4.6, isolated lignin, which is insoluble in water, was changed to be sodium lignosulfonate by sulfonation or sulfomethylation. This synthesized sodium lignosulfonate can improve water solubility. Sodium lignosulfonate from sulfomethylation of isolated lignin in condition 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin give the highest water solubility when compared with synthsized sodium lignosulfonate from other sulfonation because this sulfomethylated sodium lignosulfonate has the highest sulfur quantities in strucure which increased that for product. However, its water solubility was lower than that of commercial lignosulfonate because these synthesized sodium lignosulfonates may come from different tree sources and they also possibly their structures were changed after treatment by chemical compounds in kraft pulping process.

4.4 Surface tension of synthesized lignosulfonate

Surface tension of sodium lignosulfonate from sulfomethylation in condition 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin at 130 °C 2 h which give the highest water solubility is compared with that of commercial lignosulfonate, as shown in Figure 4.7.

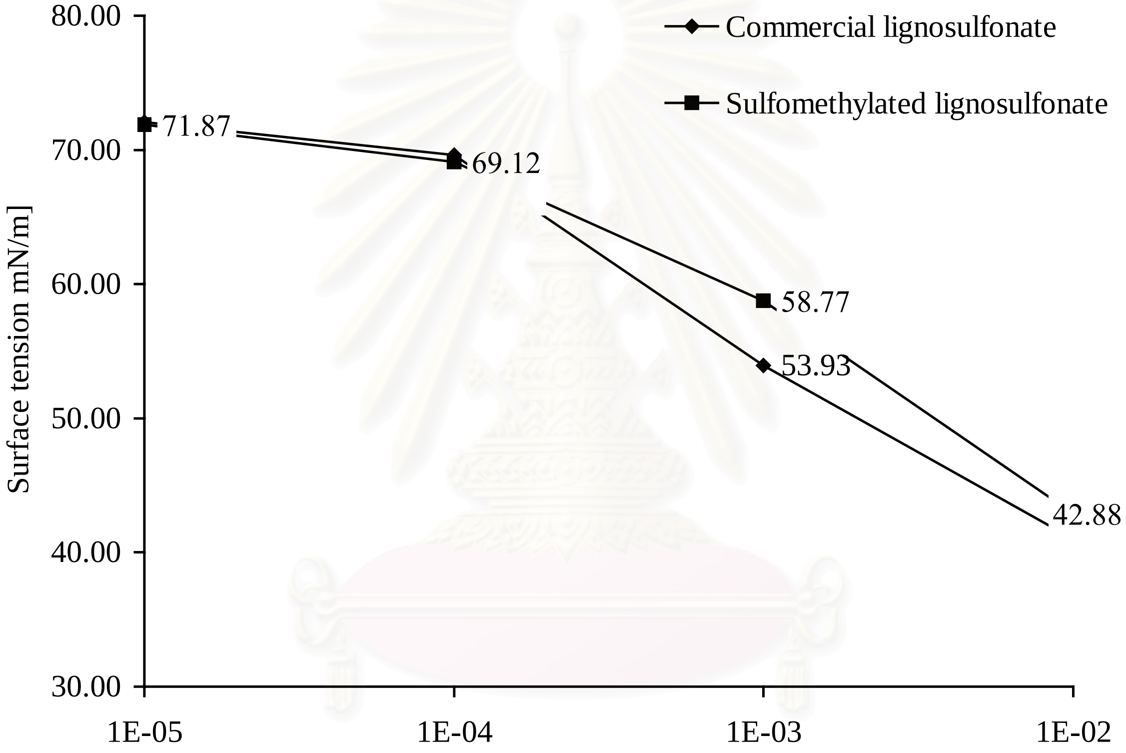


Figure 4.7 Surface tension values of lignosulfonate

From Figure 4.7, surface tension values of sulfomethylated sodium lignosulfonate and commercial lignosulfonate show similarly trend of surface activity. Therefore this sulfomethylated lignosulfonate can be used as surfactant for replacing commercial lignosulfonate.

CHAPTER V

CONCLUSION

From this study, it can be concluded that the isolation of lignin from eucalyptus kraft pulping black liquor after acid precipitation at pH 3 and washing with hot water, could get yield of purified lignin 188.13 g/ 1000 ml black liquor. Then isolated lignin was used to prepare the lignosulfonate compound by sulfonation with 96% sulfuric acid, 65% fuming sulfuric acid, sodium sulfite and sulfomethylating agent. The optimum condition for synthesis of lignosulfonate was carried out at 130 ^{o}C 0.5:0.119:1 by weight ratio of sodium sulfite: formaldehyde: lignin for 2 hours. The lignosulfonate yield was 12.66 g/ 10 g lignin. In addition, lignosulfonate from this synthesis with sulfomethylation was obtained with the highest quantities of sulfur in lignosulfonate structure, in comparison with lignosulfonate from other synthesis of sulfonation reaction. The sulfomethylated lignosulfonate also was linked between lignosulfonate molecules together by formaldehyde which unreacted sulfomethylation. Therefore, this linkation caused of getting higher molecular weight and molecular weight distribution than molecular weight and molecular weight distribution of synthesized lignosulfonate from other sulfonation.

From water solubility, lignosulfonate, which was prepared by sulfomethylation in condition 0.5:0.119:1 by weight ratio of sodium sulfite: formaldehyde: lignin 130 ^{o}C for 2 hours, was found to have the highest water solubility. However, its water solubility was lower than water solubility of commercial lignosulfonate. On the other hand, surface tension of this sulfomethylated lignosulfonate got similar surface activity to commercial lignosulfonate. Therefore this sulfomethylated lignosulfonate can be used as surfactant which similar to commercial lignosulfonate.

SUGGESTION FOR FUTURE WORK

In future work, other properties of lignosulfonate, such as dispersant and emulsifier, should be studied for information of applications of lignosulfonate.

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APPENDICES

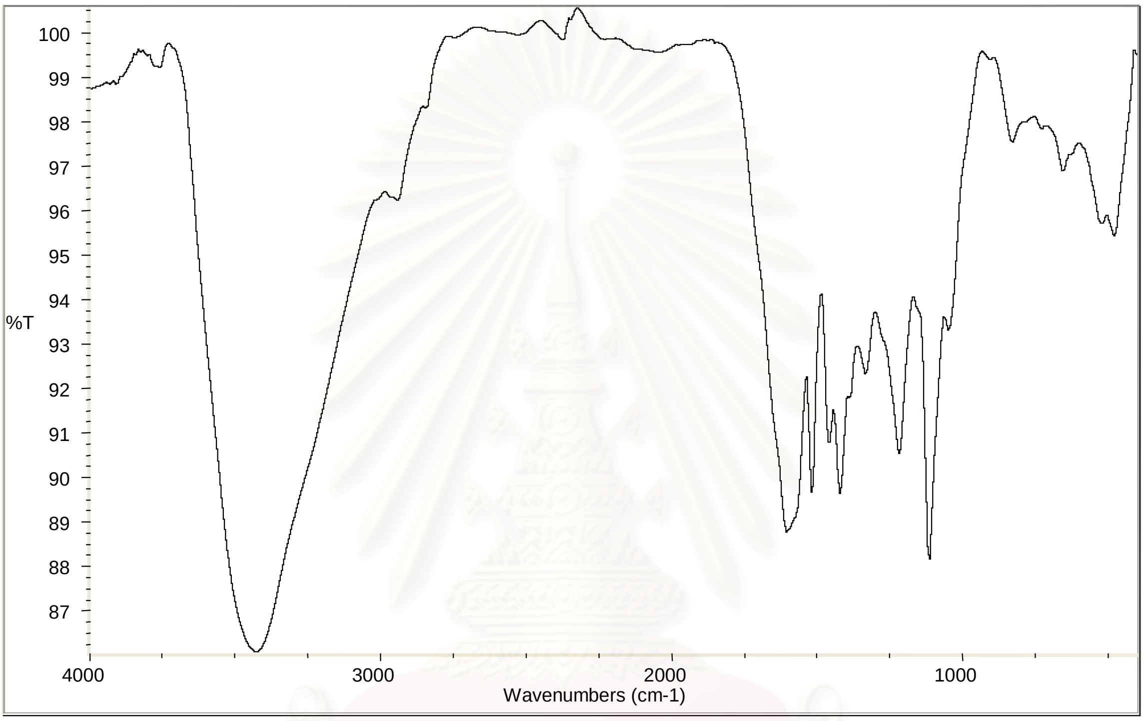


Figure A1 FT-IR spectrum of isolated lignin

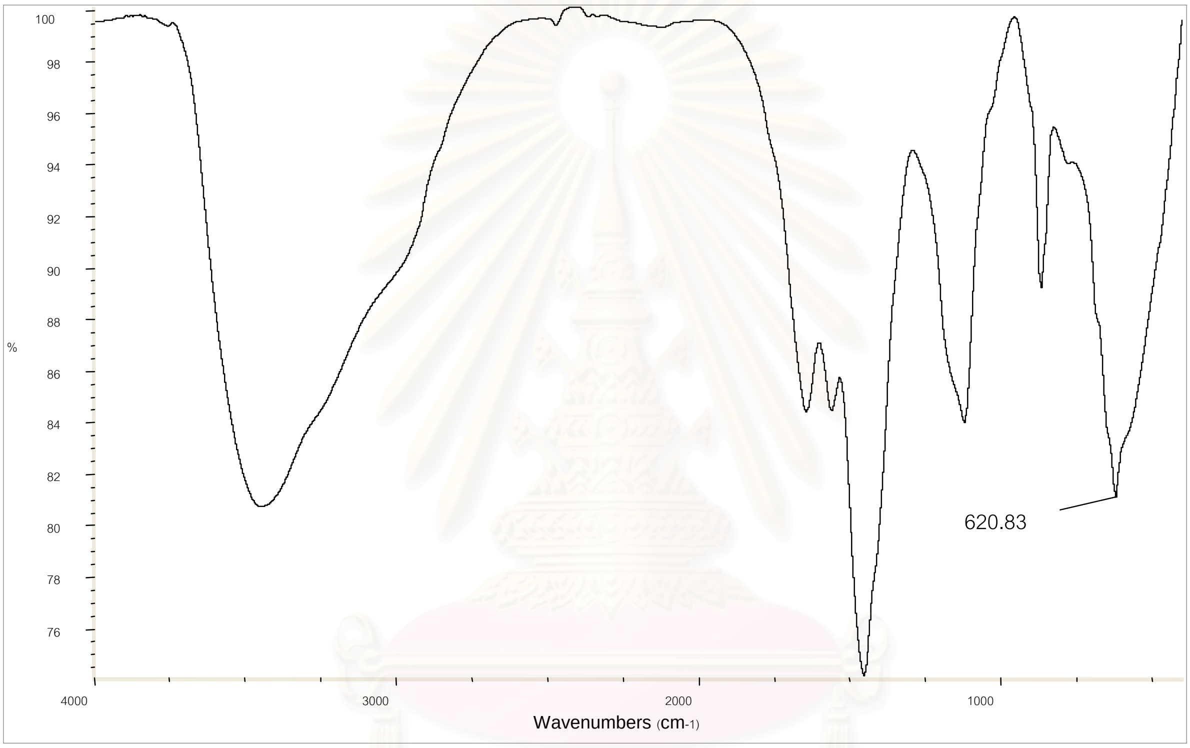


Figure A2 FT-IR spectrum of sodium lignosulfonate from sulfonation with 1:1 gram ratio of 96% sulfuric acid: isolated lignin

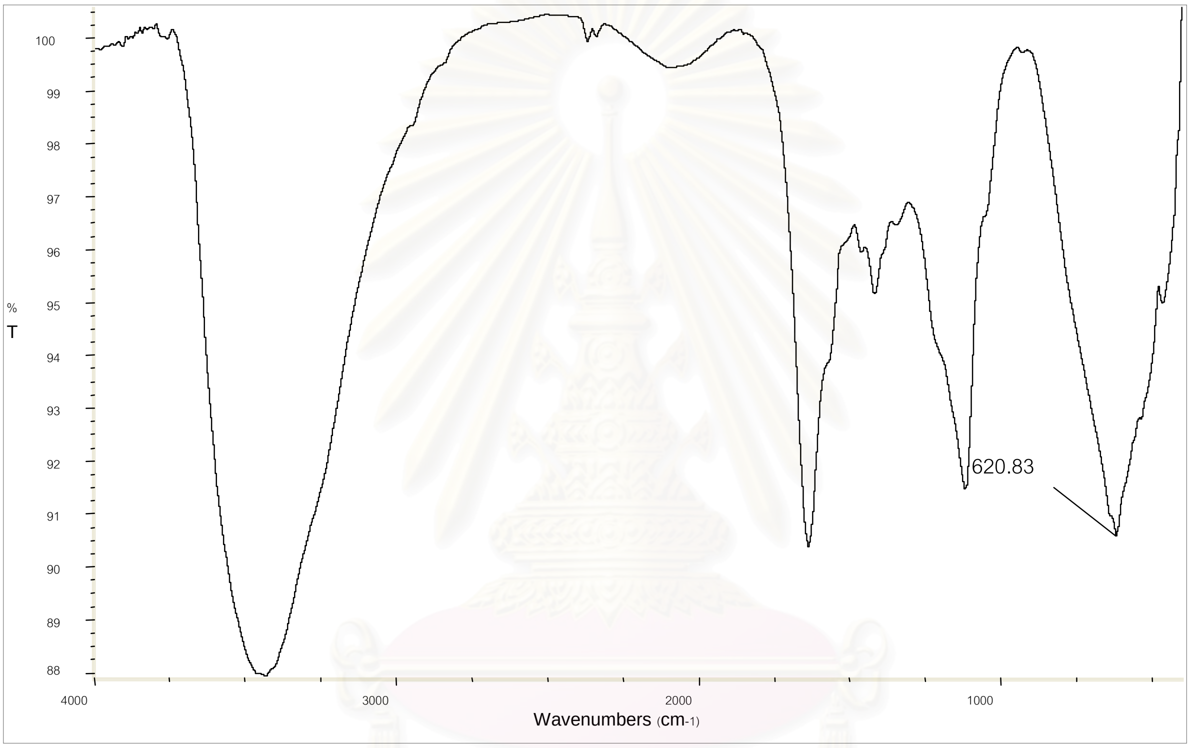


Figure A3 FT-IR spectrum of sodium lignosulfonate from sulfonation with

1:1 gram ratio of 65% fuming sulfuric acid: isolated lignin

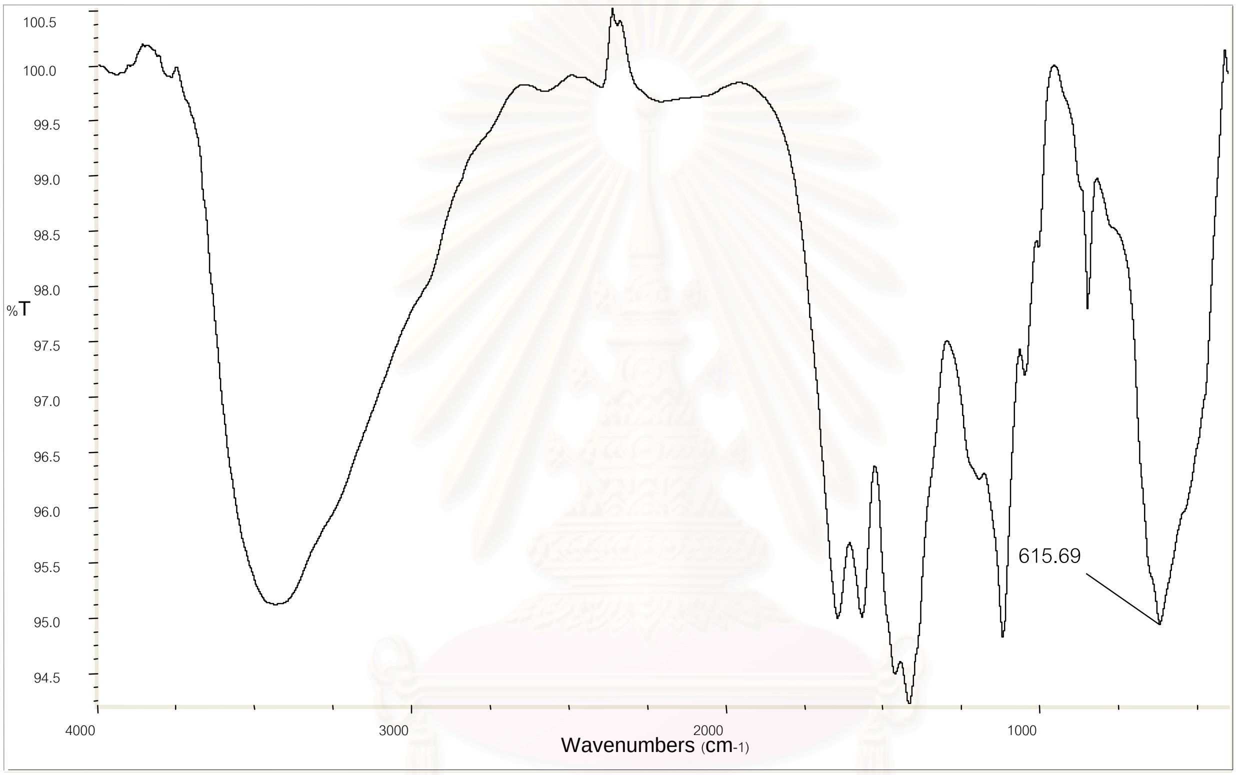


Figure A4 FT-IR spectrum of sodium lignosulfonate from sulfonation of isolated lignin with sodium sulfite

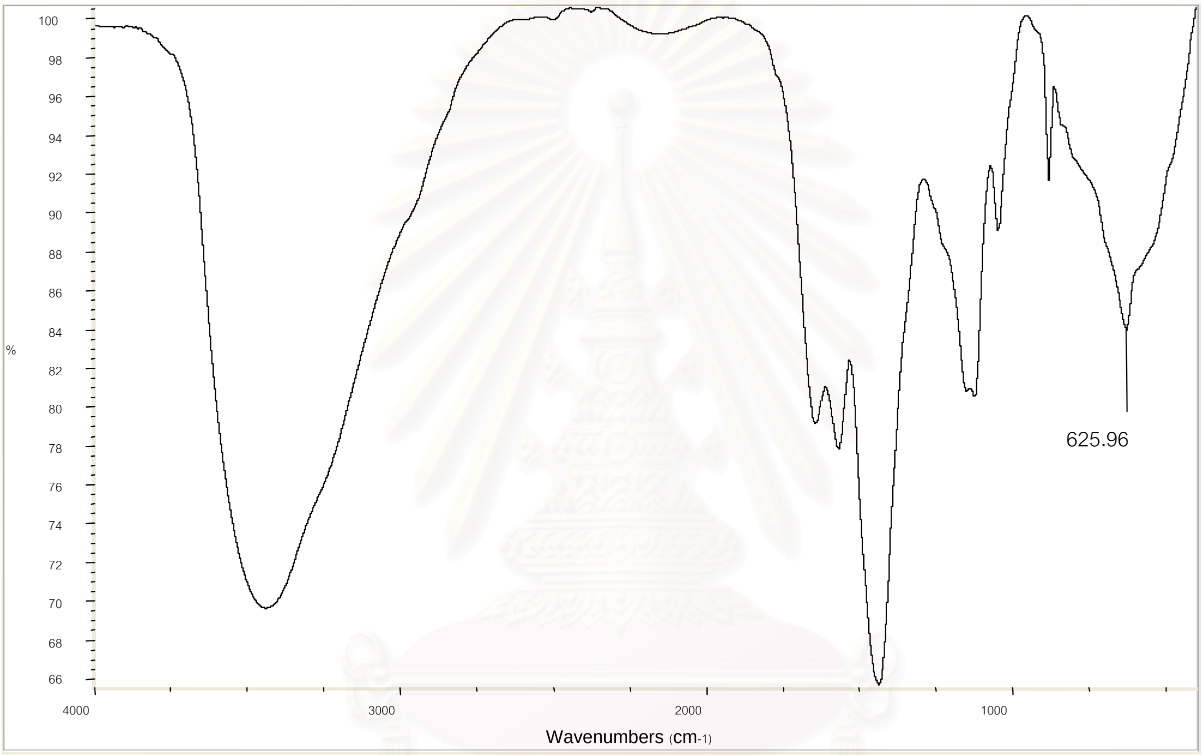


Figure A5 FT-IR spectrum of sodium lignosulfonate from sulfomethylation with 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin

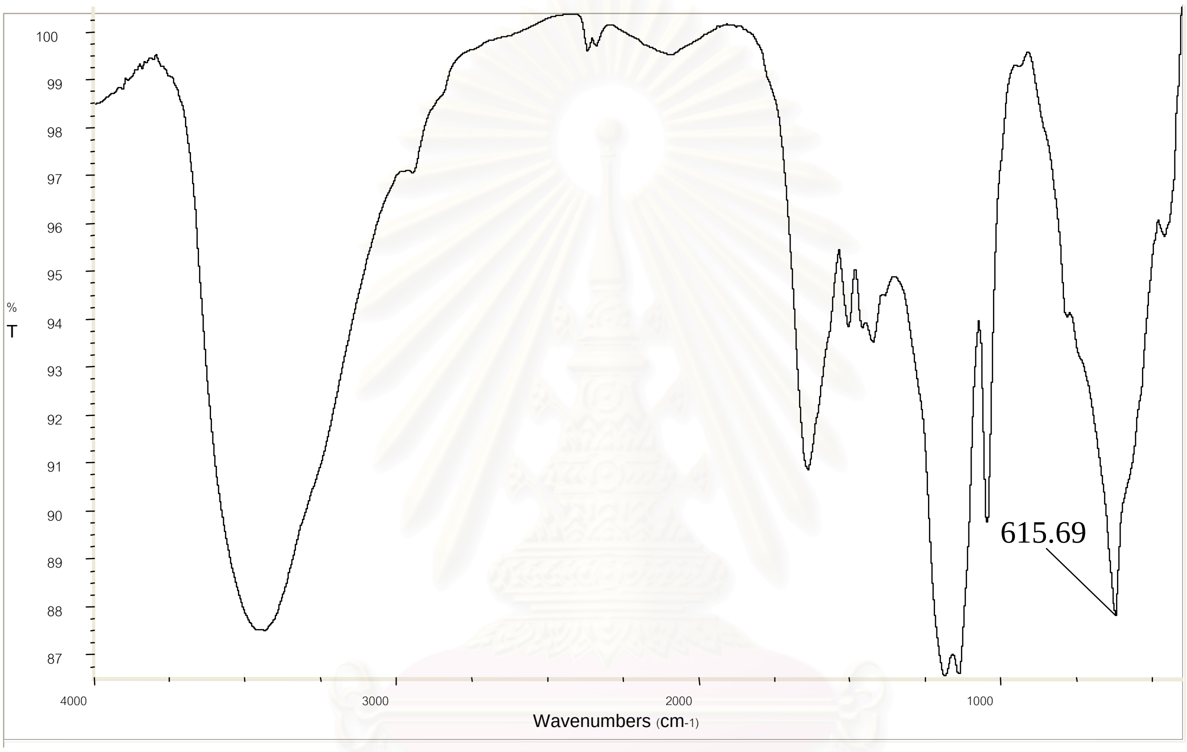


Figure A6 FT-IR spectrum of commercial lignosulfonate

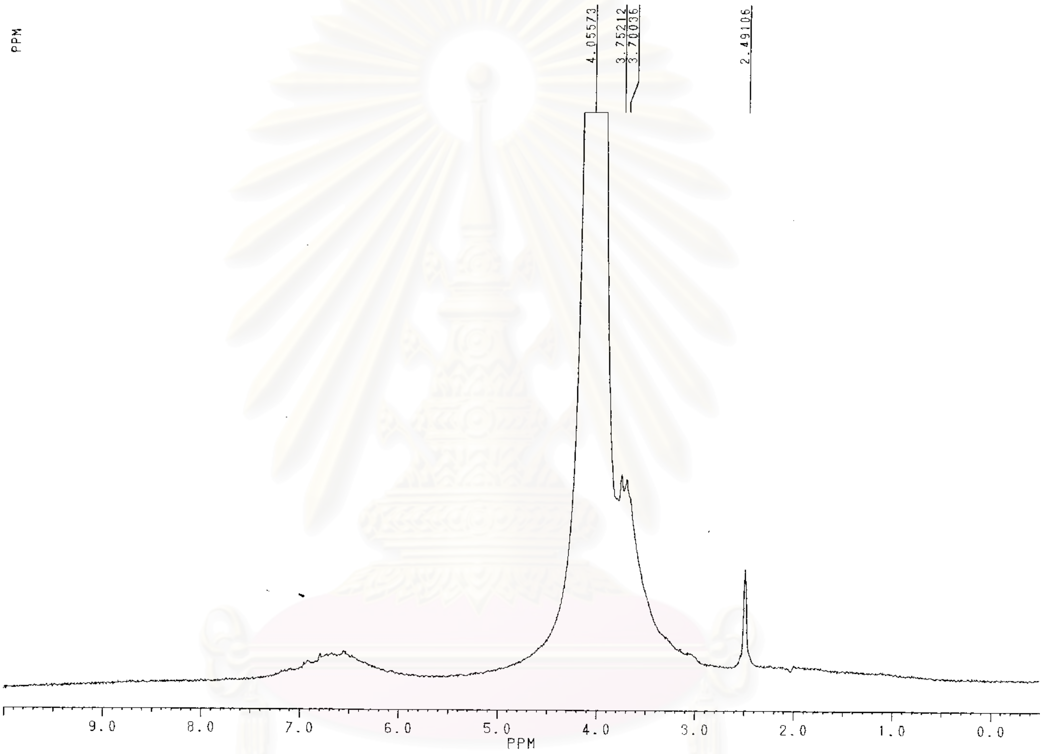


Figure B1 ^{1}H NMR spectrum of isolated lignin

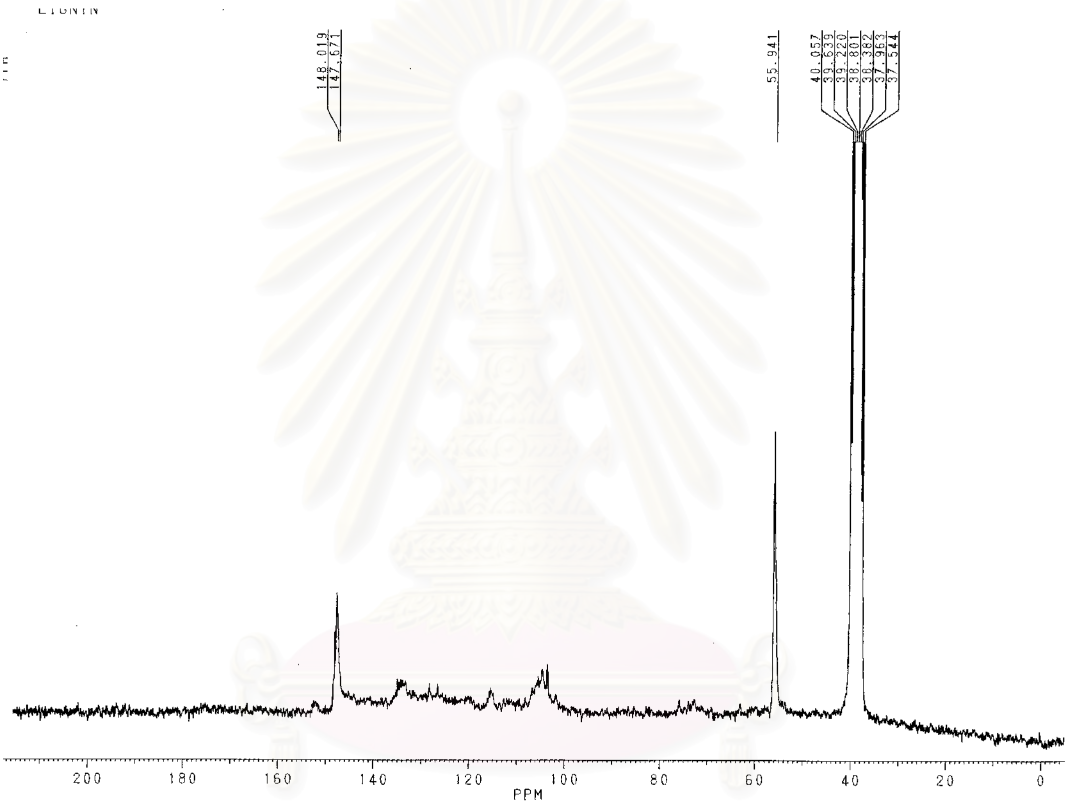


Figure C1 ^{13}C NMR spectrum of isolated lignin

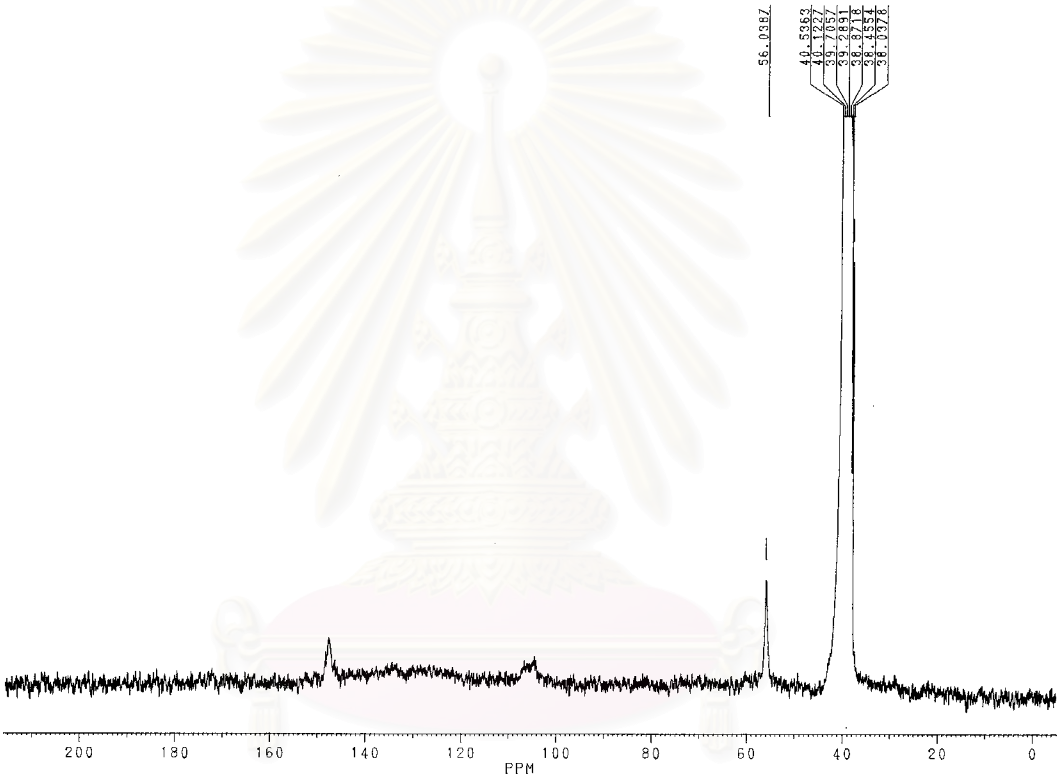


Figure C2 ^{13}C NMR spectrum of sodium lignosulfonate from sulfonation with 1:1 gram ratio of 96% sulfuric acid: isolated lignin

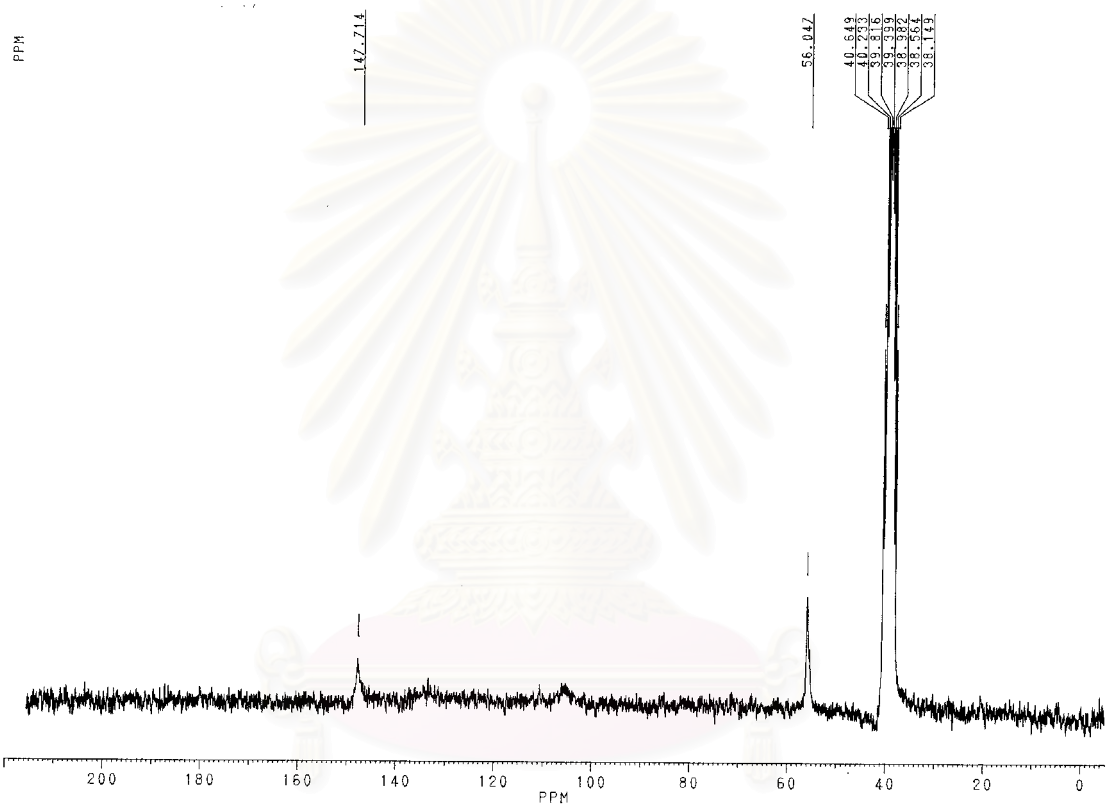


Figure C3 ^{13}C NMR spectrum of sodium lignosulfonate from sulfonation with 1:1 gram ratio of 65% fuming sulfuric acid: isolated lignin

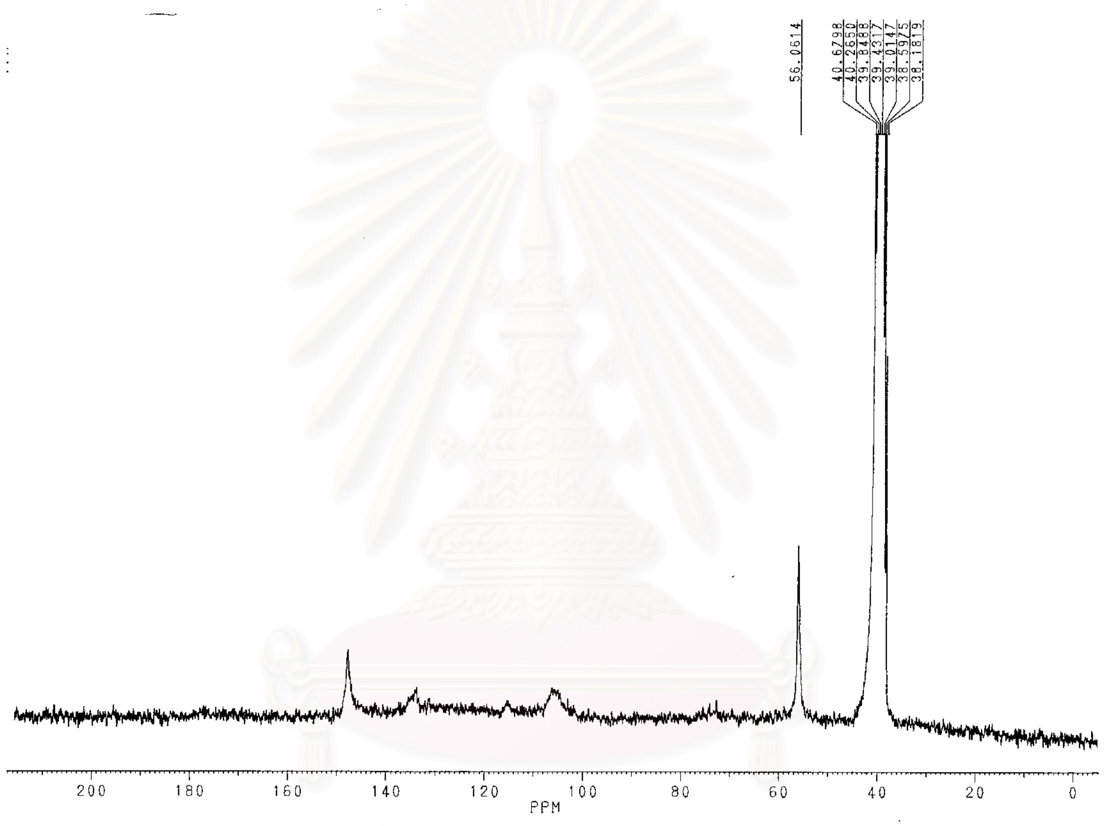


Figure C4 ^{13}C NMR spectrum of sodium lignosulfonate from sulfonation of isolated lignin with sodium sulfite

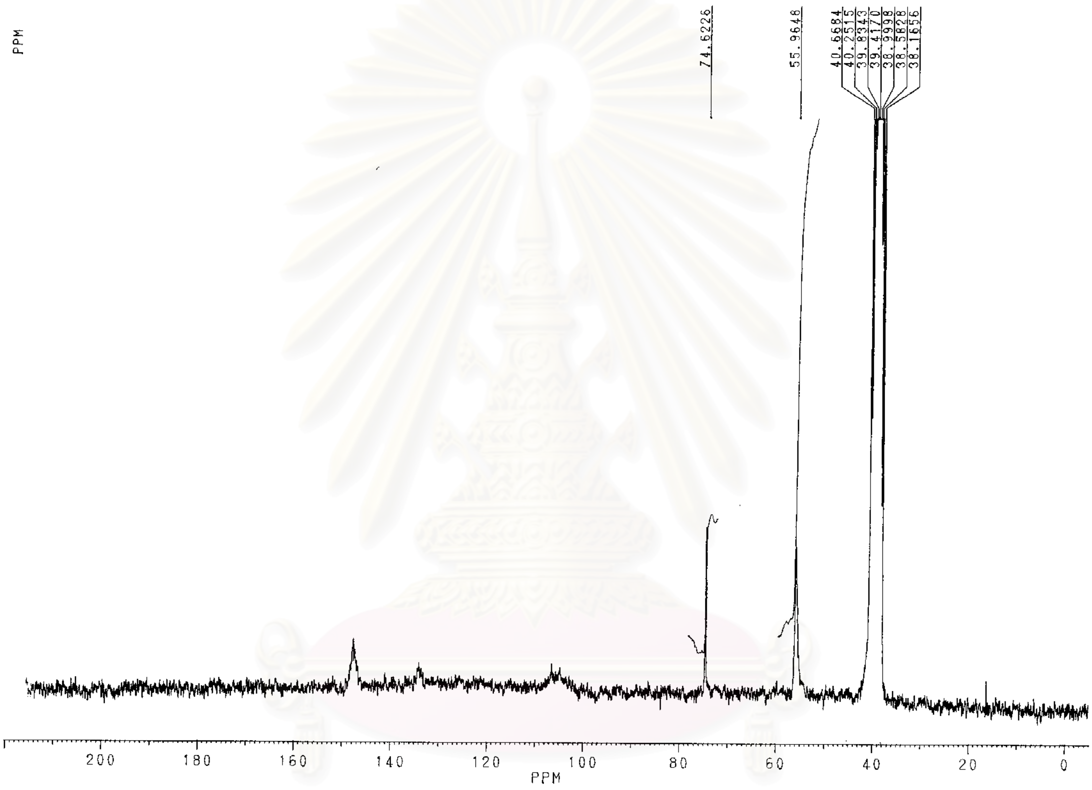


Figure C5a ^{13}C NMR spectrum of sodium lignosulfonate from sulfomethylation with 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin before washing with saturated sodium chloride solution

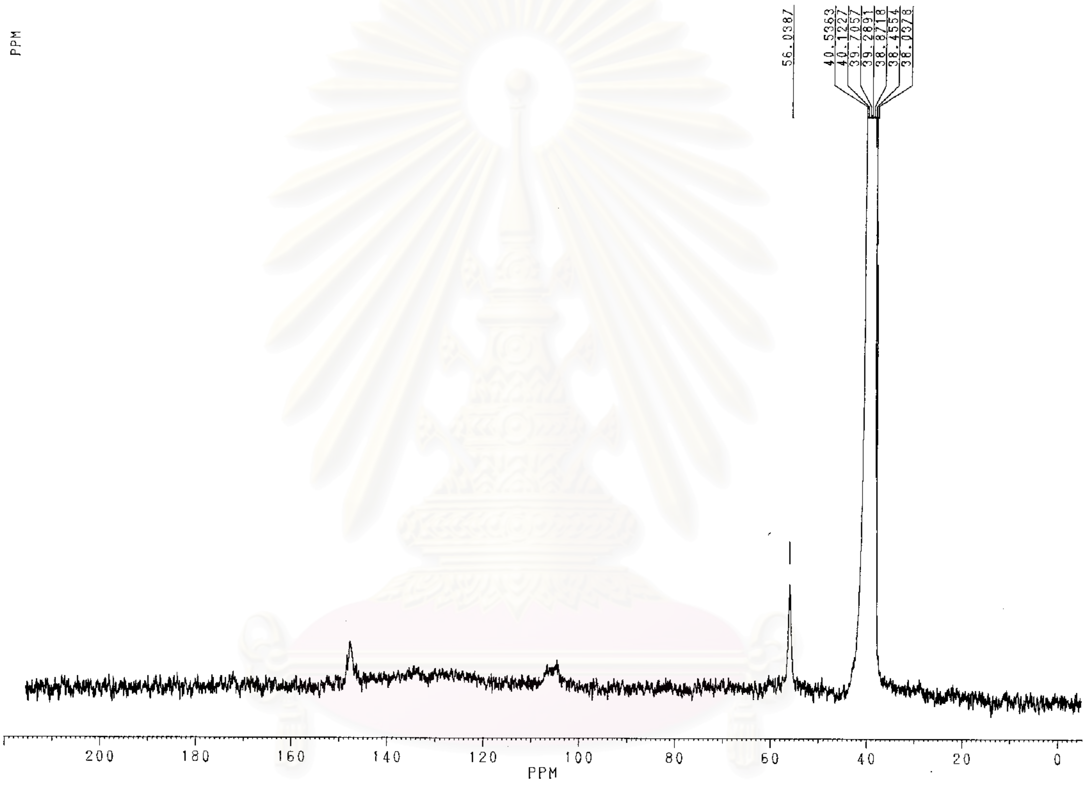


Figure C5b ^{13}C NMR spectrum of sodium lignosulfonate from sulfomethylation with 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin after washing with saturated sodium chloride solution

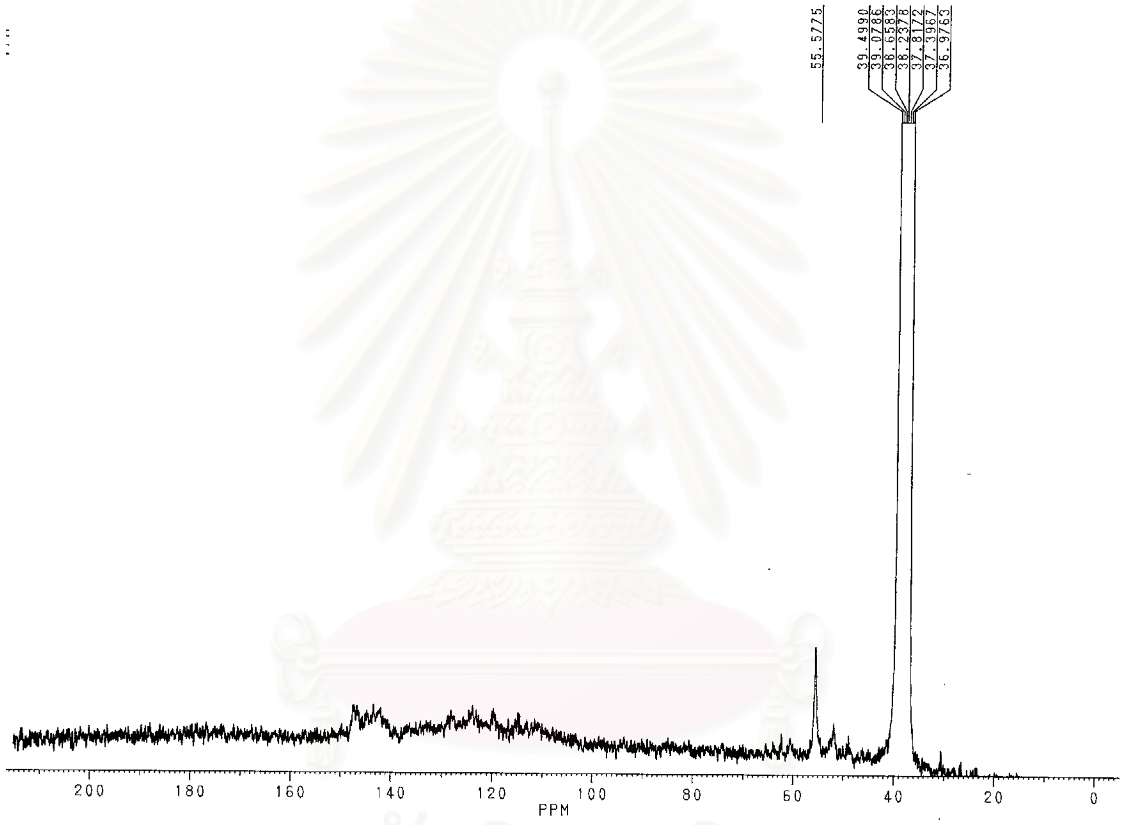
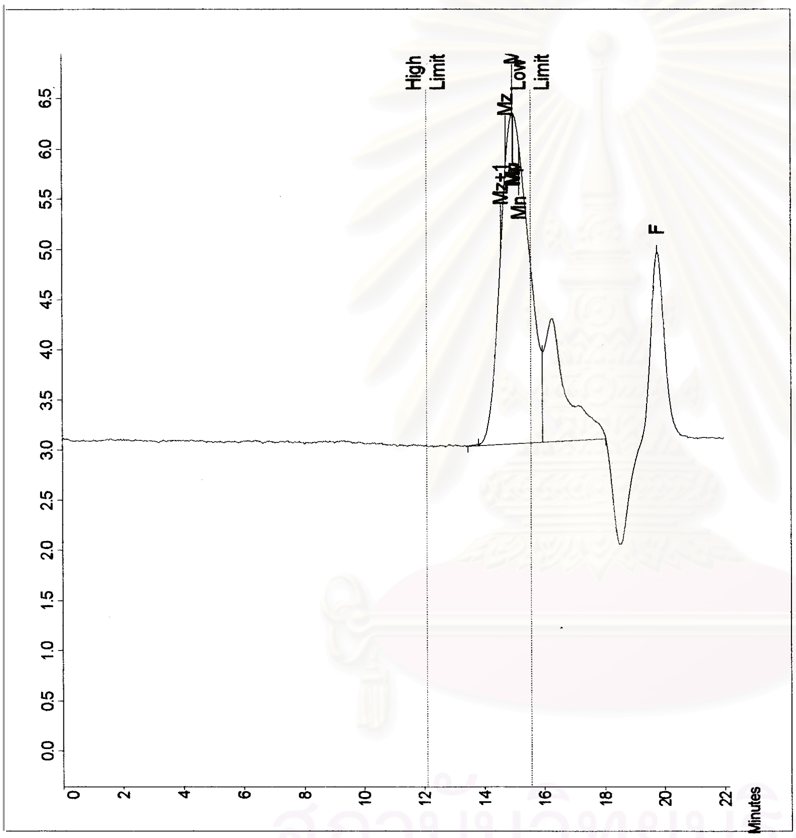


Figure C6 ^{13}C NMR spectrum of commercial lignosulfonate



M_p = 12929

M_n = 9481

M_w = 13192

M_z = 17788

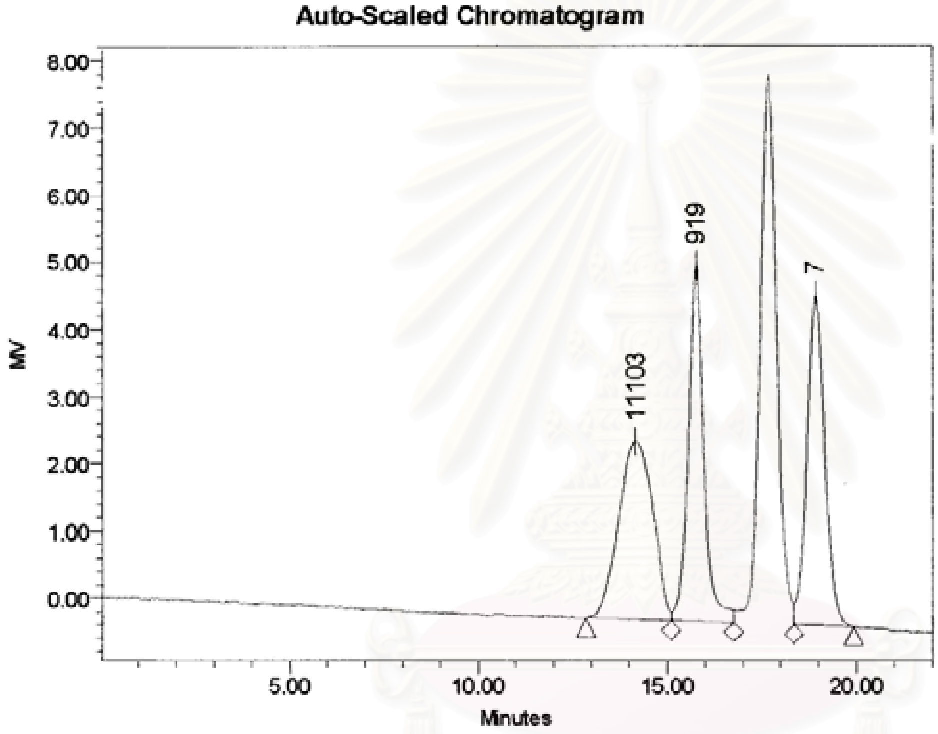
M_{z+1} = 22780

M_v = 12574

Polydispersity = 1.391

Peak area = 44333

Figure D1 GPC of isolated lignin



M_p = 11103

M_n = 9325

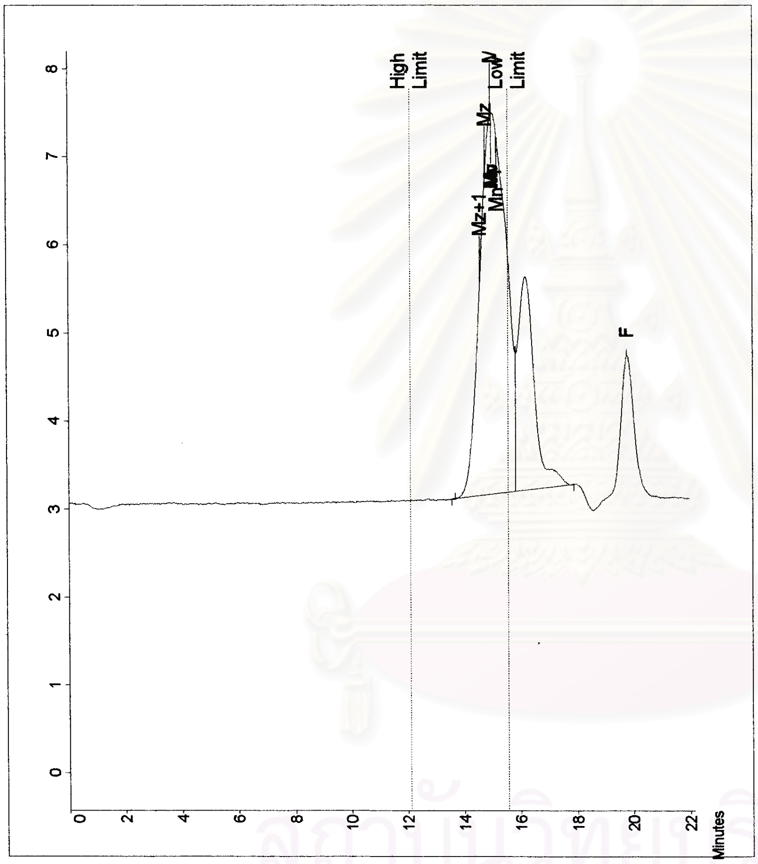
M_w = 13490

M_z = 19583

M_{z+1} = 27086

Polydispersity = 1.447

Figure D2 GPC of sodium lignosulfonate from sulfonation with 1:1 gram ratio of 65% fuming sulfuric acid: isolated lignin



M_p = 12628

M_n = 9694

M_w = 13106

M_z = 17615

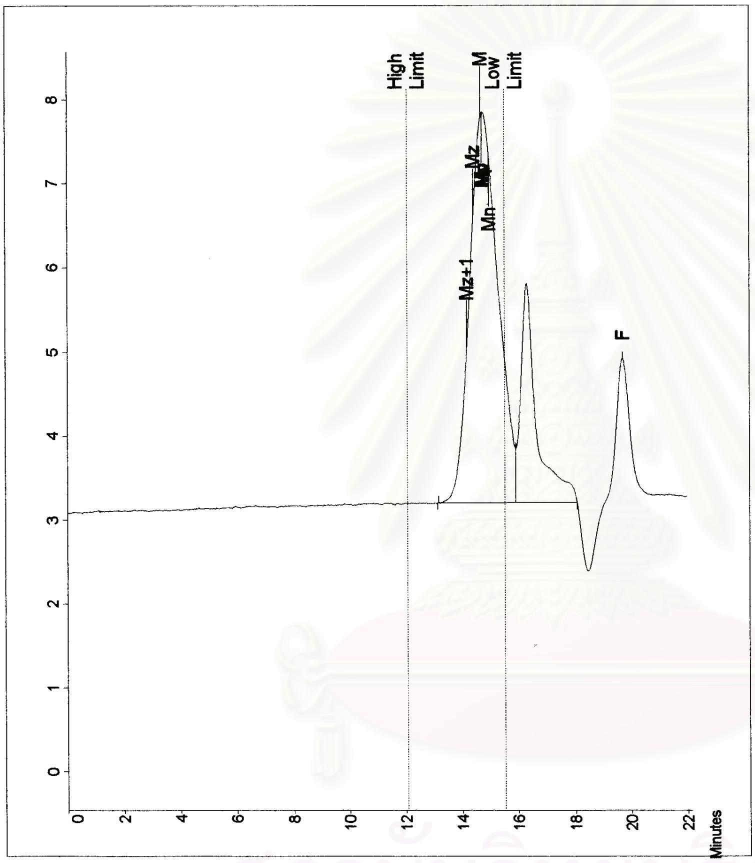
M_{z+1} = 22829

M_v = 12517

Polydispersity = 1.352

Peak area = 58054

Figure D3 GPC of sodium lignosulfonate from sulfonation of isolated lignin with sodium sulfite



M_p = 17058

M_n = 11932

M_w = 18118

M_z = 26638

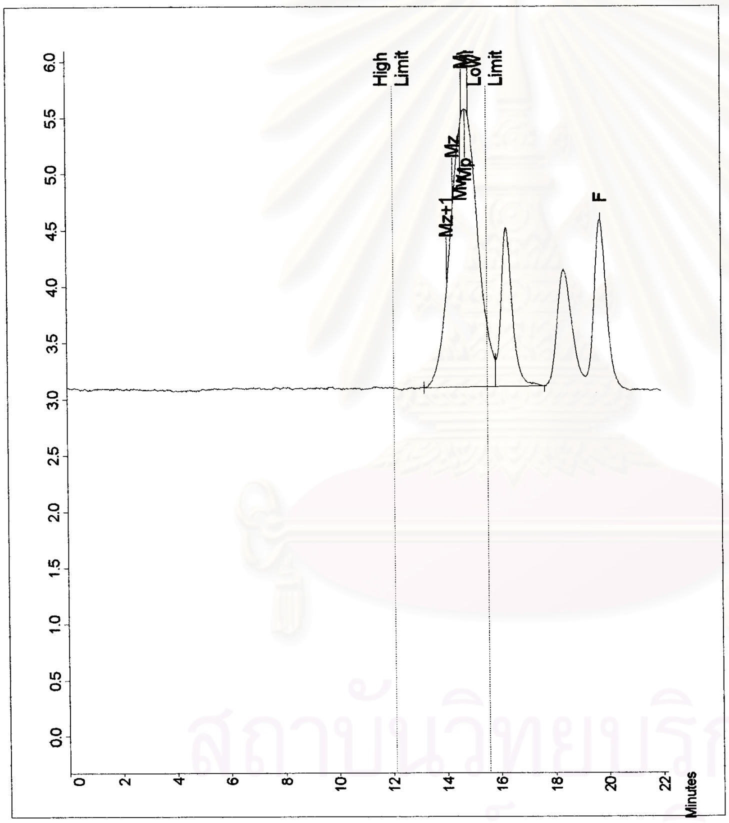
M_{z+1} = 37535

M_v = 17051

Polydispersity = 1.518

Peak area = 66879

Figure D4 GPC of sodium lignosulfonate from sulfomethylation with 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin



M_p = 16755

M_n = 14354

M_w = 21602

M_z = 32115

M_{z+1} = 45296

M_v = 20313

Polydispersity = 1.505

Peak area = 35520

Figure D5 GPC of commercial lignosulfonate

Analyte	Type	Calibration status	Compound	Concentration (%)	Calcuration method
Na	Sample	Calibrated	Na	0.057	Calcurate
Si	Sample	Calibrated	Si	0.011	Calcurate
S	Sample	Calibrated	S	0.418	Calcurate
Cl	Sample	Calibrated	Cl	0.189	Calcurate
K	Sample	Calibrated	K	0.319	Calcurate
Ca	Sample	Calibrated	Ca	0.031	Calcurate
V	Sample	Calibrated	V	0.020	Calcurate
Fe	Sample	Calibrated	Fe	0.025	Calcurate

Sum 0.9%

Figure E1 XRF of isolated lignin

Analyte	Type	Calibration status	Compound	Concentration (%)	Calcuration method
Na	Sample	Calibrated	Na	0.725	Calcurate
Al	Sample	Calibrated	Al	0.004	Calcurate
Si	Sample	Calibrated	Si	0.045	Calcurate
S	Sample	Calibrated	S	10.622	Calcurate
Cl	Sample	Calibrated	Cl	0.175	Calcurate
K	Sample	Calibrated	K	0.118	Calcurate
Ca	Sample	Calibrated	Ca	0.033	Calcurate
Fe	Sample	Calibrated	Fe	0.058	Calcurate
Ni	Sample	Calibrated	Ni	0.014	Calcurate

Sum 10.4%

Figure E2 XRF of sodium lignosulfonate from sulfonation with 1:1 gram ratio of 65% fuming sulfuric acid: isolated lignin

Analyte	Type	Calibration status	Compound	Concentration (%)	Calcuration method
Na	Sample	Calibrated	Na	0.8	Calcurate
Si	Sample	Calibrated	Si	0.009	Calcurate
S	Sample	Calibrated	S	10.766	Calcurate
Cl	Sample	Calibrated	Cl	0.149	Calcurate
K	Sample	Calibrated	K	0.118	Calcurate
Fe	Sample	Calibrated	Fe	0.015	Calcurate

Sum 11.9%

Figure E3 XRF of sodium lignosulfonate from sulfonation of isolated lignin with sodium sulfite

Analyte	Type	Calibration status	Compound	Concentration (%)	Calcuration method
Na	Sample	Calibrated	Na	2.526	Calcurate
Si	Sample	Calibrated	Si	0.052	Calcurate
S	Sample	Calibrated	S	15.895	Calcurate
K	Sample	Calibrated	K	0.114	Calcurate
Ca	Sample	Calibrated	Ca	0.034	Calcurate

Sum 18.6%

Figure E4 XRF of sodium lignosulfonate from sulfomethylation with 0.5:0.119:1 gram ratio of sodium sulfite: formaldehyde: isolated lignin

Analyte	Type	Calibration status	Compound	Concentration (%)	Calcuration method
Na	Sample	Calibrated	Na	1.887	Calcurate
Si	Sample	Calibrated	Si	0.009	Calcurate
S	Sample	Calibrated	S	14.264	Calcurate
Cl	Sample	Calibrated	Cl	0.425	Calcurate
K	Sample	Calibrated	K	0.268	Calcurate
Ca	Sample	Calibrated	Ca	0.037	Calcurate
Fe	Sample	Calibrated	Fe	0.071	Calcurate

Sum 17.0%

Figure E5 XRF of commercial lignosulfonate

Concentration [M]	Average surface tension (Nm/m)	
	Sulfomethylated Na-LS	Commercial LS
10^{-2}	42.88	40.99
10^{-3}	58.70	53.93
10^{-4}	69.12	69.61
10^{-5}	71.87	72.07

Table A Surface tension values of synthesized sodium lignosulfonate

VITAE

Mr. Supachet Pongsai was born on May 14, 1981 in Bangkok. He received a Bachelor’s Degree of Science in Chemistry from the Faculty of Science, Chulalongkorn University in 2002. He has been a graduate student studying Petrochemistry in the Program of Petrochemistry and Polymer Science at Chulalongkorn University since 2002.