

การดูดซับของโอเลฟินส์ในสารป้อนบีทีเอ็กซ์โดยใช้ดินเหนียว



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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์  
หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2545

ISBN 974-17-1213-8

ลิขสิทธิ์ของ จุฬาลงกรณ์มหาวิทยาลัย

ADSORPTION OF OLEFINS IN BTX FEEDSTOCK USING CLAYS



Miss Pennapa Klurvudtikul

สถาบันวิทยบริการ

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Petrochemistry and Polymer Science

Program of Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2002

ISBN 974-17-1213-8

**Thesis Title** : ADSORPTION OF OLEFINS IN BTX FEEDSTOCK USING  
CLAYS  
**By** : Miss Pennapa Klurvudtikul  
**Field of Study** : Petrochemistry and Polymer Science  
**Thesis Advisor** : Associate Professor Amorn Petsom, Ph.D.

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เพ็ญนภา เครือวุฒิกุล : การดูดซับของโอเลฟินส์ในสารป้อนบีทีเอ็กซ์โดยใช้ดินเหนียว  
(ADSORPTION OF OLEFINS IN BTX FEEDSTOCK USING CLAYS)

อาจารย์ที่ปรึกษา : รองศาสตราจารย์ ดร. อมร เพชรสม, 88 หน้า,

ISBN 974-17-1213-8

ได้ศึกษาการดูดซับของสารประกอบโอเลฟินส์ในสารป้อนบีทีเอ็กซ์ โดยใช้ดินในประเทศไทย 6 ชนิดได้แก่ เบนโทไนต์ ไคอะตอมไมต์ แทลคัม ดินขาว จังหวัดลำปาง ดินขาว จังหวัดระนอง และบอลเคลย์ โดยภาวะที่เหมาะสมในการดูดซับสารประกอบโอเลฟินส์ คือ ทำการทดลองที่อุณหภูมิ 120 °C เป็นเวลา 3 ชั่วโมง พบว่าดินต่างชนิดกันจะให้ค่าประสิทธิภาพในการดูดซับที่แตกต่างกัน ข้อมูลจากเอ็กซ์เรย์และอินฟราเรดสเปกโทรสโกปี ยืนยันว่า การปรับสภาพดินด้วยกรดมีผลต่อชั้นออกทอะไซด์รอนและเททระไซด์รอน ของดิน นอกจากนี้เพื่อให้ดินมีประสิทธิภาพในการดูดซับเพิ่มขึ้น จึงทำการเลือกแทลคัมและเบนโทไนต์ มาทำการพัฒนาโดยการปรับสภาพดินด้วยโพแทสเซียมคลอไรด์ แคลเซียมคลอไรด์ และเกลืออัลคิลแอมโมเนียม โดยเบนโทไนต์ที่ปรับสภาพแล้ว มีค่าการดูดซับโอเลฟินส์เพิ่มขึ้นเมื่อเทียบกับดินก่อนการปรับสภาพ อย่างไรก็ตามความสามารถในการดูดซับยังน้อยกว่าดินทอนซิล 616 จีเอสอี ที่มีจำหน่ายเชิงพาณิชย์ ส่วนแทลคัมที่ปรับสภาพด้วยโพแทสเซียมคลอไรด์และแคลเซียมคลอไรด์ให้ค่าการดูดซับโอเลฟินส์เท่ากับ 53.49 และ 58.07 เปอร์เซ็นต์ตามลำดับ ซึ่งความสามารถในการดูดซับนี้ทัดเทียมกับทอนซิล 616 จีเอสอี ที่มีจำหน่ายเชิงพาณิชย์

หลักสูตร... ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต.....

สาขาวิชา..... ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา..... 2545.....

## 4372357323 : MAJOR PETROCHEMISTRY AND POYMER SCIENCE

KEY WORDS : CLAYS / BTX FEEDSTOCK / ADSORPTION

PENNAPA KLURVUDTIKUL : ADSORPTION OF OLEFINS IN BTX FEEDSTOCK USING CLAYS. THESIS ADVISOR : ASSOCIATE PROFESSOR AMORN PETSOM, Ph.D., 88 pp. ISBN 974-17-1213-8

Six types of Thai clays, namely bentonite, diatomite, talcum, china (Lumpang), china (Ranong) and ball clay have been studied on the adsorption of olefins in BTX feedstock. The suitable condition for olefin adsorption is observed at 120 °C for 3 hours. The efficiencies of acid activated clays for olefin adsorption were investigated. The difference in adsorption efficiency appeared to be due to different types of clays. X-ray and FTIR data confirmed that the acid activation affected both the octahedral and tetrahedral sheets. For more adsorption efficiency, talcum and bentonite were selected to be modified with KCl, CaCl<sub>2</sub> and alkyl ammonium salt. Modified bentonite showed higher adsorption value than the original one. However, its adsorption capacity was less than that of commercial Tonsil 616GSE. Talcum modified with KCl and CaCl<sub>2</sub> exhibited 53.49 and 58.07% olefin adsorption, respectively. Their adsorption capability is comparable to that of commercial Tonsil 616GSE.

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Program..... Petrochemistry and Polymer Science..... Student's signature.....

Field of study... Petrochemistry and Polymer Science... Advisor's signature.....

Academic year..... 2002.....

## ACKNOWLEDGEMENT

I wish to express gratitude and appreciation to my advisor, Associate Professor Dr. Amorn Petsom, for his helpful suggestions, generous guidance and encouragement throughout this research. Gratefully thanks to Professor Dr. Pattaraphan Prasassarakich, Associate Professor Dr. Sophon Roengsumran, Assistant Professor Dr. Warinthorn Chavasiri and Dr. Thumnoon Nhujak, for their valuable suggestions and advice as thesis committee.

I also would like to gratefully thank Mrs. Jiraprapa Niampan from Department of Geology for making available the facilities of using X-ray powder diffraction. Many thanks to Süd-chemie (Thai) Co., Ltd. and Cernic international Co., Ltd. for clay supports. Moreover, thanks all of the members of Associate Professor Dr. Sophon Roengsumran's research group for their friendships and help during graduate study. I am also obliged to the Graduate School of Chulalongkorn University and Program of Petrochemistry and Polymer Science for their financial supports throughout this research.

Finally, I also thank my family for their continued supports, love and encouragement. Without them this thesis could not have been succeeded.

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## LIST OF SYMBOLS AND ABBREVIATIONS

BTX	=	Benzene Toluene Xylene
XRD	=	X-ray Powder Diffractometer
FTIR	=	Fourier transform infrared spectrometer
SEM	=	Scanning Electron Microscope
GCMS	=	Gas Chromatograph Mass Spectrometer
°C	=	Degree Celsius
ml	=	Milliliter (s)
g	=	Gram (s)
mg	=	Milligram (s)
meq	=	Milliequivalent (s)
MA	=	Methylammonium Chloride
DMA	=	Dimethylammonium Chloride
TMA	=	Tetramethylammonium Chloride
I.V.	=	Iodine value

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## CHAPTER I

### INTRODUCTION

BTX is an acronym for Benzene-Toluene-Xylene, which are aromatic hydrocarbons of most value and widely used as petrochemicals. They are important precursors for many plastics, such as nylon, polyurethane, polyester, polystyrene and alkyd resin. The other usages are mixed in fuel for increasing octane number and directly used as solvent in many industries. The demand for aromatics in Thailand and South East Asia (SEA) has been increasing, especially in Thailand which has a 10-15% average expansion up until several years [1].

Aromatic hydrocarbons, particularly benzene, toluene, and xylene (BTX), are a by-product formed in the production of gasoline in an oil refinery. The separation of BTX from other hydrocarbons, can be done by a catalytic reformer and an extraction device, results in a BTX mixture containing contaminants, particularly reactive contaminants, such as olefins and diolefins. These contaminants must be removed from the aromatics to obtain the aromatic hydrocarbons in a usable form.

Practically olefins and diolefins are removed from BTX by the treatment of BTX feed stock with clay in a fixed bed column. In Thailand, 1000 metric tons of clays are used annually. All of them are imported from foreign countries. Therefore it is very interesting to evaluate the possibility of using clays available in Thailand as sorbent for unsaturated compounds in BTX feedstock.



## Objective and scope of the research

The objective of this research is to study, the factors affecting performance of adsorption of olefin in BTX feedstock using various clays. The scopes were the following: 1) to find the highest olefin adsorption conditions for clay used in the treatment of BTX feedstock, and 2) to compare properties and structures of Thai clays with imported clay.



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## CHAPTER II

### THEORETICAL CONSIDERATION

#### 2.1 Basic of BTX plant [2]

Aromatic compounds are produced in a fully integrated process with the purpose of producing benzene, toluene and xylene. They are by-products formed in the production of gasoline in an oil refinery, catalytic reforming and naphtha cracking process.

A process for the removal of hydrocarbon contaminants, such as dienes and olefins, from an aromatic reformat by contacting an aromatic reformat stream with a hydrotreating catalyst and a molecular sieve. The hydrotreating catalyst substantially converts all dienes to oligomers and partially converts olefins to alkylaromatics. The process provides olefins depleted product, which can be passed through a clay treater to substantially convert the remaining olefins to alkylaromatics. The hydrotreating catalyst has a metal component of nickel, cobalt, chromium, vanadium, molybdenum, and tungsten being preferred. The molecular sieve is an intermediate pore size zeolite. Moreover, the clay treatment can be carried out with any clay suitable for treating hydrocarbon.

A typical complex is shown in Figure 2.1. In general, BTX is separated from the hydrocarbon mixture by fractionation distillation and extractive distillation. The  $C_8^+$  bottoms steam from the C7/C8 splitter is fed to clay treater (Bentonite clay) for removal of unsaturated compounds especially naphthene

and olefin, and color producing materials. The olefin content of BTX feedstock is measured by bromine index or iodine value.

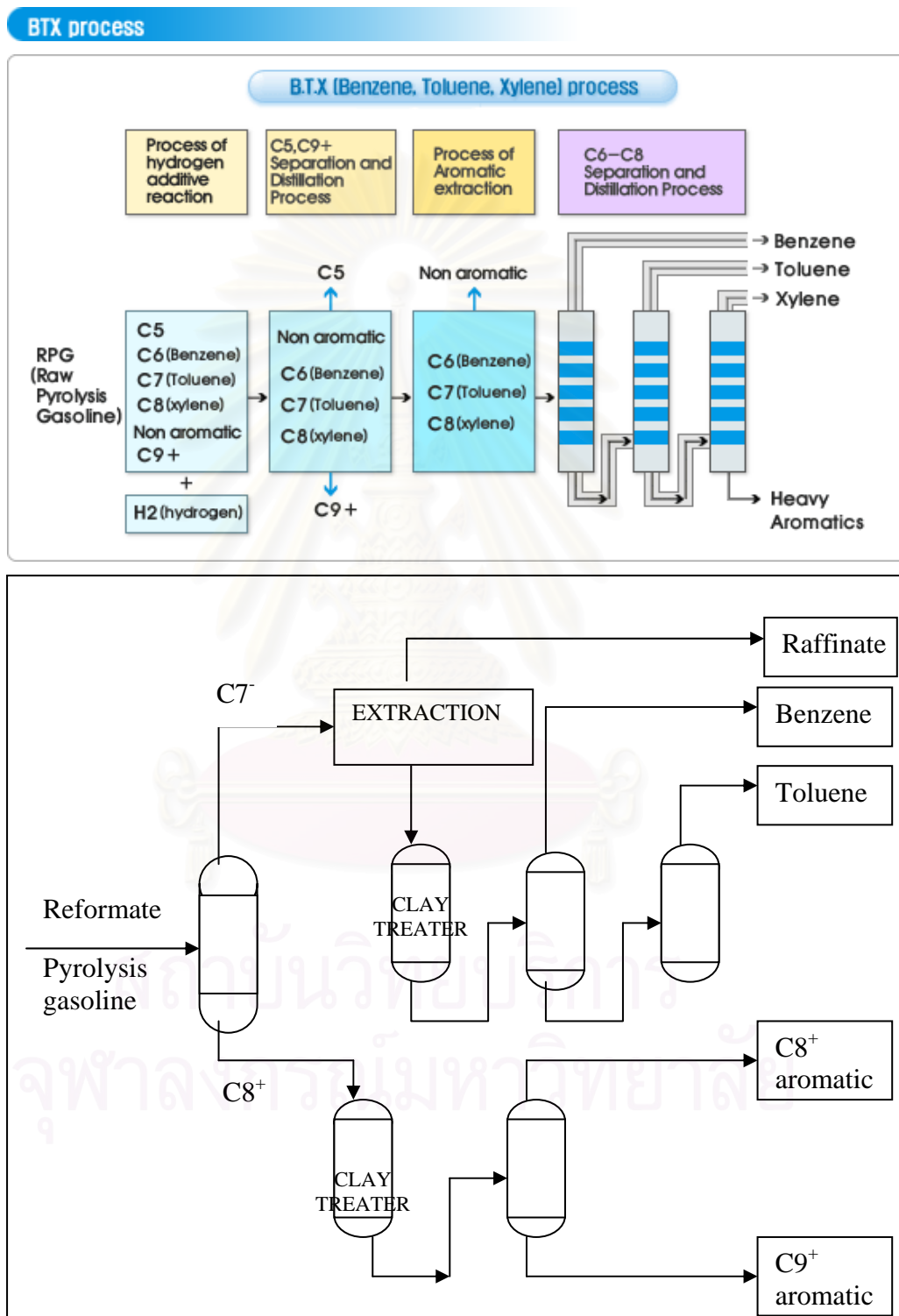


Figure 2.1 Typical BTX Plant simplified block diagram [2]

Olefins are objectionable in aromatic hydrocarbon, e.g. BTX, because of the following reasons. They are reactive and produce undesirable co-product in down stream processing, such as colored materials. Olefins in the production of various xylene derivatives can cause fouling in high temperature equipment, such as a xylene column reboiler.

The iodine value of BTX prior to treatment is usually high. After percolation through a fixed bed of clay, the iodine value will be decreasing. The spent Bentonite clay is usually steamed to remove any organic materials and then buried in an appropriate locally approved landfill.

## 2.2 Introduction of bentonite clay [3]

The term “bleaching earths” refers to clays that their natural states or after chemical or physical activations, have the capacity to adsorb coloring matters from oil. Bleaching earths are finely crystalline silicates of aluminum and/or magnesium with variable amounts of lime, alkalis and iron with a large proportion of water of hydration.

Bleaching clays are often classified as fuller's earths and Bentonites according to their inherent properties. The geological term “Bentonites” refer to any devitrification of volcanic ash. Mineralogically, bentonites are 75 percent or more of montmorillonites with fragment of kaolinite, illite feldspar and traces of other minerals.

The best known property of bleaching earth is its high adsorption capacity, which can be enhanced by acid treatment.

Bleaching clays in powder or granular form were used for the refining of petroleum products using two main processes: contact and percolation. In

the contact process, recovered oil, paraffin wax or liquid paraffin is previously treated with sulfuric acid to remove acid tar, and after its decantation the bleaching earth is added. In the percolation process, the solvent to be treated is passed through a tower containing a bed of bleaching clay granules.

### 2.3 Bentonite clay for treatment of BTX feedstock

Clay minerals are characterized by an extremely fine particulate construction and by a composition which is based primarily on oxygen and hydrated silicates of aluminum, iron and magnesium. The most important bentonite clay is the montmorillonite group of minerals. Figure 2.2, at the atomic level, montmorillonite possesses the layered sheet structural that is typical of most minerals. Each sheet consists of a three-layer sandwich of ions in octahedral form. The central layer consists of aluminium ions surrounded by oxygen ions in octahedral form. The outer layers are silicon ions surrounded oxygen ions in tetrahedral form.

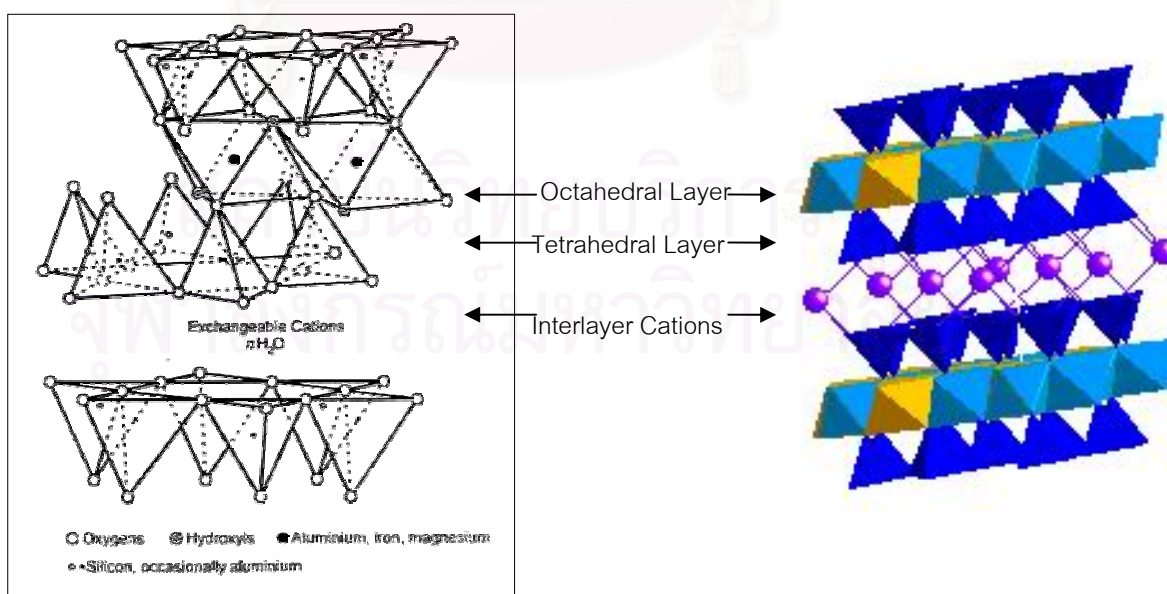
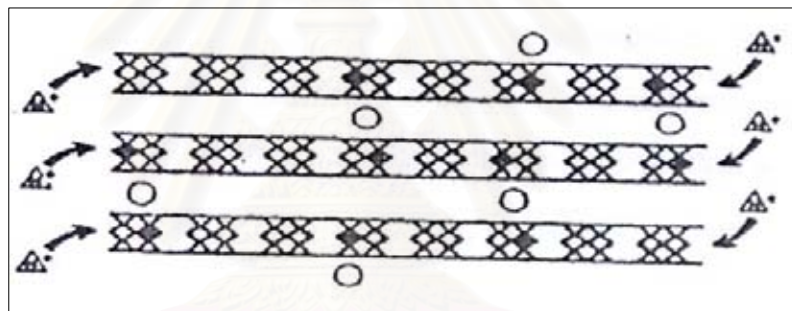


Figure 2.2 Structure of montmorillonite [4].

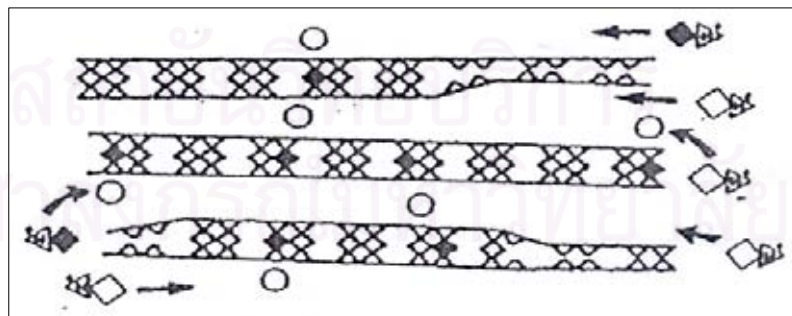
Acid activation enhances the natural ability of montmorillonites to adsorb polar molecules. The naturally occurring substitution of magnesium (+2) ions for aluminium (+3) ions in certain clay deposits leaves a negative charge, which thus requires a positive charge to achieve electroneutrality. This positive charge is supplied by cations, such as sodium (+1) or calcium (+2), which are located between the sheets.

Clay activation step by acid attack [2]

1. Acid attacks octahedral layer

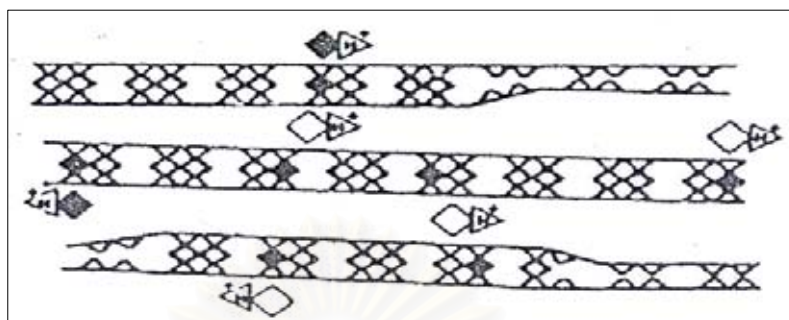


2. Structure disrupted surface area increases



3. Acid cations released from structure exchanged for cations

#### 4. Acid activated clay with acid cations in exchange sites



A well-controlled process has been developed to activate montmorillonites, exploiting the natural characteristics of its structure. The principle is to render soluble the structure cations in the octahedral layer, thus opening up the structure and increasing surface area. This allows more acidic (active) cations released from the octahedral layer to replace the less acidic cations originally present in the space between the sheets, thus increasing its characteristic acidic adsorption and catalytic nature.

There is considerable evidence that acidic (active) cations serve as the active sites in the activated clay. When a pigment molecule (polar impurity) approaches one of the active sites, a carbonium ion (organic cation) forms and replaces, or associates with, one of the active, acidic inorganic interlayer cations. Now anchored in place by electrostatic force, the captive pigment molecule can be removed from the system along with the clay by simple filtration.

Figure 2.3 shows general stages of manufacturing of acid activated bentonite clay process. These clays are used as catalyst and adsorbent in the chemical, petroleum and petrochemical industries.



Figure 2.3 Acid activated bentonite clay process [2]



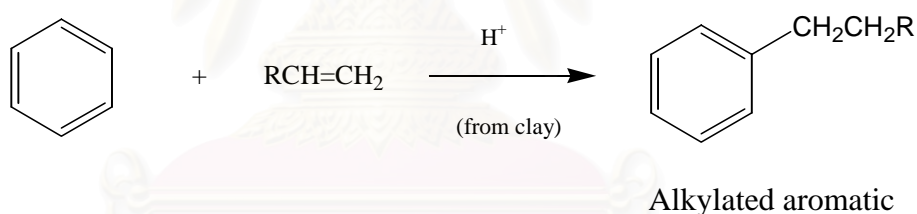
## 2.4 Reactions occurring on bentonite clays treatment of BTX [3]

Clay treatment of BTX is practiced when it is desired to clean up a BTX stream. During clean up, the olefin content of BTX is reduced.

Unsaturated compounds are normally present in feedstocks. Clay treating process consists of a two-part mechanism.

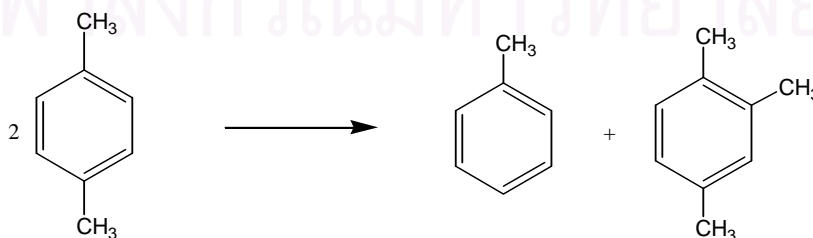
1. Adsorption of olefinic materials on active surface.
2. Polymerization and alkylation, by catalytic reaction with acid catalyst of the impurities to high boiling compounds that can be more easily removed downstream.

### Alkylation

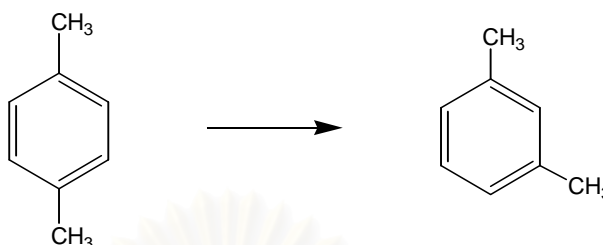


Side reaction occurring at high temperature:

### Disproportionation



## Isomerization



### 2.5 Literature reviews.

Novak and Petraitin [5] studied a BTX aging test, which can differentiate the olefin removal performance of clays during BTX clay treatment under accelerated aging conditions. During clay treatment, the olefin content of BTX as measured by bromine index is reduced.

Kumar et al. [6] evaluated the surface acidity and porosity of bentonite clay on treating with sulfuric acid. It was observed that clay treated with 4 N sulfuric acid showed the maximum surface acidity. Acid strength distribution as measured by Benesi's technique of nonaqueous titration shows acidity range mainly between  $H_0 + 4.6$  and  $+3.3$ . Nitrogen adsorption-desorption hysteresis data indicated the transformation of pores from slit-shaped to spheroid or inkbottle type as the acid concentration is increased from 1 to 8 N. X-ray diffraction and FTIR explained these observations in terms of structural modifications of clay on treatment with acid.

Breen et al. [7] studied acid-activated organoclays by treating with tetraalkylammonium-exchanged smectites. They investigated the catalytic

ability of acid-activated organoclays, which should provide reasonable levels of acidity, hydrophobicity, and swelling ability for use with nonpolar reagents. A range of organoclays containing tetramethylammonium, dodecyltrimethyl ammonium, or octadecyltrimethylammonium cations at 25, 50, or 100% exchange level was prepared and subjected for the selection of acid-leaching procedures at either 20 or 95 °C. Acid-leached tetramethylammonium clays were the most active with yields four times higher than those for the corresponding parent clay. Acid-leached dodecyltrimethyl ammonium and octadecyltrimethylammonium clays were only active when the organocations occupied 25% of the exchange sites.

Kooli and Jones [8] studied catalytic properties and characterization of saponite clay by powder X-ray diffraction, infrared spectroscopy and thermogravimetry. The leaching of Mg from the octahedral sheets is enhanced by an increase in the acid/clay ratio and by increase in temperature of activation. The desorption of cyclohexylamine indicates that for samples activated at 90 °C, the number of acid sites in the acid-activated saponites decreases following severe acid treatment. Infrared spectroscopy of adsorbed pyridine on samples after calcinations at 500 °C suggests that acid activation at 90 °C produce a single type of Brønsted site but two types of Lewis sites whereas activation at room temperature results in only one type. The dehydration of pentan-1-ol has been used as a further probe to measure acidity by monitoring the degree of conversion and selectivity for the different samples.

Fararas et al. [9] evaluated the acid-activated montmorillonite to bleach cottonseed oil. A progressive decrease in cation exchange capacity (CEC) values was observed by treating Ca-montmorillonite with sulfuric acid solutions and this can be understood in terms of the layered structure of the clay. Elemental analysis showed that moderate activation occurred and only 25-30% of the octahedral cations was removed. X-ray and FTIR data confirmed that acid activation affects both the octahedral and the tetrahedral sheets. The oil acid value was not affected by the bleaching procedure but a slight shift in the adsorption maximum of the beached cottonseed oil was observed. Medium activation of the clay (treatment with 4N H<sub>2</sub>SO<sub>4</sub>) was the most effective in bleaching the cottonseed oil, resulting in the best color index and the lowest peroxide value.

Díaz and Santos [10] studied on the acid activation of Brazilian smectitic clays used as bleaching earth for the industrial processing of vegetable, animal and mineral oils and waxes. The paper comments about the nomenclature used for these materials, the nature of the acid activation of smectitic clays (bentonites), activation laboratory procedures and presents a review of the acid activation bentonites from 20 deposits from several regions of Brazil. The activated clays were tested and showed good decolorizing power for soybean, castor, cottonseed, corn and sunflower oils.

Boyd et al. [11] studied mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. The adsorption of a series of *para*- and *meta*-substituted nitrobenzenes by K-smectite clay was measured. Adsorption isotherms were fit to the Freundlich equation. This relationship and positive

reaction constant ( $\rho = 1.15$ ) indicated that the adsorption reaction is favored by electron-withdrawing substituents. These results are consistent with an electron donor (smectite)-acceptor (substituted nitrobenzenes) mechanism offered previously. Rather, electron density donated by a second substituted on nitrobenzene appears to be appropriated by the nitro group leaving ring electrondensity uncharged. Fourier transform infrared spectroscopy revealed shifts in the  $-\text{NO}_2$  vibrational modes of 1,3,5-trinitrobenzene upon adsorption to K-smectite that was consistent with the complexation of  $\text{K}^+$  by  $-\text{NO}_2$  groups. Adsorption of substituted nitrobenzenes by smectite clays appears to result from the additive interactions of  $-\text{NO}_2$  groups and secondary substituents with interlayer  $\text{K}^+$  ions. Adsorption occurs to greater or lesser extent depending on the abilities of substituents to complex additional interlayer cations and water solubilities of substituted nitrobenzenes.



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## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

(1) Bentonite clay (standard), Tonsil 616GSE, was a commercial sorbent from Süd-chemie (Thai) Co., Ltd., produces in granular form (white solid). Typical properties and characteristics were:

Moisture content	14	%wt
Residual acidity	11	mgKOH/g
Particle size, Tyler Standard Sieve		
Passing 20 mesh	85	%wt
Passing 60 mesh	5	%wt
Apparent Bulk Density	0.8	gcc <sup>-1</sup>
Surface area (BET method)	350	m <sup>2</sup> g <sup>-1</sup>

(2) Thai clays were obtained from Cernic international Co., Ltd. They were:

1. Bentonite clay (Chantaburi Province)
2. Diatomite clay (Prajearburi Province)
3. Talcum clay (Utaradit Province)
4. China clay (Lumpang Province)
5. China clay (Ranong Province)
6. Ball Clay (Surathani Province)

(3) BTX feedstock was supplied from the TPI plant in Rayong. All studies of  $C_8^+$  stream in this research separated from C7/C8 splitter of BTX process which is shown in Figure 2.1. The chemical composition consists of aromatic (95%) and non-aromatic (5%), density 0.85-0.87, distillation range 130 to 210 °C and iodine value 17.7 mgI/100g.

(4) Chemical for clay modification

1. Methylammonium Chloride  $\geq 97\%$  BDH
2. Dimethylammonium Chloride  $>99\%$  Merck
3. Tetramethylammonium Chloride  $\geq 98\%$  Fluka
4. Potassium Chloride  $> 99\%$  Merck
5. Calcium Chloride  $>96\%$  Mallinckrodt

### 3.2 Apparatus and instruments

1. Scanning Electron Microscope (SEM)  
JEOL Japan JSM-541OLV SEM
2. Laser particle size analyzer  
Mastersizer S long bed Ver. 2.19
3. X-ray Powder Diffractometer (XRD)  
Bruker AXS GmbH D8 Advance XRD
4. Fourier Transform Infrared Spectrometer (FTIR)  
FTIR-Impact 410 Nicolet
5. Gas Chromatograph Mass Spectrometer (GCMS)  
GC from Carlo Erba Instruments 8060  
Trio 2000 from Fisons Instruments

### 3.3 Procedure

#### 3.3.1 The acid activation of clay

Fifty grams of clay was refluxed with 250 ml of 4 N  $\text{H}_2\text{SO}_4$  in a round-bottom flask at  $90^\circ\text{C}$  for 2 hours. The slurry was cooled in air and filtered through a sintered glass crucible. The filter cake was repeatedly washed with distilled water until the filtrate was neutral to litmus paper.

#### 3.3.2 Determination of clay properties

##### 3.3.2.1 Structure of clays

The structure of clay was characterized by X-ray powder diffractometry, scanning electron microscopy, particle size analysis and Fourier transform infrared spectrometry.

##### 3.3.2.2 Acidity

Acidity of clays was determined by volumetric titration. In this method, 0.5 g of the clay, previously dried at  $120^\circ\text{C}$  for 6 hours, was taken in a conical flask to which 15 ml of 0.1 N NaOH was added. After stirring the flask for 10 minutes, excess NaOH was titrated with 0.1 N  $\text{H}_2\text{SO}_4$ . Acidity was determined as milliequivalents of NaOH used per 100 g of clay.



$$\text{Acidity of clay (meq/100 g clay)} = \frac{(V1 - V2) \times [H_2SO_4] \times 100}{\text{amount of clay}}$$

Where: **V1** is the volume of NaOH, **V2** is the volume of H<sub>2</sub>SO<sub>4</sub>, and [H<sub>2</sub>SO<sub>4</sub>] is the H<sub>2</sub>SO<sub>4</sub> concentration.

### 3.3.3 Determination of iodine value

The iodine value is defined by the amount of halogen (calculated by the number of grams of iodine) absorbed by 100 g of the sample. The iodine values of the samples were determined following the Japanese Industrial Standard JIS K 0070-1966 (see Appendix B).

About 3 g of the sample was weighed accurately into a 250 ml iodine flask and 10 ml of Wijs' solution was added and tightly stopper with a glass stopper wet with potassium iodide solution (5%) in order to prevent volatilization of iodine and gently swirl the flask. The flask was kept in a dark place at room temperature for 30 minutes and the flask was swirled occasionally.

Aliquot of 50 to 70 ml of potassium iodide solution (5%) was added, swirl the flask and titrate with N/10 thiosulfate solution until the solution turns pale yellow. Then, one ml of starch solution was added and the titration was continued, with swirling, until the blue color of iodine-starch disappears. The blank titration was carried out in the same manner.

Calculate the iodine value, I.V., by the following formula:

$$\text{I.V.} = \frac{(\text{B}-\text{A}) \times f \times 1.269}{\text{S}}$$

Where: **A** is the volume of N/10 sodium thiosulfate solution consumed in actual titration (ml), **B** is the volume of N/10 sodium thiosulfate solution consumed in blank titration (ml), **f** is the factor of N/10 sodium thiosulfate solution and **S** is the weight of sample (g).

### 3.3.4 Treatments of reformat BTX feedstock with clays

Clay was refluxed with BTX feedstock at various times and temperatures. The performance of olefin removal from the treatment of BTX feedstock was monitored by iodine value (JIS K0070).

#### 3.3.4.1 The optimum treated time

Each 0.5 gram of clay was refluxed with 25 ml of BTX feedstock at 150 °C in round-bottom flask at various times as shown in Table 3.1.

Table 3.1 The optimum treated time

Sample	Temperature (°C)	Time (hours)	Weight of clays (grams)
Clay-1	150	1	0.5
Clay-2	150	2	0.5
Clay-3	150	3	0.5

### 3.3.4.2 The optimum temperature

Each 0.5 gram of clay was refluxed with 25 ml of BTX feedstock for 3 hours in round-bottom flask at various temperatures as shown in Table 3.2.

Table 3.2 The optimum temperature

Sample	Temperature (°C)	Time (hours)	Weight of clays (grams)
Clay-180	180	3	0.5
Clay-150	150	3	0.5
Clay-120	120	3	0.5
Clay-90	90	3	0.5
Clay-30	30	3	0.5

### 3.3.4.3 The optimum amount of clay

Clay was refluxed with 25 ml of BTX feedstock at 120 °C for 3 hours in a round-bottom flask for various amounts as shown in Table 3.3.

**Table 3.3 The optimum amount of clay**

Sample	Temperature (°C)	Time (hours)	Weight of clays (grams)
Clay-2.00	120	3	2.00
Clay-1.00	120	3	1.00
Clay-0.50	120	3	0.50
Clay-0.25	120	3	0.25
Clay-0.12	120	3	0.12

### 3.3.4.4 Analysis of BTX feedstock

The BTX feedstock before and after treatment with clays was characterized by GC-MS using DB-5 MS column, injection with splitless mode at 250 °C, oven 45 - 220 °C at 10 °C/min. This instrument identified hydrocarbon compositions with the library search program.

### 3.3.4.5 Modification of clay

Two grams of clays were prepared by adding the raw clay to a solution containing sufficient 1 M methylammonium chloride (MA), dimethylammonium chloride (DMA), tetramethylammonium chloride (TMA), potassium chloride (KCl) or calcium chloride ( $\text{CaCl}_2$ ). The suspensions were heated at 60 °C for 5 hours with stirring. The slurry was cooled and washed twice with deionized water. The solid was dried at 120 °C for 6 hours. Then clay was treated with acid following the above procedure (see 3.3.1).

Activated clays were refluxed with BTX feedstock at 120 °C for 3 hours and determined olefin adsorption by iodine value. This procedure was repeated three times.

## CHAPTER IV

### RESULTS AND DISCUSSION

In this research, all trials for development of Thai clay used for BTX purification process took into account the iodine value of BTX feedstock after refluxing with clays. The first attempt was the modification of clay by choosing the most effective Thai clay, bentonite and talcum. However, after refluxing with methylammonium chloride, dimethylammonium chloride and tetramethylammonium chloride they did not give better results than the original clays. The second attempt was carried out by refluxing clay with potassium chloride and calcium chloride at 60 °C for 5 hours and activated with 4 N H<sub>2</sub>SO<sub>4</sub>. After acid treatment, the iodine values of all clays used were found to decrease especially talcum, which has lower value than standard. This indicates that modified talcum has higher adsorption performance than does the import clay standard.

#### 4.1 Determination of clay properties

The differences in properties of acid-activated and non acid-activated clay in terms of structure and acidity of the clay sample were determined.

##### 4.1.1 Acidity characterization

The total acidity of clay (determined by sodium hydroxide titrations and expressed in meq of NaOH used per 100 g of clay) was presented in Figure

4.1. Talcum after acid activation exhibited the maximum acidity (78.21 meq/100 g) followed by bentonite, diatomite, ball, china R and china L, respectively.

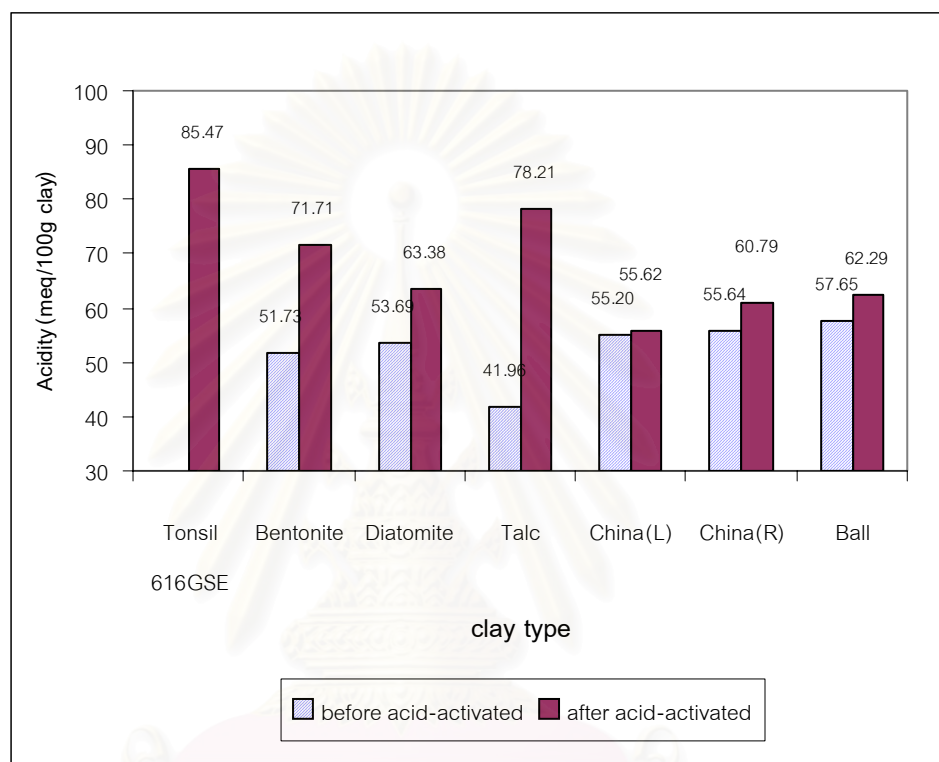


Figure 4.1 Acidity values of clays before and after acid activation

#### 4.1.2 Study of clay structure

The surfaces of clay samples were observed using scanning electron photomicrography as shown in Figure A1. The surface of Tonsil 616GSE, bentonite and talcum were found to have more porosity than the others. Therefore, they should have more acid sites than the others.

IR spectroscopy is very sensitive to the structure changes, which occur in the clay upon acid treatment [8]. Figures A2 – A8 show IR spectra of acid-activated clay samples and Table 4.1 summarizes the main vibrations observed. In Figures A3 – A5, bentonite, diatomite and talcum, the band between 3800 and 3300  $\text{cm}^{-1}$  decreased in intensity from each parent clays. It showed that water was adsorbed on the free silica when acid treatment increases. Similar behavior was shown by the deformation band nearby 1638  $\text{cm}^{-1}$ , which may be used to indicate the amount of water in clay. The Si-O band, shift from 1035 to 1040  $\text{cm}^{-1}$  for bentonite, 1033 to 1037  $\text{cm}^{-1}$  for diatomite and 1024 to 1045  $\text{cm}^{-1}$  for talcum, indicated that the acid treatment had attacked the present clay structure [8]. The band nearby 915  $\text{cm}^{-1}$  corresponding to the AlAlOH bending deformation [9] decreased and became very weak for bentonite, diatomite and talcum, suggesting significant depopulation of the octahedral sheet by acid treatment.

**Table 4.1 Characteristic FTIR bands for acid activated clays**

Wave number ( $\text{cm}^{-1}$ )						Band assignment [9]
Bentonite		Diatomite		Talcum		
Parent	Acid <sup>a</sup>	Parent	Acid <sup>a</sup>	Parent	Acid <sup>a</sup>	
3416	3416 <sup>b</sup>	3436	3436 <sup>b</sup>	3441	3441 <sup>b</sup>	OH stretching
1639	1639 <sup>b</sup>	1634	1634 <sup>b</sup>	1644	1644 <sup>b</sup>	Hydration, HOH deformation
1034	1040	1033	1037	1024	1045	SiO stretching
917	916 <sup>b</sup>	922b	922 <sup>b</sup>	912	912 <sup>b</sup>	OH deformation

a=acid activated clay

b=intensity decreased



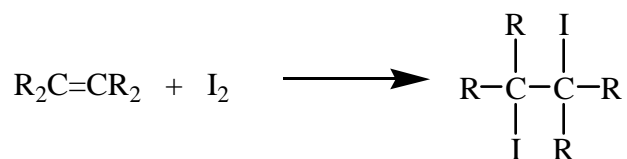
On the other hand, Figures A6 – A8, china L, china R and ball clay indicated no changes of IR spectra from the parent clays. Therefore, the acid activation of these clays did not change the structure by acid treatment.

Figure A9 shows a comparison of IR spectra of standard and acid activated Thai clays. The OH stretching band of Tonsil 616GSE has less intensity than the others. This means that OH groups in Tonsil 616GSE structure were attacked by acid. Therefore, octahedral layers were collapsed and the number of acid sites increased. This is a reason why Tonsil 616GSE has more acidity than the others.

Figures A12 – A18 show The XRD patterns of clay before and after acid activation. Gradual degradation of the layered structure was observed by the intensity of the 001 reflection. The untreated samples exhibited a well-defined and very intense 001 peak. When the samples were acid activated, the crystallinity of the samples decreased and the loss of intensity of 001 reflection, without undergoing line broadening during the acid activation process, has been taken to indicate that the removal of ions from the octahedral sheets occurs by proton attack at layer edge sites [8]. The broad hump in the 20-30° (2θ) region has been attributed to amorphous silica [9].

#### 4.2 Treatments of reformat BTX feedstock with various types of clay

The iodine value was an indication of olefin content in BTX feedstock. The reaction of olefins with iodine is an electrophilic addition to the carbon-carbon double bond as shown below.



#### 4.2.1 Treated time and temperature for performance of olefin adsorption

Firstly, treatment time was considered for olefin adsorption. Each clay was refluxed with BTX feedstock at 150 °C for 1, 2, and 3 hours. Results are shown in Table A1 and Figure 4.2 the iodine values at 3 hours has lower than 2 and 1 hours in every sample. The results showed that the olefin adsorption efficiency is in the order:

$$3 \text{ hrs} > 2 \text{ hrs} > 1 \text{ hrs}$$

Iodine values can be converted to % olefin adsorption as shown in Table A1 and Figure 4.3. At 1, 2, and 3 hours, Tonsil 616GSE (standard) has the highest % olefin adsorption, in comparison with other samples. Besides, % olefin adsorptions of bentonite, diatomite and talcum have lower than standard but higher than the other samples.

Especially, talcum showed nearly the same % olefin adsorption with Tonsil 616GSE at 3 hours. However, china (L), china (R), and ball clay showed less % olefin adsorption at each treated time. Therefore, the suitable treated time was found at 3 hours.

Secondly, treatment temperature was considered. Clays were treated with BTX feedstock for 3 hours at various temperatures of 30, 90, 120, 150, and 180 °C. The result is shown in Table A2 and Figure 4.4. The iodine value on BTX feedstock decreased with increase of treatment temperature from 30 to 120 °C. Above 120 °C, the iodine value would quite constant or little difference.

The iodine value can be converted to %olefin adsorption curve in Table A2 and Figure 4.5. The trend of curve was S-shape, indicating that was not good adsorption of olefins at the low temperature. Although the temperatures that gave the good results were 120, 150, and 180 °C, but the difference of % olefin adsorption was not significant. From Figures 4.4 and 4.5, the suitable treatment temperature of 120 °C was obtained.

The above data indicated that the best condition for adsorption of olefins should be refluxed BTX feedstock with clays at 120 °C for 3 hours.

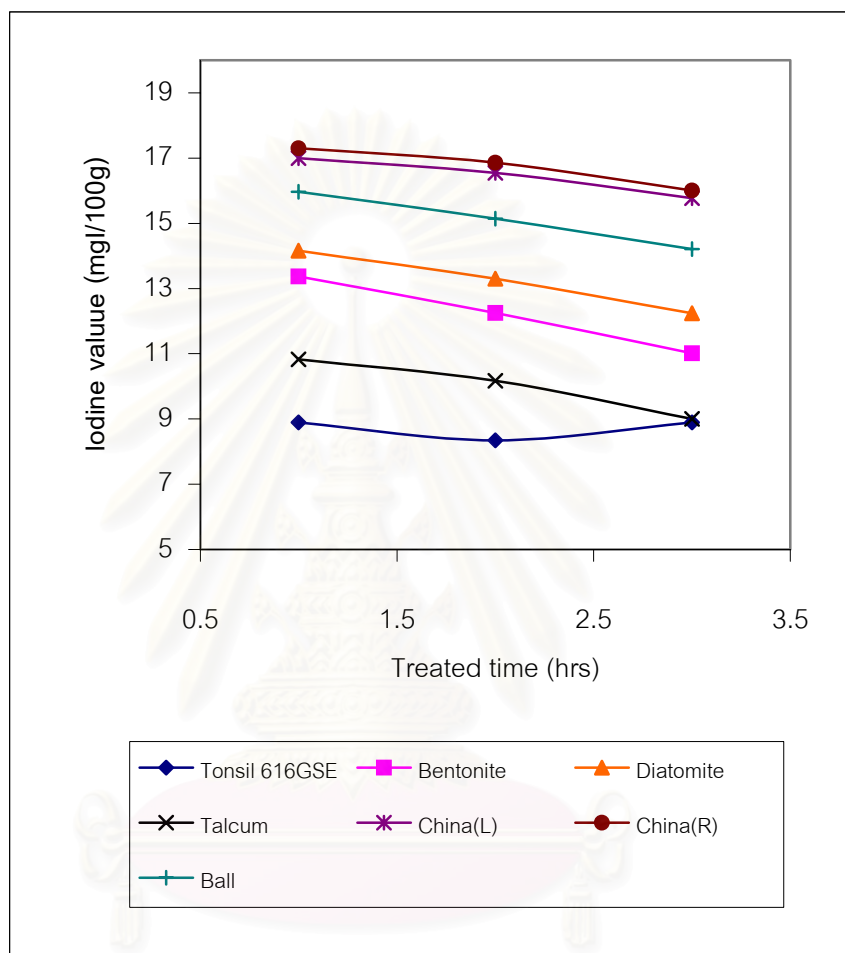


Figure 4.2 Iodine values of BTX feedstock refluxed with clays at 150 °C for various treated times

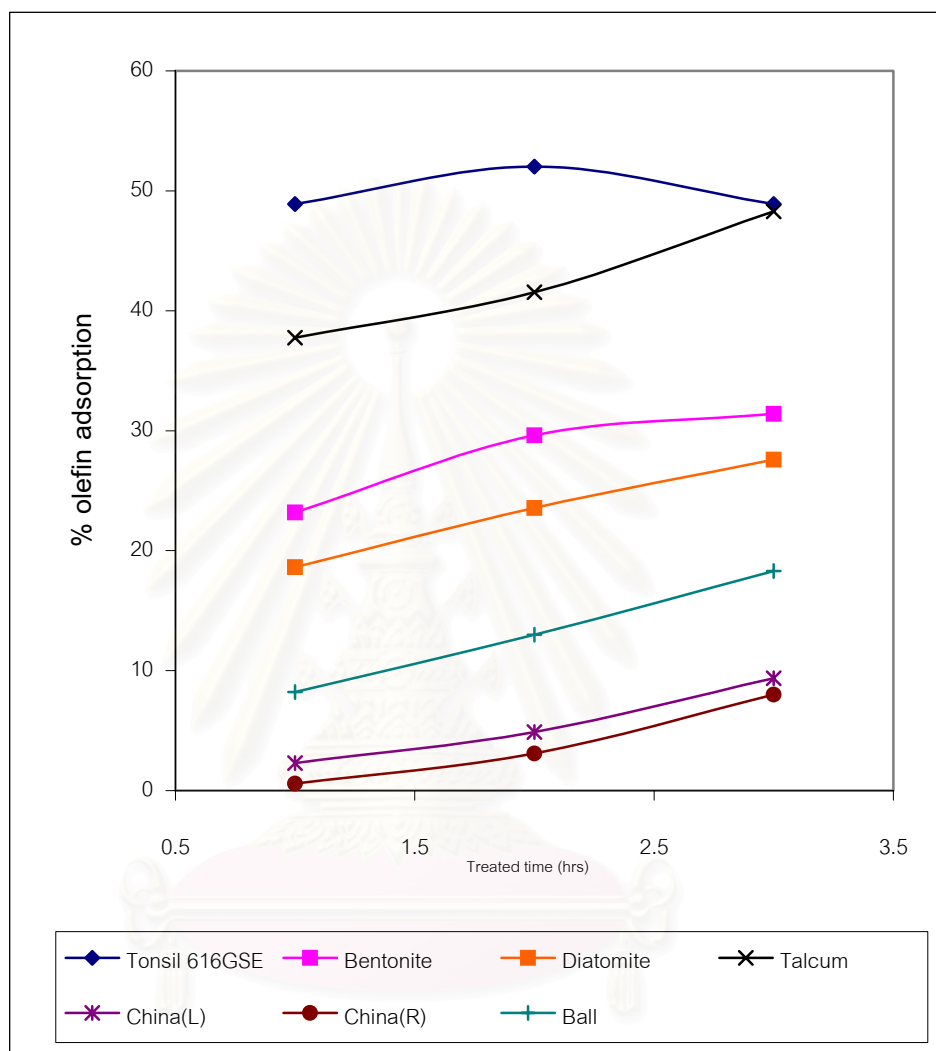


Figure 4.3 The % olefin adsorption of BTX feedstock refluxed with clays at 150 °C for various treated times

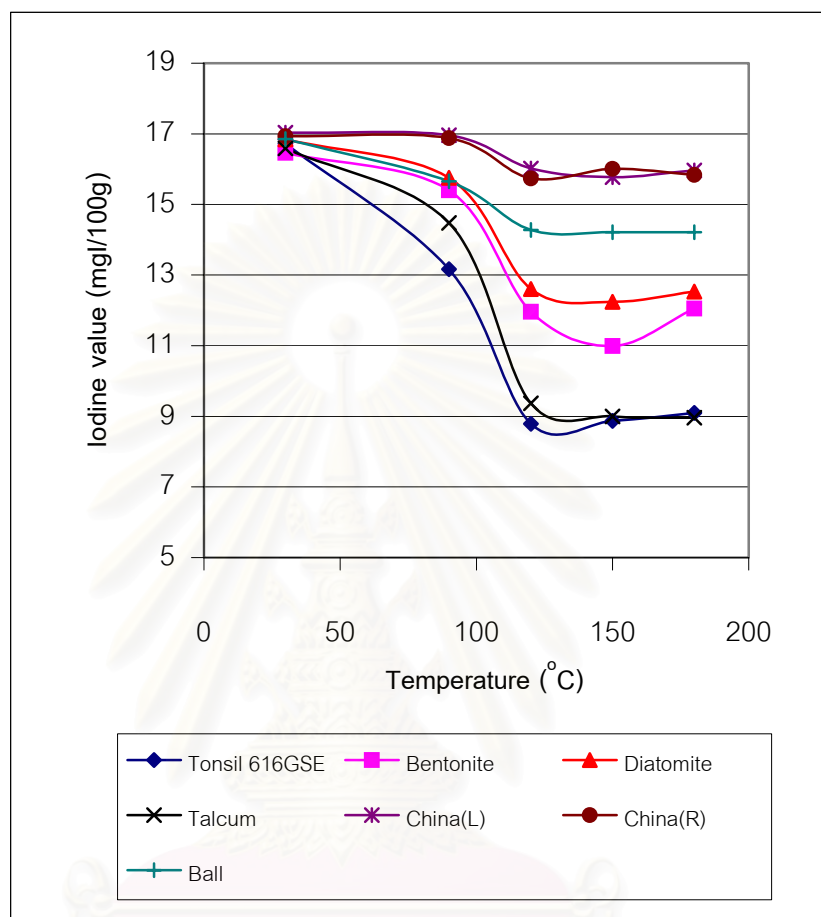


Figure 4.4 Iodine values of BTX feedstock refluxed with clays for 3 hours at various temperatures

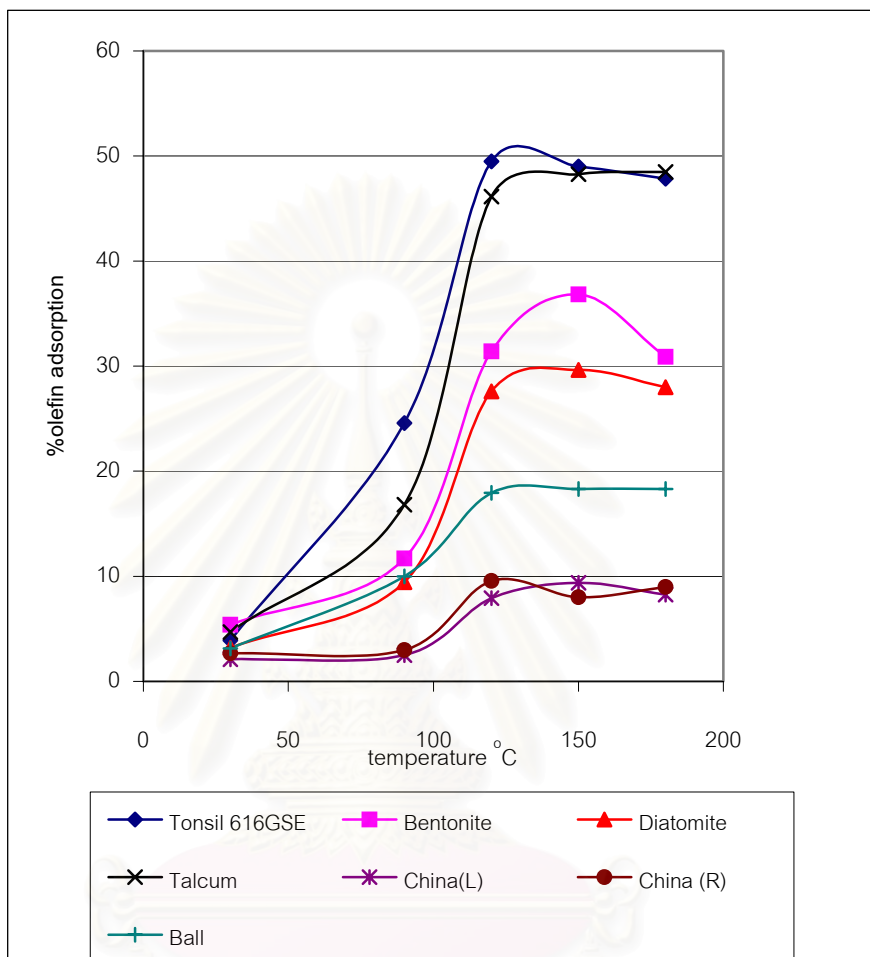


Figure 4.5 The % olefin adsorption of BTX feedstock refluxed with clays for 3 hours at various temperatures

Figure 4.6 shows the performances of six types of clay compared with Tonsil 616GSE, before and after acid activation refluxed with BTX feedstock at 120 °C for 3 hours. Before acid activation, all types of clay gave very low effective adsorption and % adsorption was evaluated after acid activation with sulfuric acid. The olefin adsorption of bentonite, diatomite, talcum, china (L), china (R), and ball clay were found to be 31.40, 27.59, 46.15, 7.93, 9.56, and 17.93, respectively. Talcum was the most effective and also good performance as Tonsil 616GSE, while the lowest was china (L). The efficiencies of all clays are in order talcum > bentonite > diatomite > ball > china (R) > china (L).

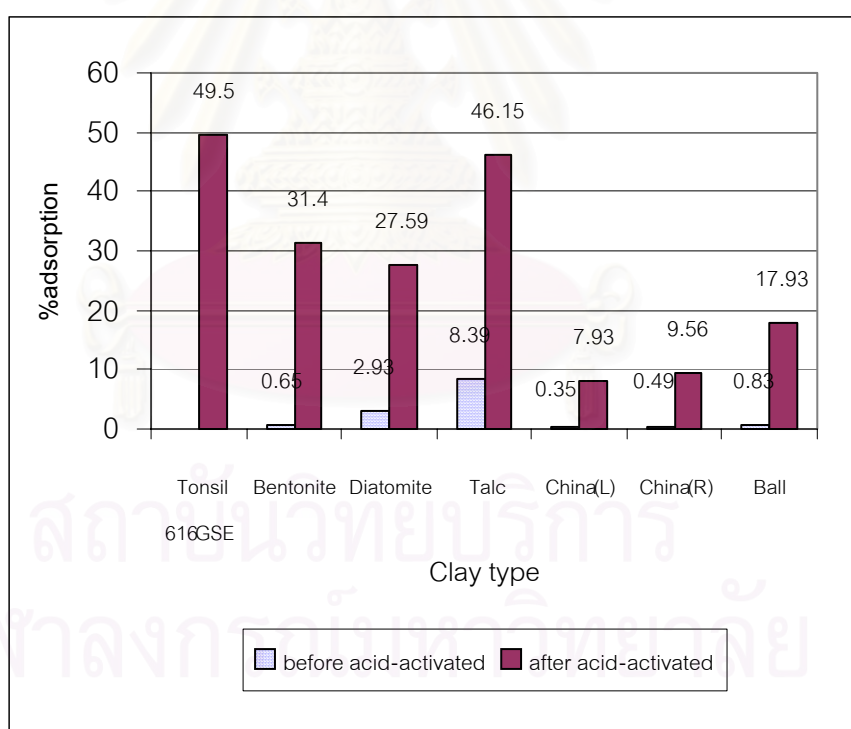


Figure 4.6 The % olefin adsorption before and after acid activated of samples.



#### 4.2.2 Optimum amounts of clay for treatment of reformat BTX feedstock

To study the optimum weight of clay, various amounts of Tonsil 616GSE, bentonite, diatomite and talcum refluxed with BTX feed stock at 120 °C for 3 hours. Results are shown in Figure 4.7. The % olefin adsorptions of every sample increased when the weight increased. However, the sharply increasing of % adsorption started only early section and became constant when amount of clay more than 0.5 g (2%). In Tonsil 616GSE, the optimum weight was 0.5 g (2%) which was the same as talcum. However, bentonite and diatomite optimum weight were 1 g (4%).

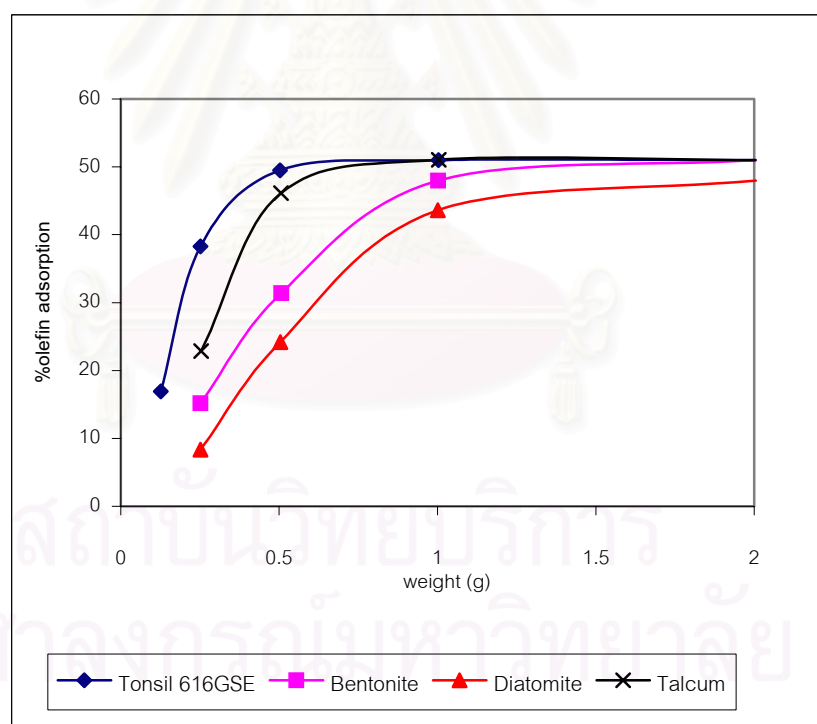


Figure 4.7 The % Olefin adsorption of BTX feedstock (various weights) refluxed with clays at 120 °C for 3 hours.

### 4.3 Characterization of BTX feedstock

BTX feedstock obtained from BTX process was identified for its composition by GC-MS with NIST library search program. GC-MS chromatograms of BTX feedstock was shown in Figures A19 – A25, These data indicated that there were many types of hydrocarbons in BTX feedstock, i.e., paraffins, branched-chain paraffins and aromatics. However, GC-MS library could not exactly specify the types of hydrocarbons, which have the same molecular weight.

**Table 4.2 Identification of BTX feedstock**

Peak no.	Retention time (min)	Peak area	Composition (%)	Expected compound
1	2.62	298.48	0.08	2,5,6-trimethyldecane
2	2.74	7352.69	1.98	benzene
3	2.82	526.32	0.14	2,4,6-trimethyldecane
4	2.91	229.50	0.06	3,3,5-trimethyl-1-hexene
5	2.98	347.81	0.09	6-ethyl-2-methyldecane
6	3.48	1758.14	0.47	2-methylheptane
7	3.59	74554.63	20.11	toluene
8	4.19	1295.84	0.35	n-octane
9	5.58	20609.06	5.56	ethylbenzene
10	5.81	69366.34	18.71	m-xylene

Table 4.2 (continued)

Peak no.	Retention time (min)	Peak area	Composition (%)	Expected compound
11	6.28	32445.91	8.75	p-xylene
12	6.91	2772.66	0.75	(1-ethylmethyl)-benzene
13	7.53	5914.49	1.60	propylbenzene
14	7.69	21724.98	5.86	1-ethyl-4-methylbenzene
15	7.86	34202.00	9.23	1,3,5-trimethylbenzene
16	8.04	10477.83	2.83	1-ethyl-2-methylbenzene
17	8.39	39969.84	10.78	1-ethyl-3-methylbenzene
18	8.65	612.59	0.17	diethylbenzene
19	8.89	10581.62	2.85	1,2,3-trimethylbenzene
20	9.16	1233.91	0.33	1-ethenyl-4-methylbenzene
21	9.36	874.57	0.24	1,3-diethylbenzene
22	9.42	3112.09	0.84	1-methyl-3-propylbenzene
23	9.53	6153.56	1.66	1,4-diethylbenzene
24	9.71	1391.14	0.38	1-methyl-2-propylbenzene
25	9.88	2315.71	0.62	1-ethyl-2,4-dimethylbenzene
26	9.93	2453.50	0.66	2-ethyl-1,3-dimethylbenzene
27	10.04	5245.69	1.42	1,2,3,4-tetramethylbenzene
28	10.24	1560.07	0.42	2,6,8-trimethyldecane
29	10.41	726.65	0.20	1-ethyl-2,3-dimethylbenzene
30	10.63	2440.43	0.66	1,2,4,5-tetramethylbenzene

Table 4.2 (continued)

Peak no.	Retention time (min)	Peak area	Composition (%)	Expected compound
31	10.68	4324.15	1.17	1,2,3,5-tetramethylbenzene
32	11.07	375.82	0.10	1-ethenyl-3-ethylbenzene
33	11.23	1841.90	0.50	1-ethyl-3,5-dimethylbenzene
34	11.97	1622.22	0.44	naphthalene
Total		370712.15	100.00	

GC-MS chromatogram showed that some components decreased from BTX feedstock. It indicated that clay adsorbed them or  $H^+$  on acid site of clay protonate on the double bond of these components. Therefore, carbocation was occurred and could be polymerized with other reactive components. Moreover, lone pair electron of oxygen in clay structure could attacked the carbocation which results in these components being adsorbed on clay structure.

#### 4.4 Clay modification

From previous results, two kinds of Thai clays, bentonite and talcum were selected for modification. Table 4.3 and Figure 4.8 represented %olefin adsorption of modified clays.

Table 4.3 The % olefin adsorption of modified clays

Clay	% olefin adsorption					
	Acid <sup>*</sup>	MA	DMA	TMA	KCl	CaCl <sub>2</sub>
Tonsil 616GSE	49.50	-	-	-	-	-
Bentonite	31.40	36.16	31.83	30.51	39.75	40.22
Talcum	46.15	46.52	46.34	46.03	53.49	58.07

\* acid activated clay

Acid activated bentonite gave 31.40% olefin adsorption. When clay was treated with MA it showed higher efficiency of olefin adsorption than normal acid activated bentonite. But modification of bentonite by DMA and TMA could not increase % olefin adsorption because DMA and TMA have more methyl groups in their structures than MA, so it could not enter through the octahedral sheet for ion exchange. Therefore, modification of bentonite with DMA and TMA provided similar efficiency in olefin adsorption to that of normal acid activated bentonite. When bentonite was treated with KCl and CaCl<sub>2</sub>, modified clay showed higher efficiency than acid activated bentonite because K<sup>+</sup> and Ca<sup>2+</sup> can be exchanged in bentonite.

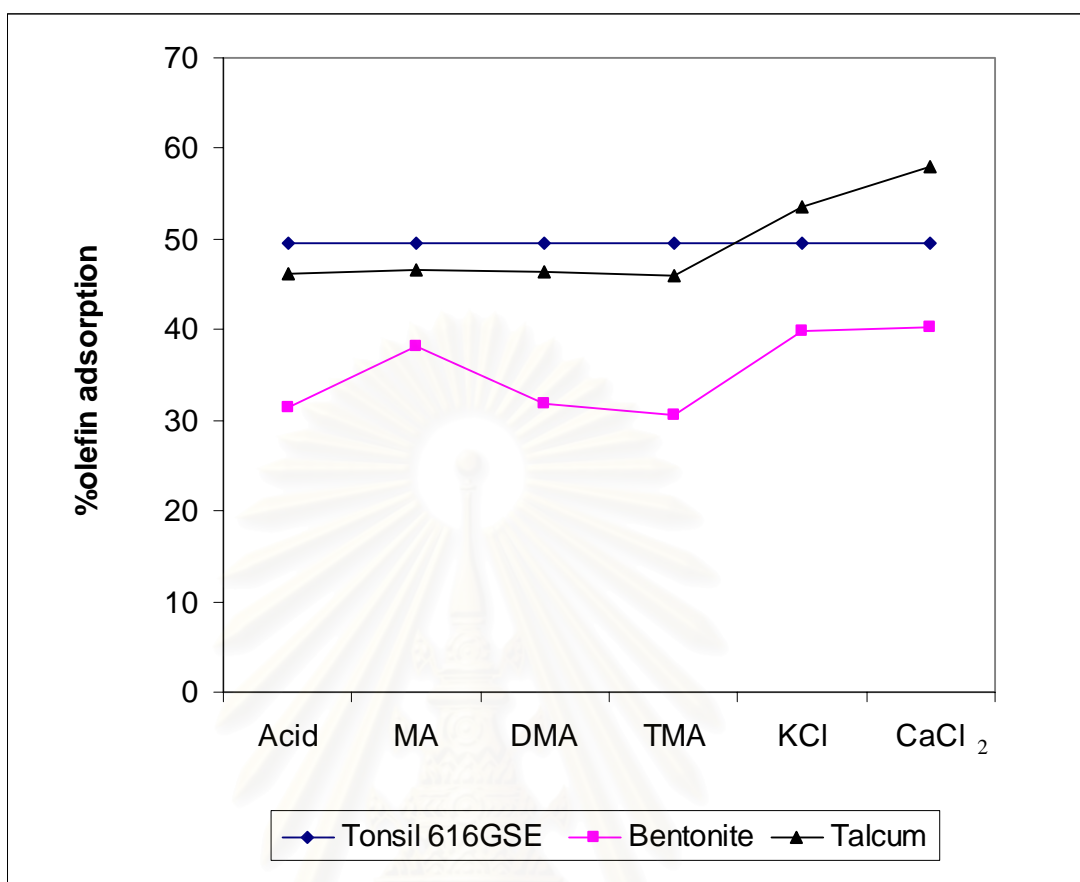
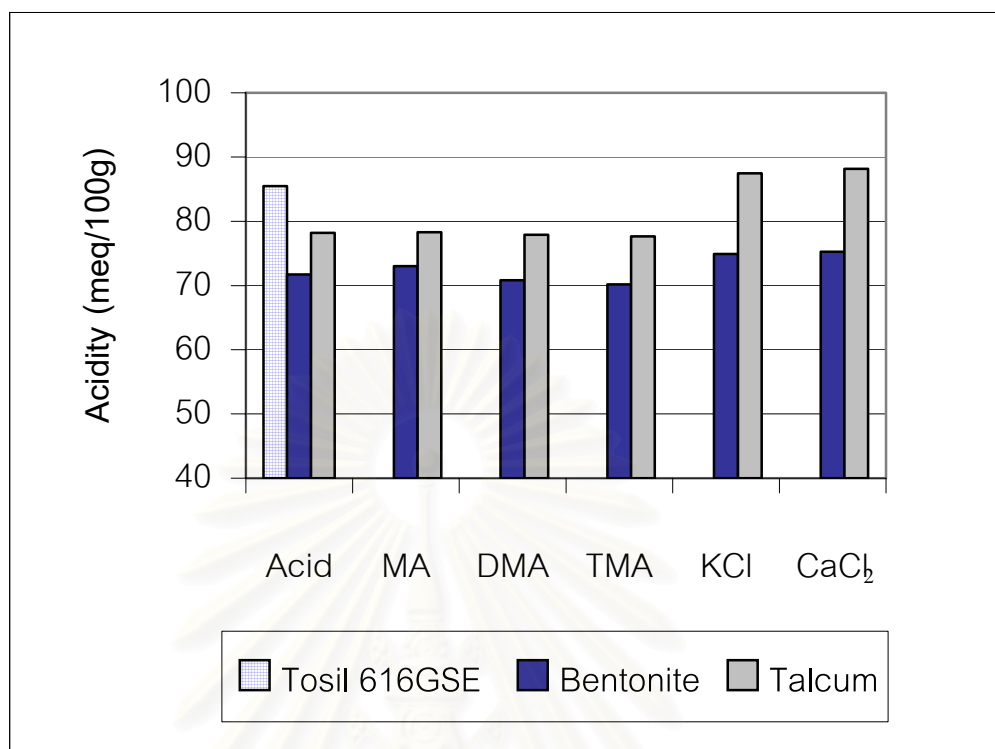


Figure 4.8 The % olefin adsorption of modified clays.

In the case of talcum, MA, DMA and TMA could not change in talcum structure, therefore, the olefin adsorption of this modified clay was the same. On the other hand, modified talcum with KCl and CaCl<sub>2</sub> gave higher performance of olefin adsorption than the original clay. Therefore, modified talcum with these reagents provided great adsorption efficiency similar to that of Tonsil 616GSE.



Clay	Acidity (meq/100g)					
	Acid	MA	DMA	TMA	KCl	CaCl <sub>2</sub>
Tonsil 616GSE	85.47	-	-	-	-	-
Bentonite	71.71	73.01	70.84	70.16	74.88	75.27
Talcum	78.21	78.30	77.91	77.65	87.46	88.17

Figure 4.9 Acidity values of modified clays.

Acidity of clay may also affect their adsorption properties. After modification, talcum (Figure 4.9) showed higher acidity than its parent and exhibited the maximum acidity, in excellent agreement with its adsorption efficiency. Therefore, the % olefin adsorption was increased following the increase in acidity.

IR spectra of modified clays also discussed. When bentonite and talcum were modified with KCl or CaCl<sub>2</sub>, intensity of OH stretching decreased and SiO band also shifted from normal acid activation shown in Figures A10 - 11. It means that cations from developing agent entered into the structure and increased the acid sites [19]. Then, the acid site was increased, thus olefin adsorption would be increased. However, DMA and TMA cases showed indifferent from normal acid activation. It means that the structure of clays did not change from the original one, so the efficiencies of these modified clays did not increase.

**Table 4.4 Surface area, acidity and olefin adsorption of clays**

Sample	Surface area (m <sup>2</sup> /g)	Acidity (meq/100g) <sup>a</sup>	Olefin adsorption (%) <sup>b</sup>
Tonsil 616GSE	347	85.47	49.50
CaCl <sub>2</sub> -Modified Talcum	390	88.17	58.07
KCl-Modified Talcum	367	87.46	53.49
Talcum*	324	78.21	46.15
Bentonite*	221	71.71	31.40
Diatomite*	187	63.38	27.59
Ball*	135	62.29	17.93
China R*	89	60.79	9.56
China L*	81	55.62	7.39

\* acid activated clay; a) SD = ±0.01; b) see appendix A



Table 4.4 presents the total surface area, acidity and adsorption efficiency of clays. Talcum gave a surface area of 324 m<sup>2</sup>/g, and after modification with KCl and CaCl<sub>2</sub> the surface area increased to 367 and 390 m<sup>2</sup>/g, respectively. Not only surface area increased but also acidity and olefin adsorption increased. Therefore, the adsorption efficiency may also depend on the surface activity and acidity of the clay samples.



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## CHAPTER V

### CONCLUSION

The optimum condition for treating BTX feedstock in order to remove olefin is refluxing the BTX feedstock with clays at 120°C for 3 hours. At this condition, two types of clays, bentonite and talcum showed higher % olefin adsorption than the other clay samples. In case of bentonite, 4% by weight bentonite is the optimum weight. Talcum showed similar olefin adsorption to Tonsil 616GSE (commercial) at 2% by weight.

From this optimum condition, clays could be ranked according to the % olefin adsorption as Tonsil 616GSE  $\cong$  talcum > bentonite > diatomite > ball > china R > china L.

The modification of bentonite with KCl, CaCl<sub>2</sub> and methyl ammonium salt, provided higher % olefin adsorption than that of the original clay. The modification of bentonite with dimethyl and tetramethylammonium salt did not show better efficiency of adsorption than that the original bentonite.

The talcum modified with alkyl ammonium salt could not increase the % olefin adsorption. On the other hand, modification of talcum with KCl and CaCl<sub>2</sub> showed better % olefin adsorption than the original talcum and higher than the commercial available Tonsil 616GSE. Therefore, talcum modified with KCl and CaCl<sub>2</sub> could be used in olefin adsorption from BTX feedstock.

## SUGGESTION FOR THE FUTURE WORK

Tonsil 616GSE is used in many purposes not only olefin adsorption but also for reuse lubricating oil, decolorizing white oil, mineral oil and vegetable oil. From this research, modified talcum had more olefin adsorption ability than Tonsil 616GSE. However, further works should be carried out as follows:

1. The used of modified Thai clay for used lubricating oil, decolorizing in white oil, mineral oil and vegetable oil should be explored.
2. Other Thai clays should be investigated.



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APPENDICES

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APPENDIX A

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Table A1 Iodine values of BTX feedstock refluxed with clays at 150 °C for various treated times.

Clay	Treated Time (hours)											
	1				2				3			
	1	2	3	Average <sup>a</sup>	1	2	3	Average <sup>b</sup>	1	2	3	Average <sup>c</sup>
Tonsil 616GSE	8.78	8.90	8.99	8.89	8.36	8.31	8.38	8.35	8.85	8.81	8.95	8.87
Bentonite	13.26	13.35	13.49	13.37	12.22	12.19	12.33	12.25	11.03	11.05	10.98	11.02
Diatomite	14.22	14.18	14.08	14.16	13.35	13.28	13.27	13.30	12.24	12.30	12.18	12.24
Talcum	11.17	11.21	11.22	11.20	9.86	9.80	9.77	9.81	9.10	8.95	8.95	9.00
China (L)	17.04	17.09	16.87	17.00	16.55	16.59	16.51	16.55	15.74	15.69	15.88	15.77
China (R)	17.31	17.40	17.19	17.30	16.84	16.92	16.82	16.86	15.98	16.04	16.00	16.01
Ball	15.93	15.90	16.08	15.97	15.13	15.16	15.13	15.14	14.23	14.35	14.07	14.22

a) SD = ± 0.12; b) SD = ±0.07; c) SD = ±0.14

Table A2 The % olefin adsorption of BTX feedstock refluxed with clays at 150 °C for various treated times.

Clay	Treated Time (hours)											
	1				2				3			
	1	2	3	Average <sup>a</sup>	1	2	3	Average <sup>b</sup>	1	2	3	Average <sup>c</sup>
Tonsil 616GSE	49.54	48.85	48.33	48.91	51.95	52.24	51.84	52.01	49.14	49.37	48.22	48.91
Bentonite	23.79	23.28	22.45	23.17	29.77	29.94	29.13	29.61	36.61	36.49	36.92	36.67
Diatomite	18.28	18.51	19.08	18.62	23.28	23.68	23.74	23.56	29.66	29.31	30.00	29.66
Talcum	35.80	35.57	35.52	35.63	43.33	43.68	43.85	43.62	47.70	48.56	48.56	48.28
China (L)	2.07	1.78	3.05	2.30	4.89	4.66	5.11	4.89	9.54	9.83	8.74	9.37
China (R)	0.52	0.00	1.21	0.57	3.22	2.76	3.33	3.10	8.16	7.82	8.02	8.00
Ball	8.45	8.62	7.59	8.22	13.05	12.87	13.05	12.99	18.22	17.53	19.15	18.30

Table A3 Iodine value and % olefin adsorption of BTX feedstock refluxed with clays for 3 hours at various temperatures.

Clay	Temperature (°C)									
	Iodine value (mgI/100g)					% Olefin Adsorption				
	30	90	120	150	180	30	90	120	150	180
Tonsil 616GSE	16.72	13.16	8.79	8.87	9.10	3.89	24.57	49.50	49.02	47.84
Bentonite	16.46	15.40	11.93	11.02	12.05	5.40	11.71	31.40	36.82	30.89
Diatomite	16.84	15.76	12.60	12.24	12.53	3.20	9.45	27.59	29.64	28.00
Talcum	16.59	13.40	9.37	9.00	8.87	4.68	23.00	46.15	48.28	49.00
China (L)	17.03	16.97	16.02	15.77	15.96	2.10	2.50	7.93	9.37	8.26
China (R)	16.94	16.88	15.74	16.01	15.83	2.67	3.00	9.56	8.01	9.00
Ball	16.86	15.66	14.28	14.22	14.22	3.13	10.00	17.93	18.30	18.30

Table A4 Average data of iodine value and %olefin adsorption of BTX feedstock refluxed with clays at 30 °C for 3 hours.

Clay	Iodine value (mg/100g)				% olefin adsorption			
	1	2	3	Average*	1	2	3	Average
Tonsil								
616GSE	16.70	16.71	16.76	16.72	4.02	3.97	3.68	3.89
Bentonite	16.50	16.47	16.41	16.46	5.17	5.34	5.68	5.40
Diatomite	16.88	16.84	16.81	16.84	2.99	3.22	3.39	3.20
Talcum	16.61	16.51	16.64	16.59	4.54	5.11	4.38	4.68
China (L)	17.08	17.08	16.94	17.03	1.84	1.84	2.62	2.10
China (R)	17.02	16.89	16.90	16.94	2.18	2.93	2.90	2.67
Ball	16.94	16.89	16.74	16.86	2.64	2.93	3.82	3.13

\*SD = ±0.07

Table A5 Average data of iodine value and %olefin adsorption of BTX feedstock refluxed with clays at 90 °C for 3 hours.

Clay	Iodine value (mg/100g)				% olefin adsorption			
	1	2	3	Average*	1	2	3	Average
Tonsil 616GSE	13.15	13.16	13.17	13.16	24.43	24.37	24.92	24.57
Bentonite	15.33	15.50	15.37	15.40	11.90	10.92	12.31	11.71
Diatomite	15.76	15.81	15.70	15.76	9.43	9.14	9.79	9.45
Talcum	13.44	13.44	13.31	13.40	22.76	22.76	23.48	23.00
China (L)	17.03	16.95	16.92	16.97	2.13	2.59	2.79	2.50
China (R)	16.94	16.84	16.85	16.88	2.64	3.22	3.14	3.00
Ball	15.65	15.70	15.63	15.66	10.06	9.77	10.17	10.00

\*SD = ±0.06

Table A6 Average data of iodine value and %olefin adsorption of BTX feedstock refluxed with clays at 120 °C for 3 hours.

Clay	Iodine value (mgI/100g)				% olefin adsorption			
	1	2	3	Average*	1	2	3	Average
Tonsil 616GSE	8.85	8.62	8.90	8.79	49.14	50.46	48.90	49.50
Bentonite	11.95	11.90	12.03	11.96	31.32	31.61	31.27	31.40
Diatomite	12.55	12.72	12.53	12.60	27.87	26.90	28.00	27.59
Talcum	9.38	9.35	9.38	9.37	46.09	46.26	46.09	46.15
China (L)	16.10	15.94	16.02	16.02	7.47	8.39	7.93	7.93
China (R)	15.83	15.79	15.59	15.74	9.02	9.25	10.40	9.56
Ball	14.32	14.25	14.27	14.28	17.70	18.10	17.99	17.93

\*SD = ±0.05

Table A7 Average data of iodine value and %olefin adsorption of BTX feedstock refluxed with clays at 150 °C for 3 hours.

Clay	Iodine value (mgI/100g)				% olefin adsorption			
	1	2	3	Average*	1	2	3	Average
Tonsil 616GSE	8.85	8.81	8.95	8.87	49.14	49.37	48.22	48.91
Bentonite	11.03	11.05	10.98	11.02	36.61	36.49	36.92	36.67
Diatomite	12.24	12.30	12.19	12.24	29.66	29.31	30.00	29.66
Talcum	9.10	8.95	8.95	9.00	47.70	48.56	48.56	48.28
China (L)	15.74	15.69	15.88	15.77	9.54	9.83	8.74	9.37
China (R)	15.98	16.04	16.00	16.01	8.16	7.82	8.02	8.00
Ball	14.23	14.35	14.07	14.22	18.22	17.53	19.15	18.30

\*SD = ±0.08

Table A8 Average data of iodine value and %olefin adsorption of BTX feedstock refluxed with clays at 180 °C for 3 hours.

Clay	Iodine value (mgI/100g)				% olefin adsorption			
	1	2	3	Average*	1	2	3	Average
Tonsil 616GSE	8.89	8.95	9.46	9.10	48.91	48.56	46.05	47.84
Bentonite	12.11	12.08	11.96	12.05	30.40	30.57	31.69	30.89
Diatomite	12.51	12.56	12.51	12.53	28.10	27.82	28.08	28.00
Talcum	8.78	8.78	9.06	8.87	49.54	49.54	47.92	49.00
China (L)	15.86	15.80	16.23	15.96	8.85	9.20	6.73	8.26
China (R)	16.01	15.74	15.75	15.83	7.99	9.54	9.47	9.00
Ball	14.23	14.40	14.02	14.22	18.22	17.24	19.44	18.30

\*SD = ±0.16

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Table A9 Iodine values of BTX feedstock refluxed with modified clays at 120 °C for 3 hours.

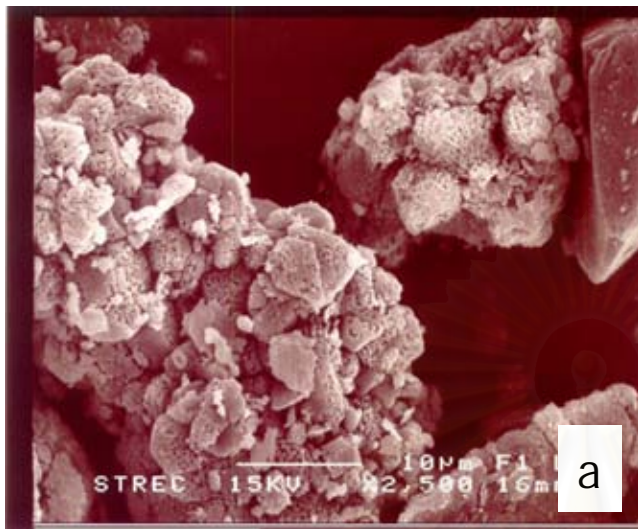
Clay	Iodine value (mgI/100g)											
	Tonsil 616GSE				Bentonite				Talcum			
	1	2	3	Average	1	2	3	Average <sup>a</sup>	1	2	3	Average
Acid	8.85	8.62	8.90	8.79	11.85	11.99	11.97	11.94	9.35	9.42	9.34	9.37
MA	-	-	-	-	10.84	10.79	10.65	10.76	9.49	9.32	9.11	9.31
DMA	-	-	-	-	11.92	11.86	11.80	11.86	9.33	9.47	9.21	9.34
TMA	-	-	-	-	12.11	12.16	12.00	12.09	9.31	9.40	9.46	9.39
KCl	-	-	-	-	10.43	10.49	10.53	10.48	8.07	8.10	8.11	8.09
CaCl <sub>2</sub>	-	-	-	-	10.36	10.41	10.44	10.40	7.28	7.31	7.30	7.30

a) SD = ±0.06; b) SD = ±0.07

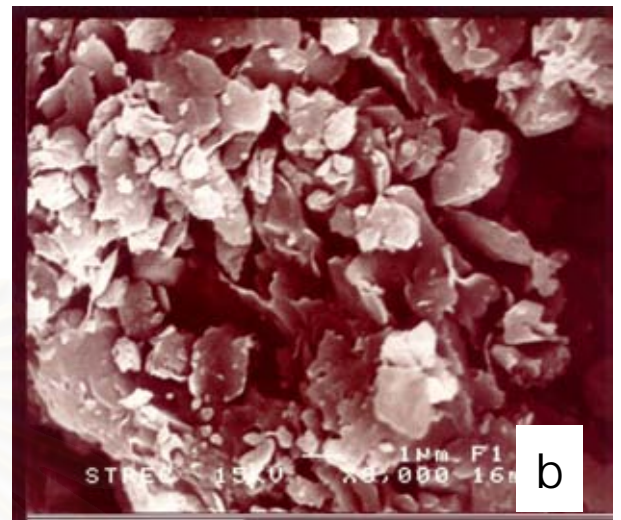
Table A10 % Olefin adsorption of BTX feedstock refluxed with modified clays at 120 °C for 3 hours.

Clay	% olefin adsorption											
	Tonsil 616GSE				Bentonite				Talcum			
	1	2	3	Average	1	2	3	Average	1	2	3	Average
Acid	49.14	50.46	48.90	49.50	31.90	31.09	31.21	31.40	46.26	45.86	46.32	46.15
MA	-	-	-	-	37.70	37.99	38.79	38.16	45.46	46.44	47.66	46.52
DMA	-	-	-	-	31.49	31.84	32.16	31.83	46.38	45.57	47.07	46.34
TMA	-	-	-	-	30.40	30.11	31.01	30.51	46.49	45.98	45.62	46.03
KCl	-	-	-	-	40.06	39.71	39.48	39.75	53.62	53.45	53.40	53.49
CaCl <sub>2</sub>	-	-	-	-	40.46	40.17	40.03	40.22	58.16	57.99	58.06	58.07

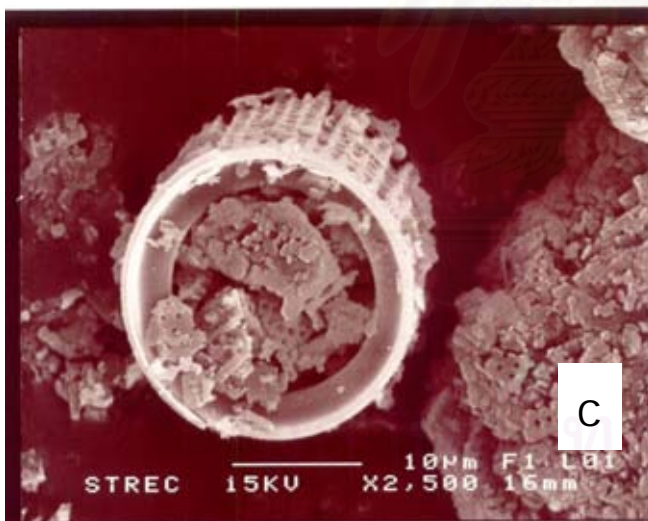




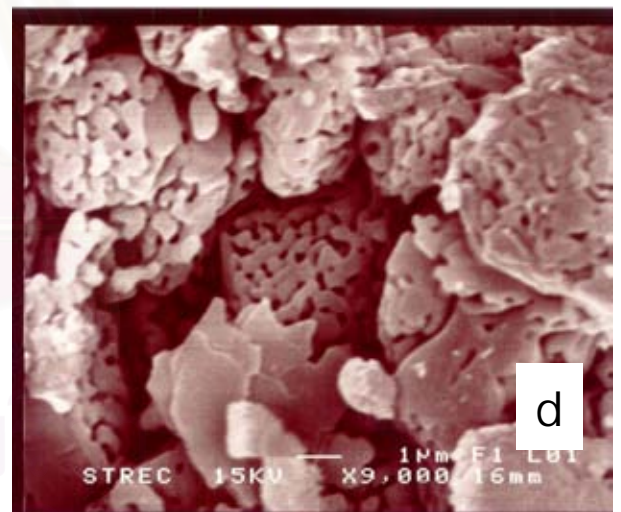
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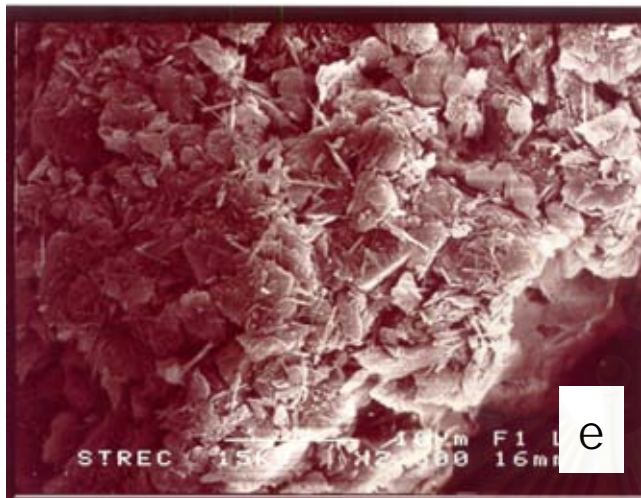


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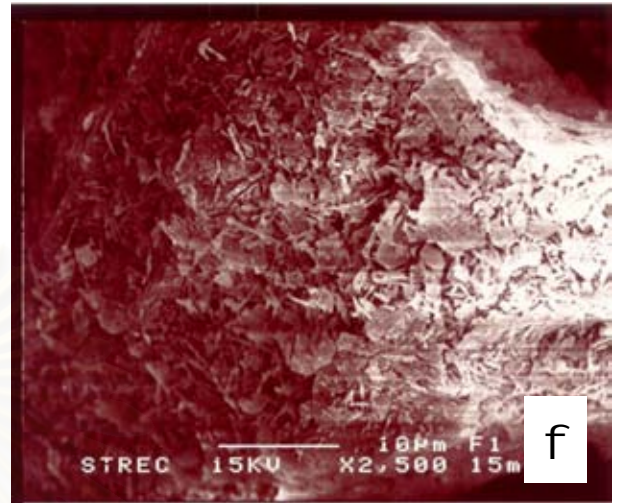


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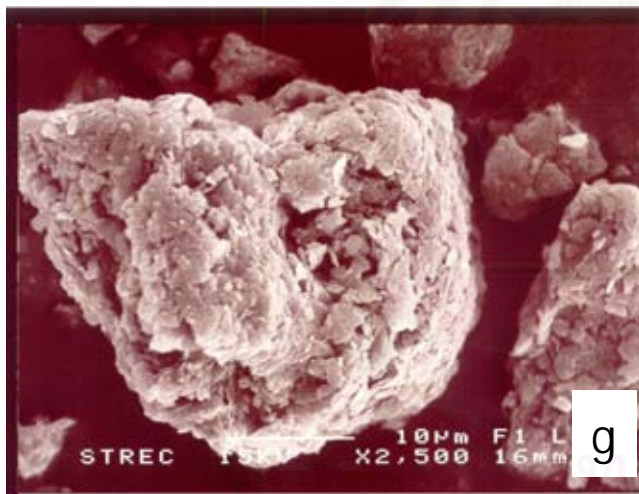
Figure A1 Scanning electron photomicrographs of clay samples (a) Tonsil 616GSE; (b) bentonite; (c) diatomite; (d) talcum;



Particle size 26.20-30.53  $\mu\text{m}$



Particle size 26.20-30.53  $\mu\text{m}$



Particle size 22.49-26.20  $\mu\text{m}$

Figure A1 (condition) Scanning electron photomicrographs of clay samples  
(e) china L; (f) china R; (g) ball.

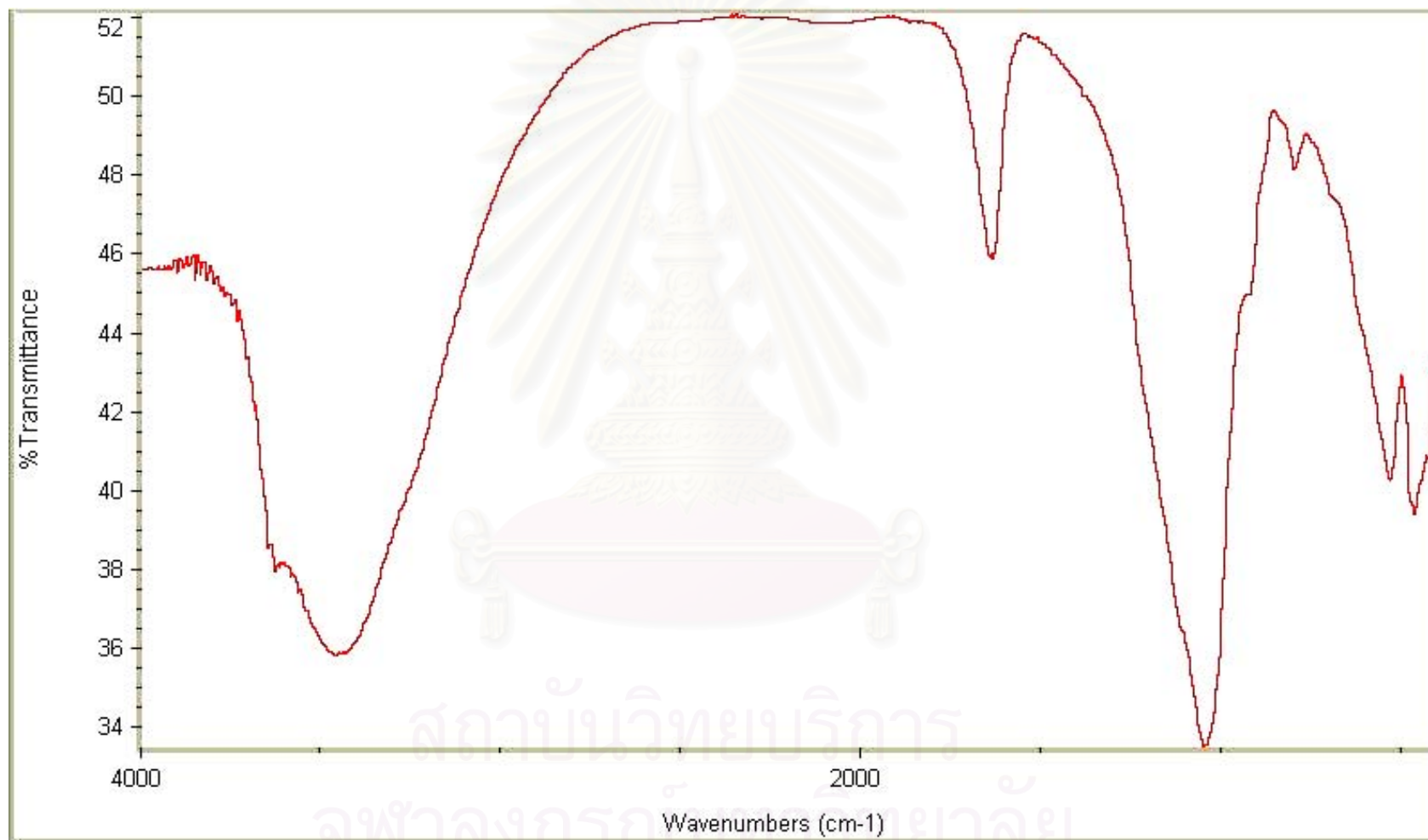


Figure A2 FTIR spectrum of Tonsil 616GSE.

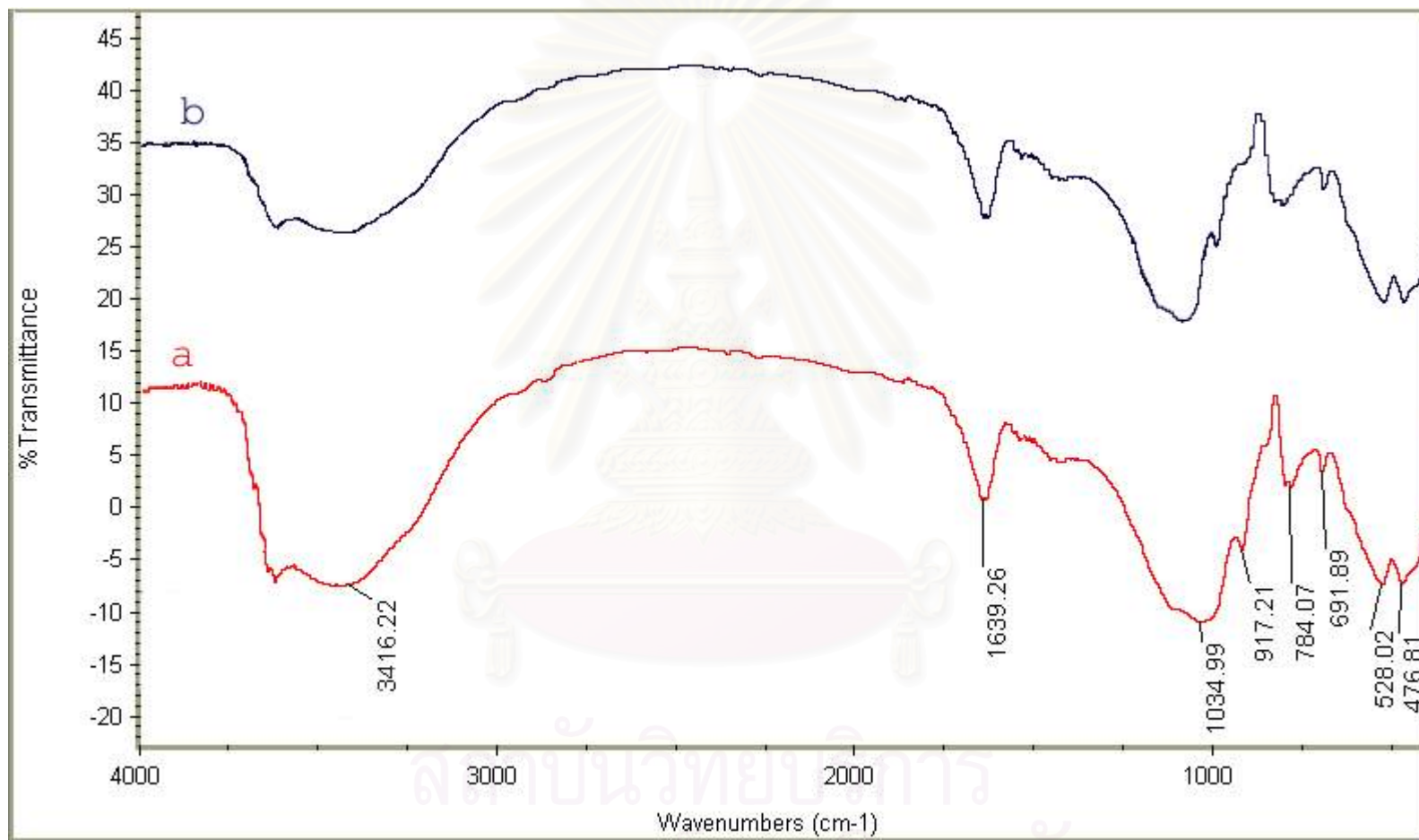


Figure A3 FTIR spectrum of bentonite (a) non-acid activated; (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

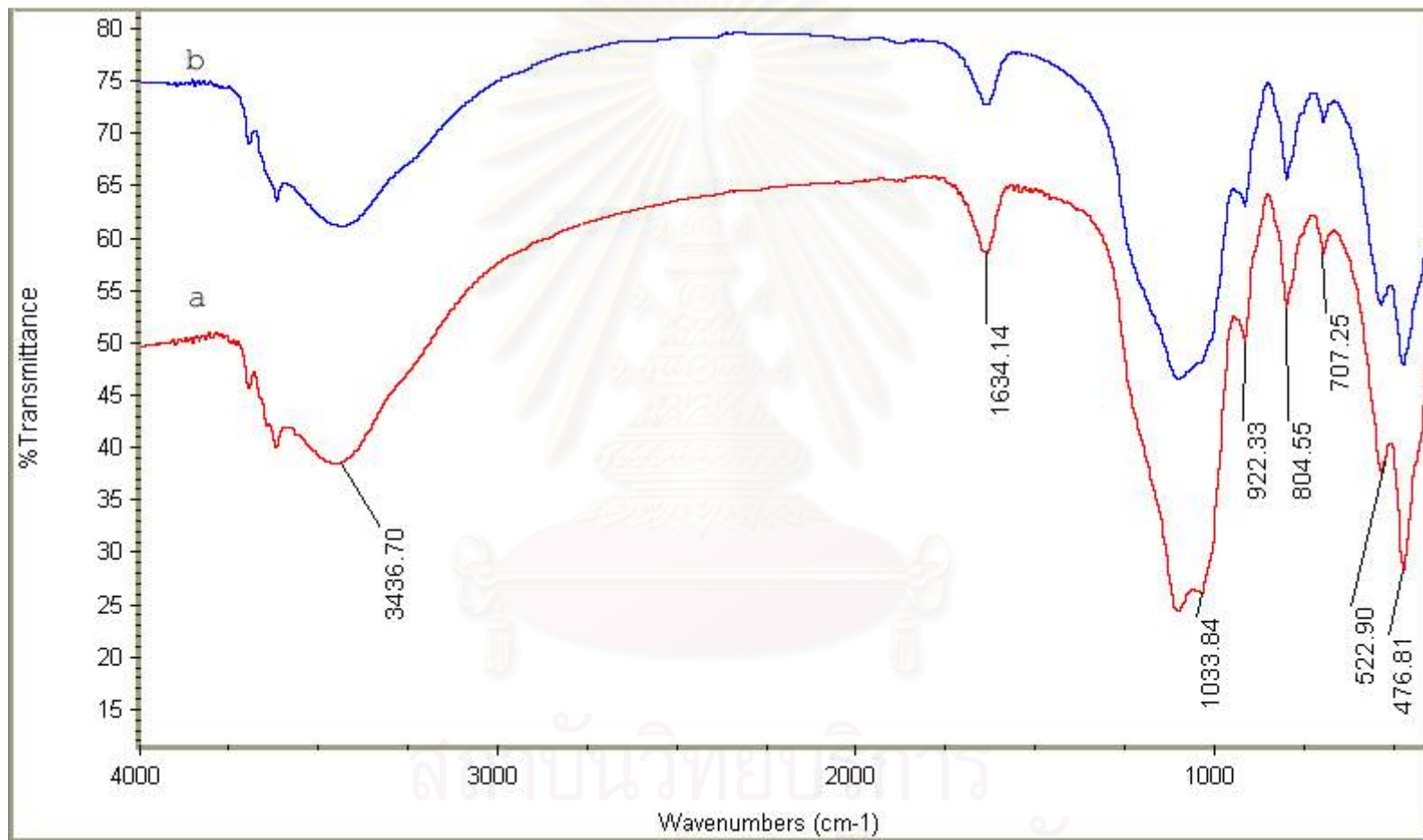


Figure A4 FTIR spectra of diatomite (a) non-acid activated; (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

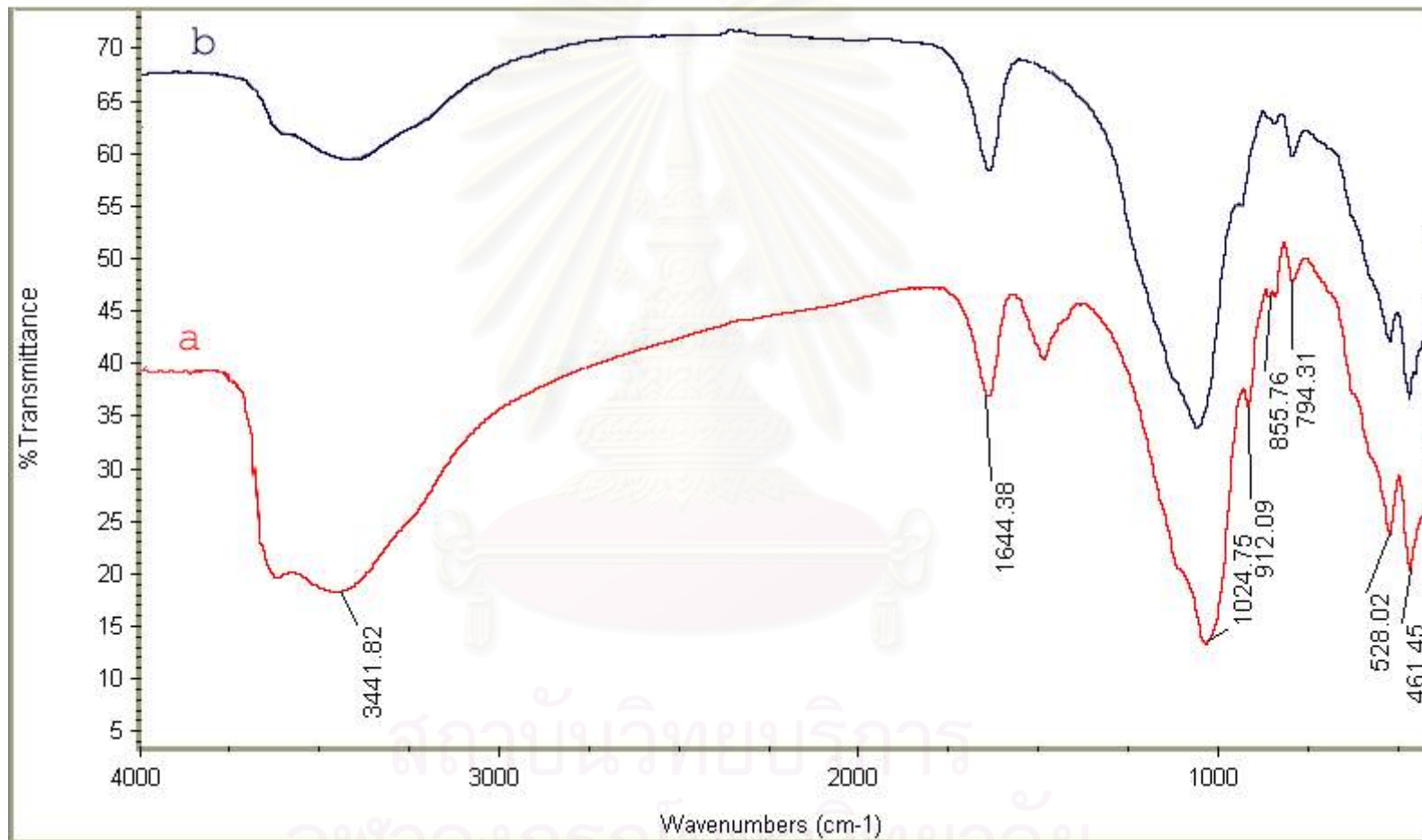


Figure A5 FTIR spectra of talcum (a) non-acid activated; (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

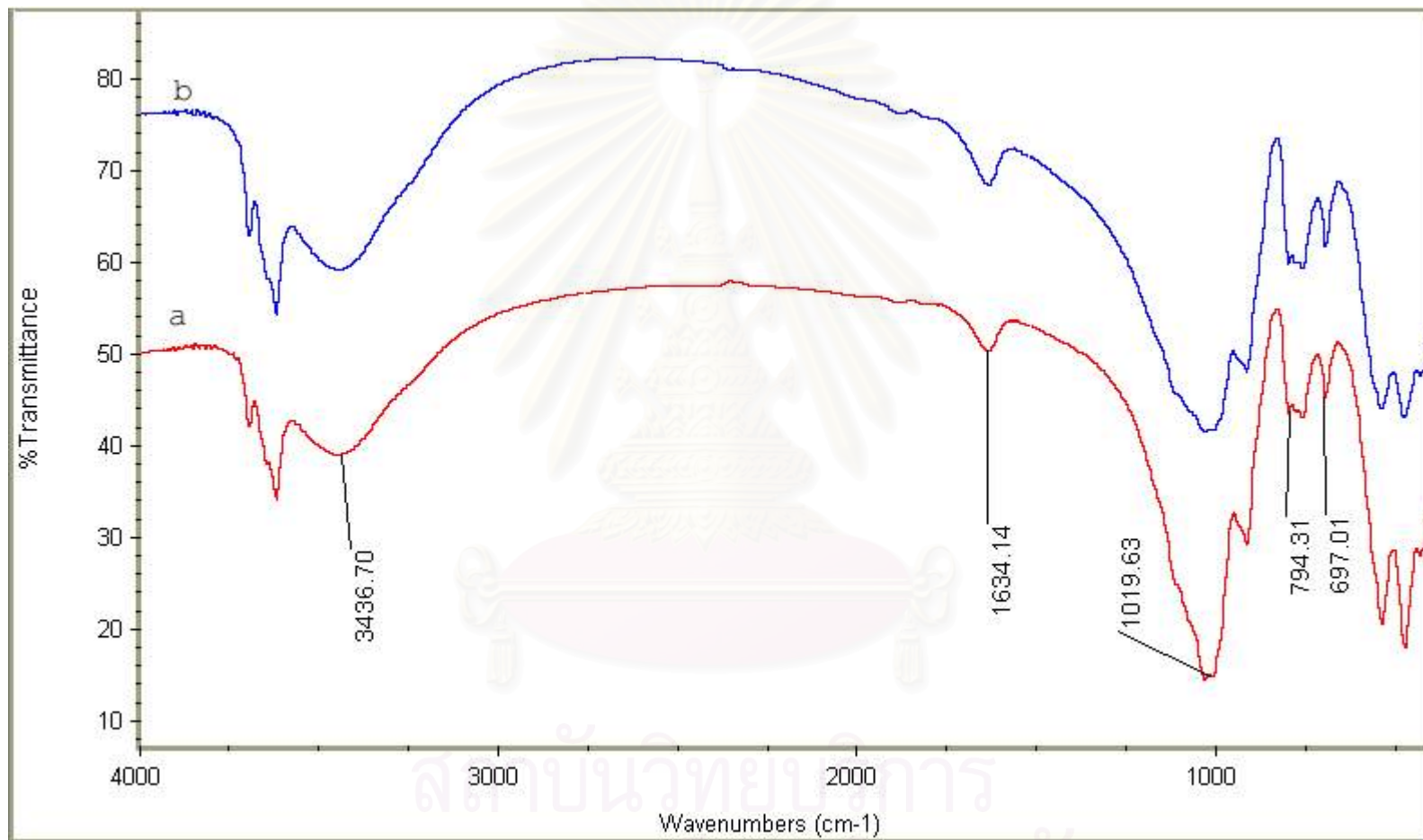


Figure A6 FTIR spectra of china L (a) non-acid activated; (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

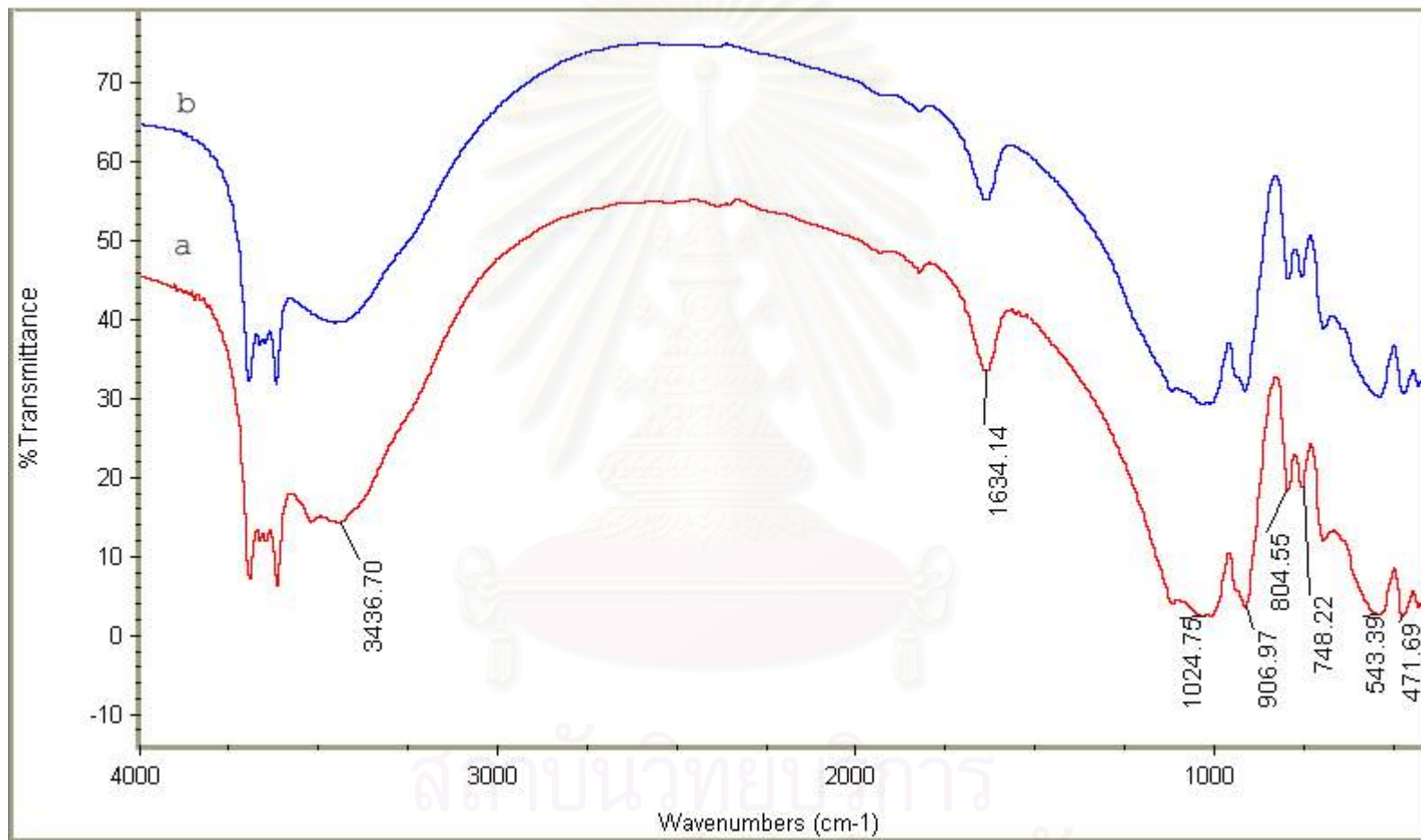


Figure A7 FTIR spectra of china R (a) non-acid activated; (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.



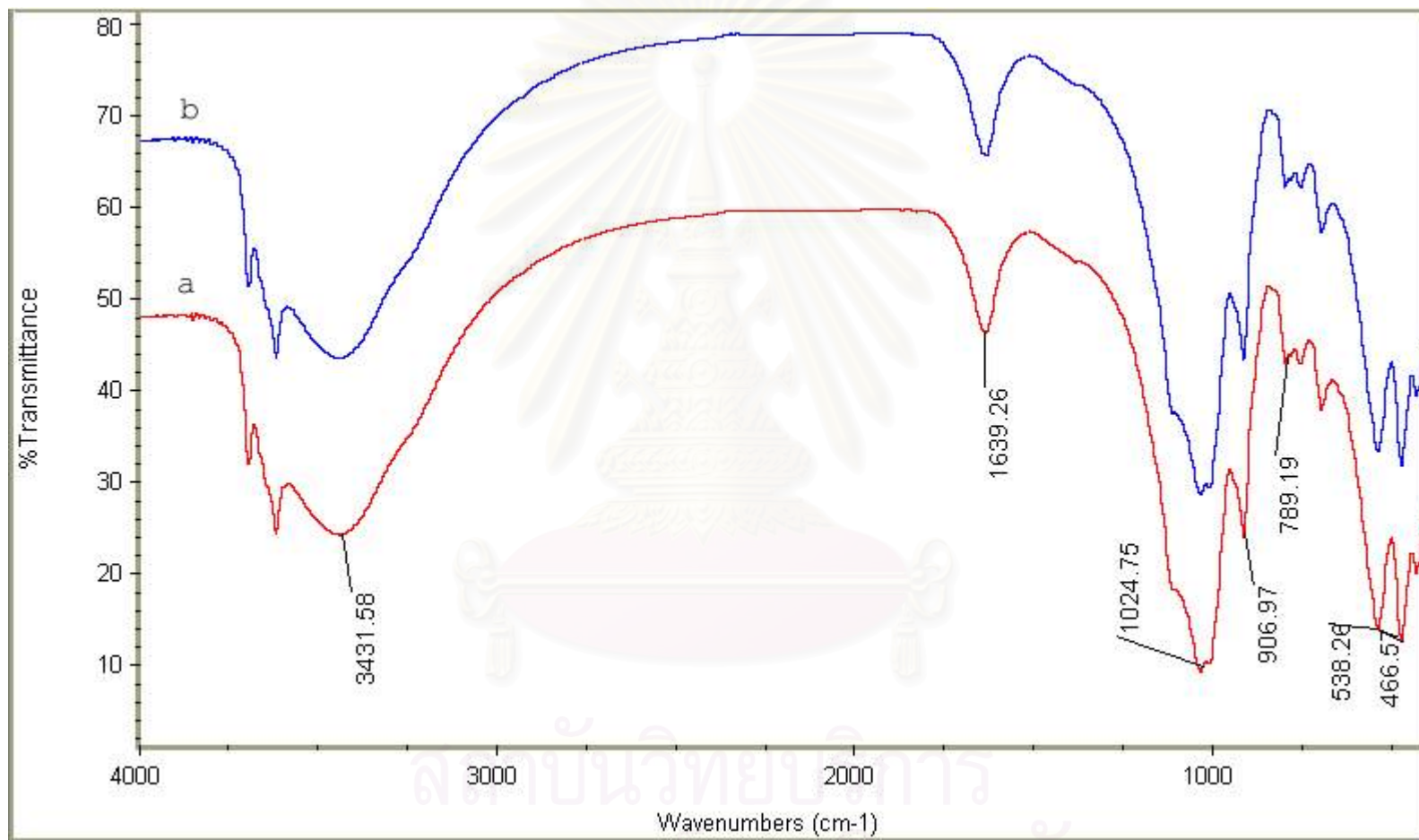


Figure A8 FTIR spectra of ball (a) non-acid activated; (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

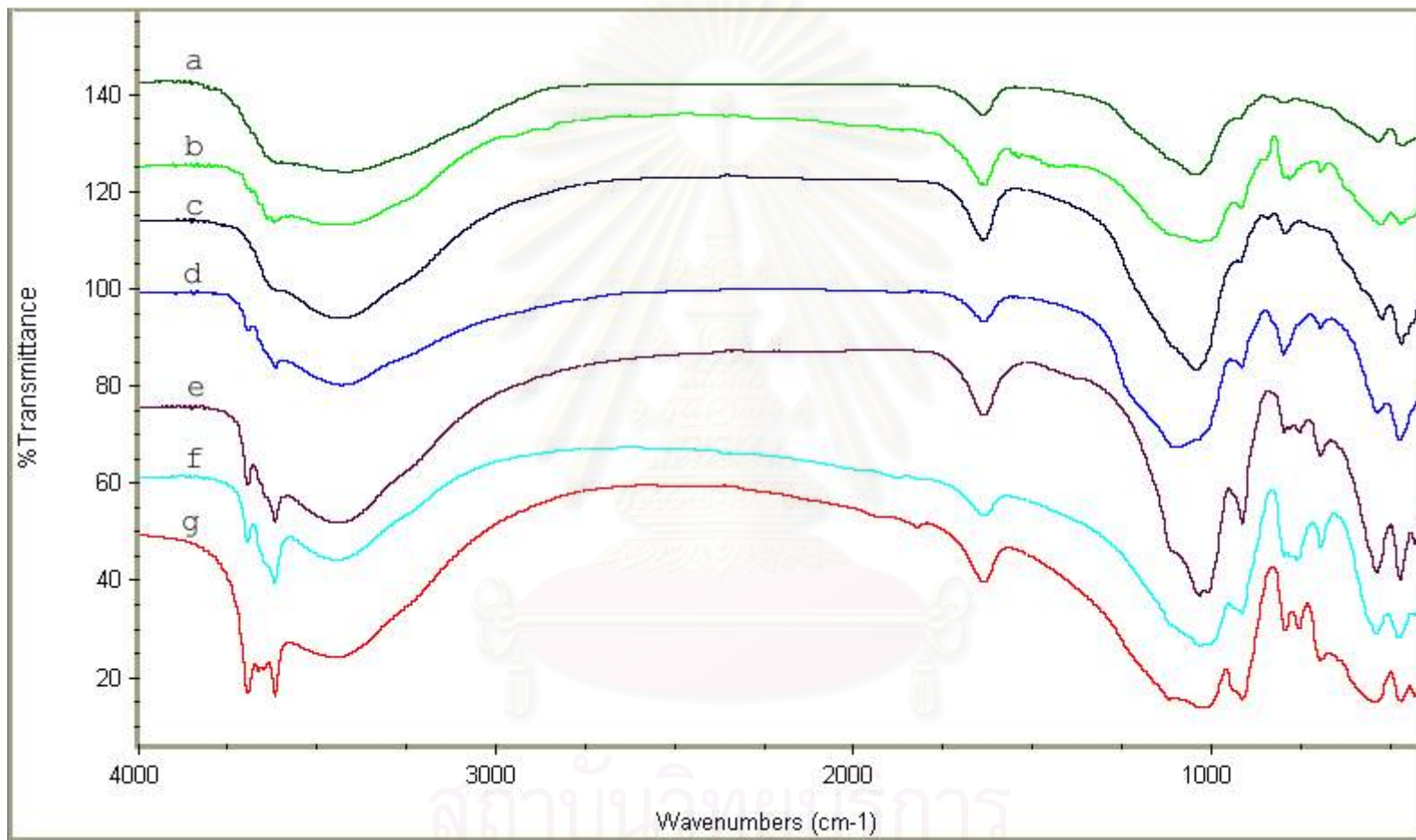


Figure A9 IR spectra of Tonsil 616GSE compared with acid activated clay;  
(a) Tonsil 616GSE; (b) bentonite; (c) talcum; (d) diatomite; (e) ball; (f) china L; (g) china R.

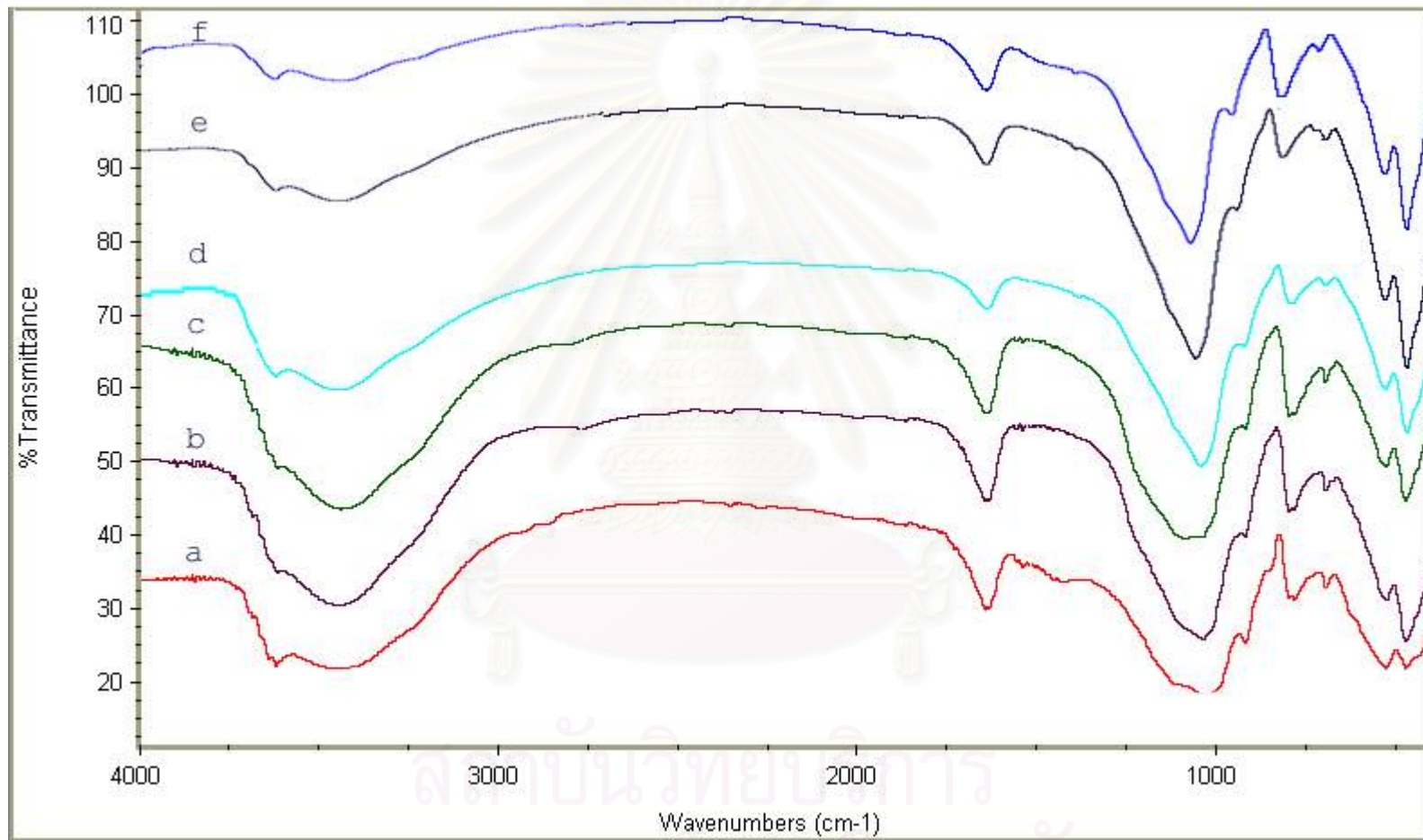


Figure A10 FTIR spectra of bentonite (a) acid activated (b) TMA (c) DMA (d) MA (e) KCl (f) CaCl<sub>2</sub>.

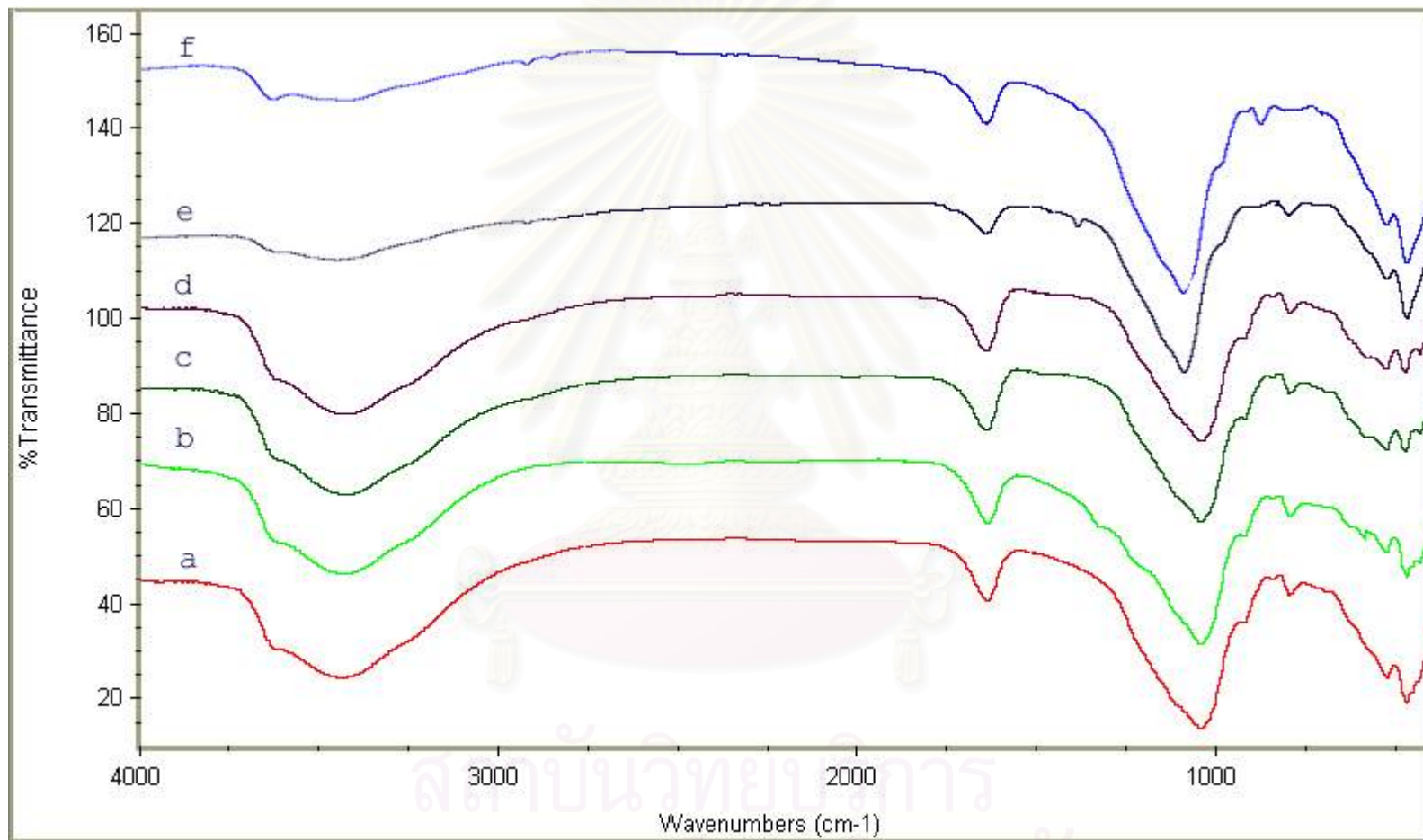


Figure A11 FTIR spectra of talcum (a) acid activated (b) TMA (c) DMA (d) MA (e) KCl (f) CaCl<sub>2</sub>.

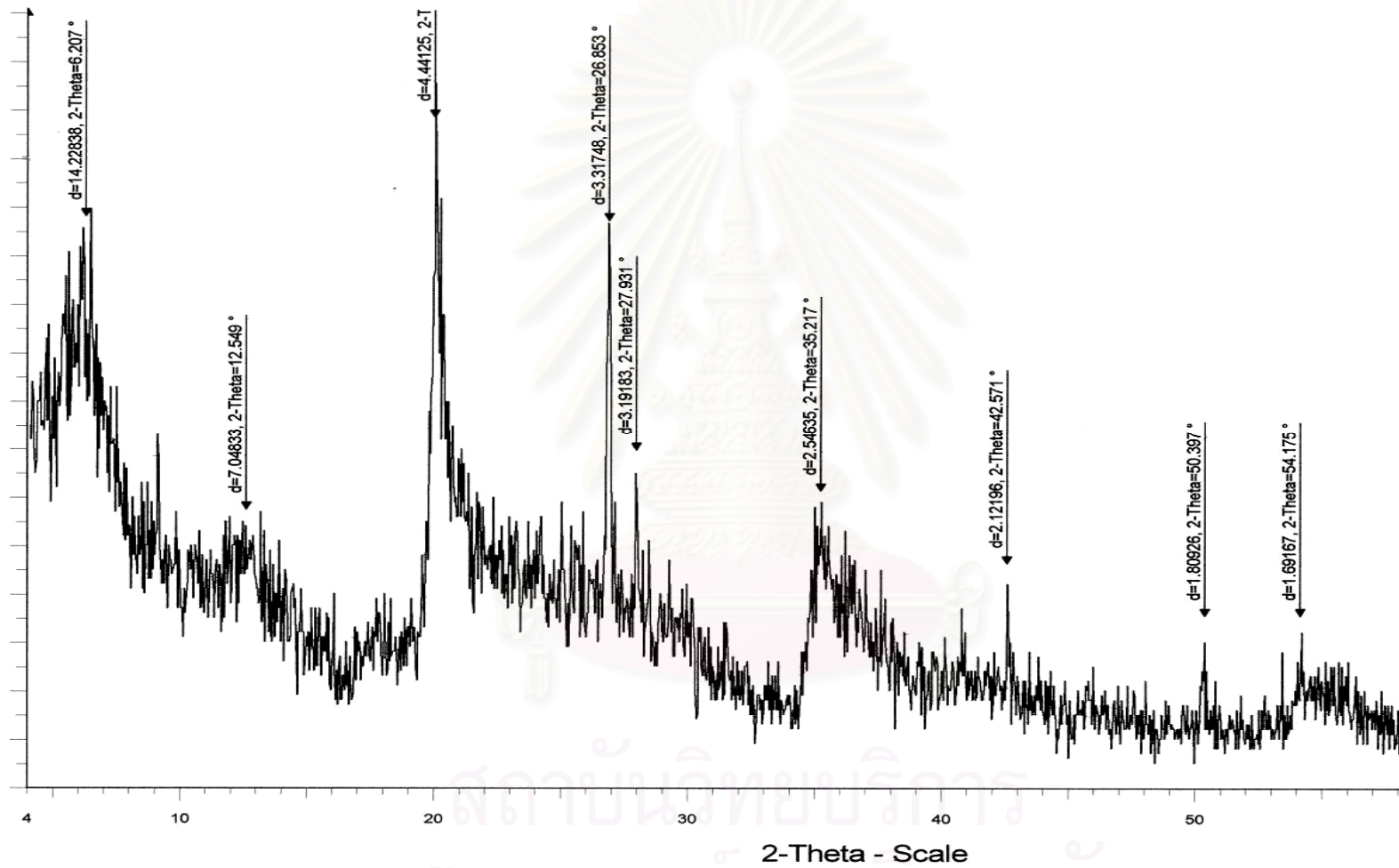


Figure A12 XRD pattern of Tonsil 616GSE.

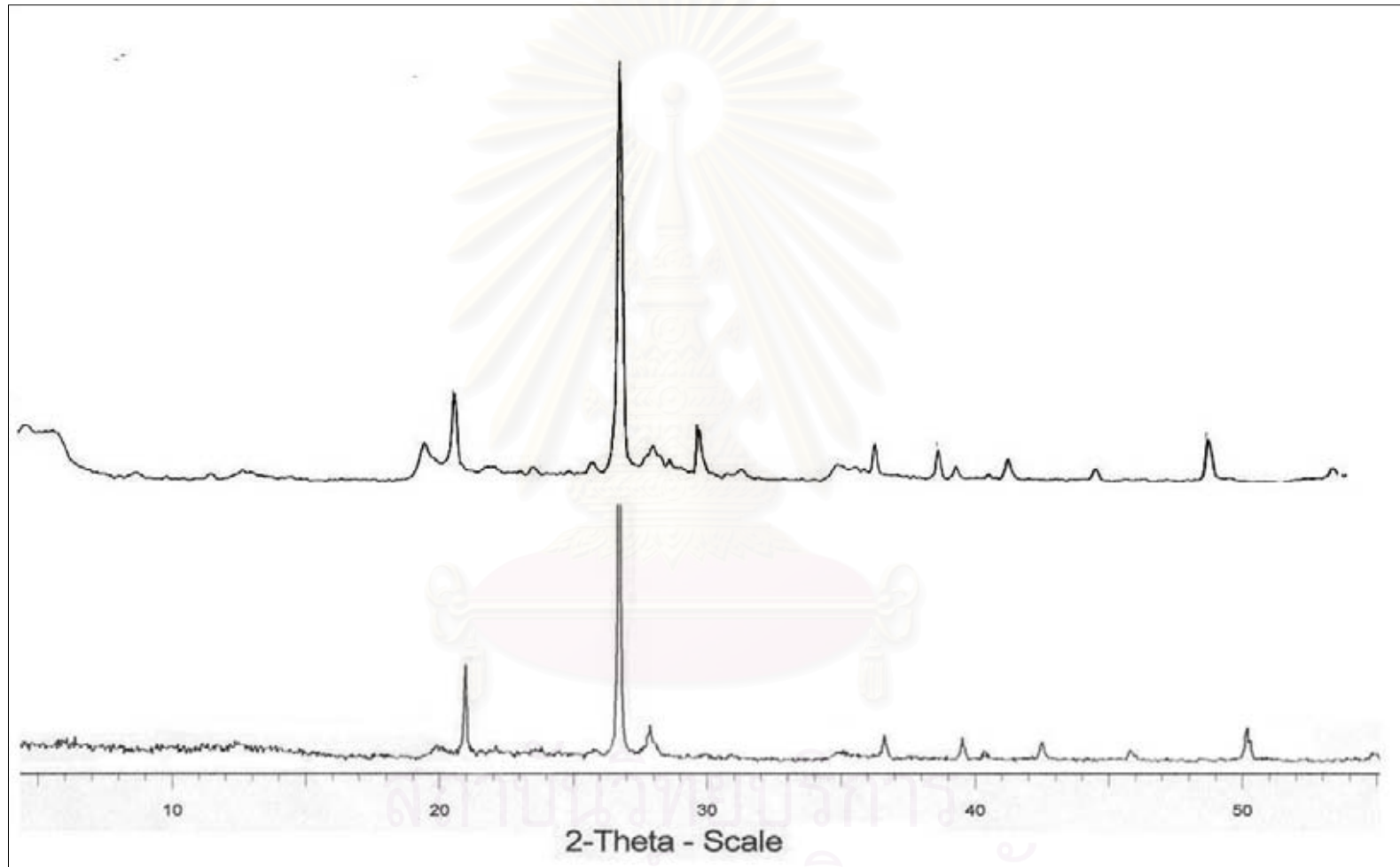


Figure A13 XRD patterns of bentonite (a) non-acid activated (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

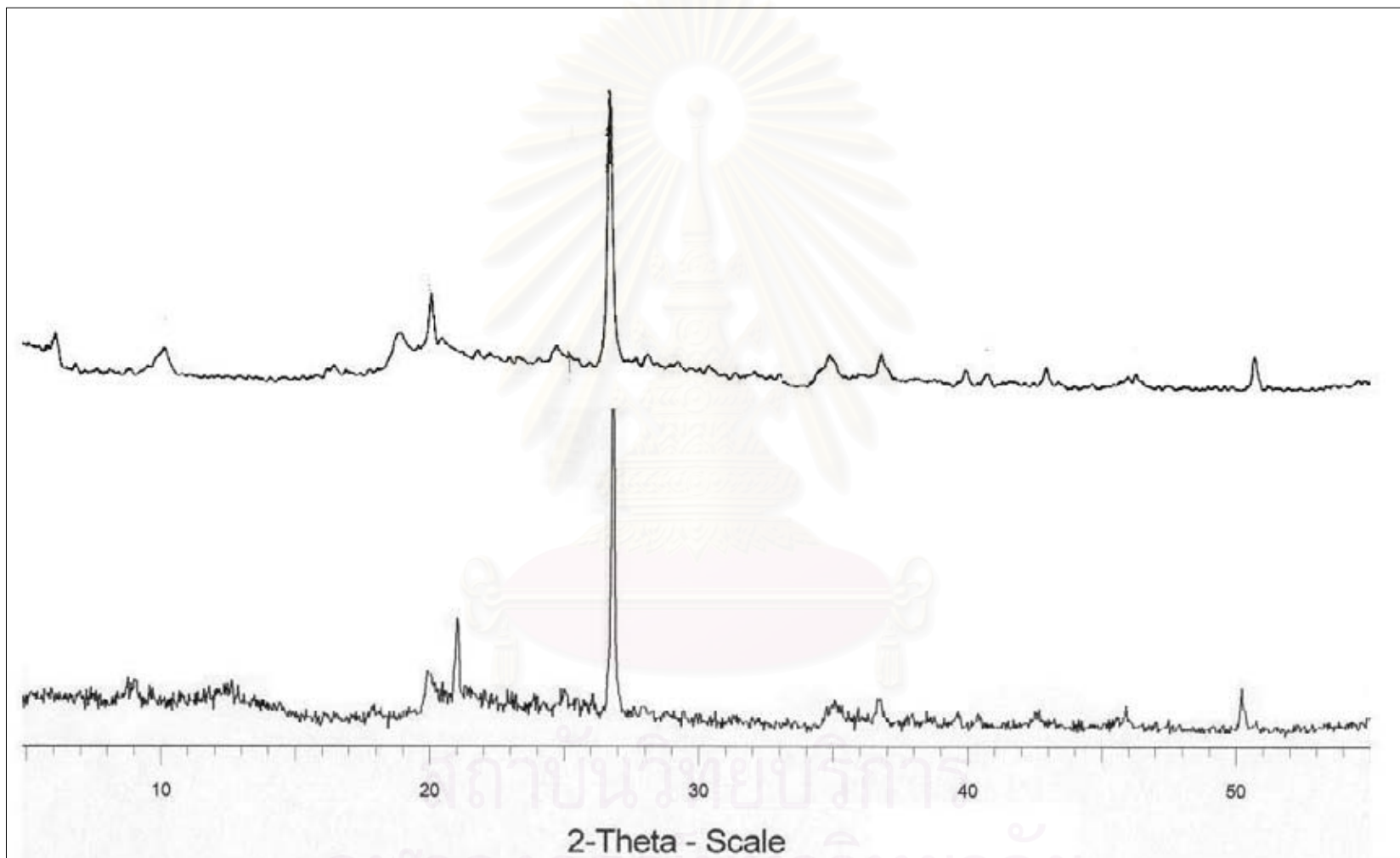


Figure A14 XRD patterns of diatomite (a) non-acid activated (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

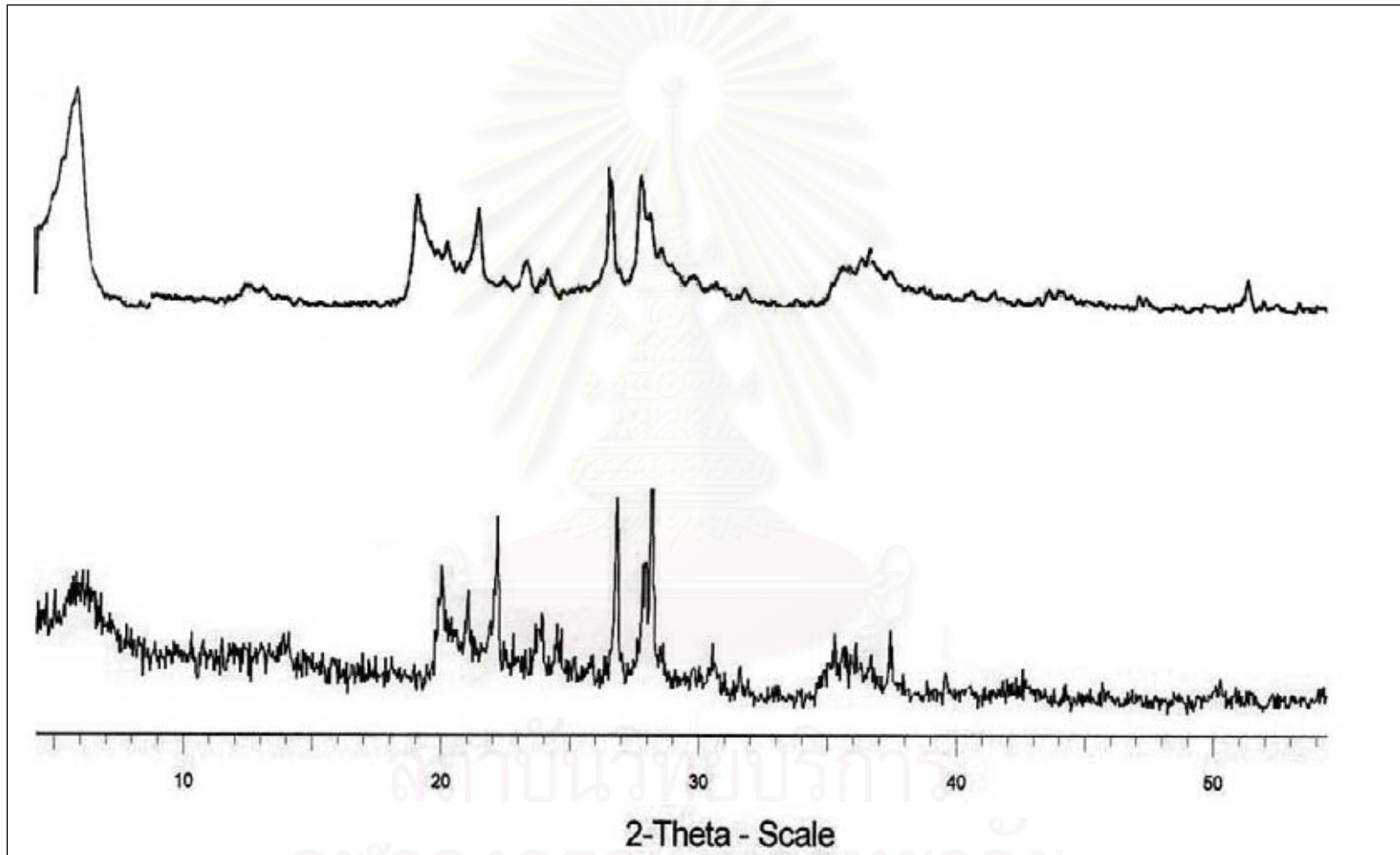


Figure A15 XRD patterns of talcum (a) non-acid activated (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.



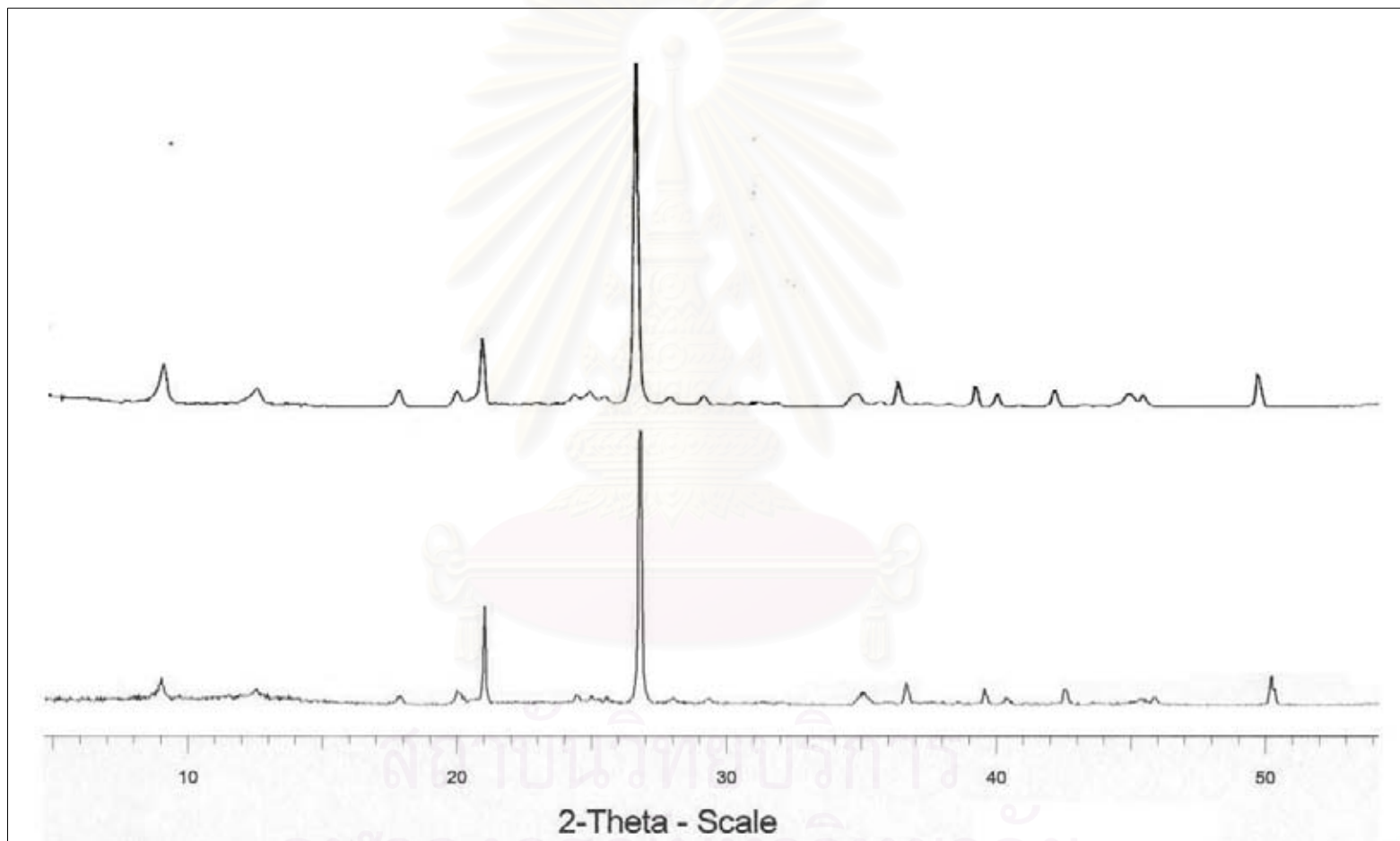


Figure A16 XRD patterns of china L (a) non-acid activated (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

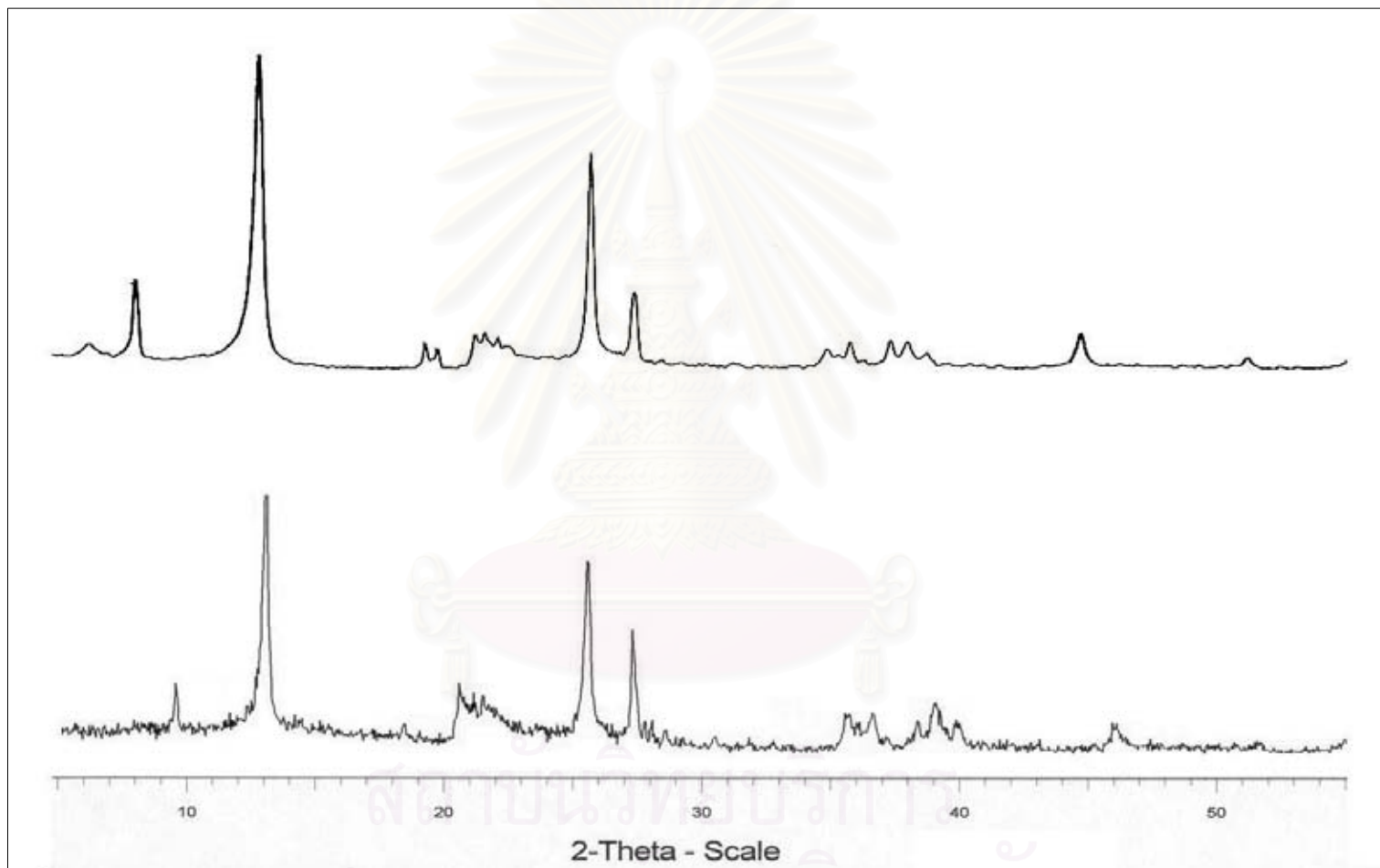


Figure A17 XRD patterns of china R (a) non-acid activated (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

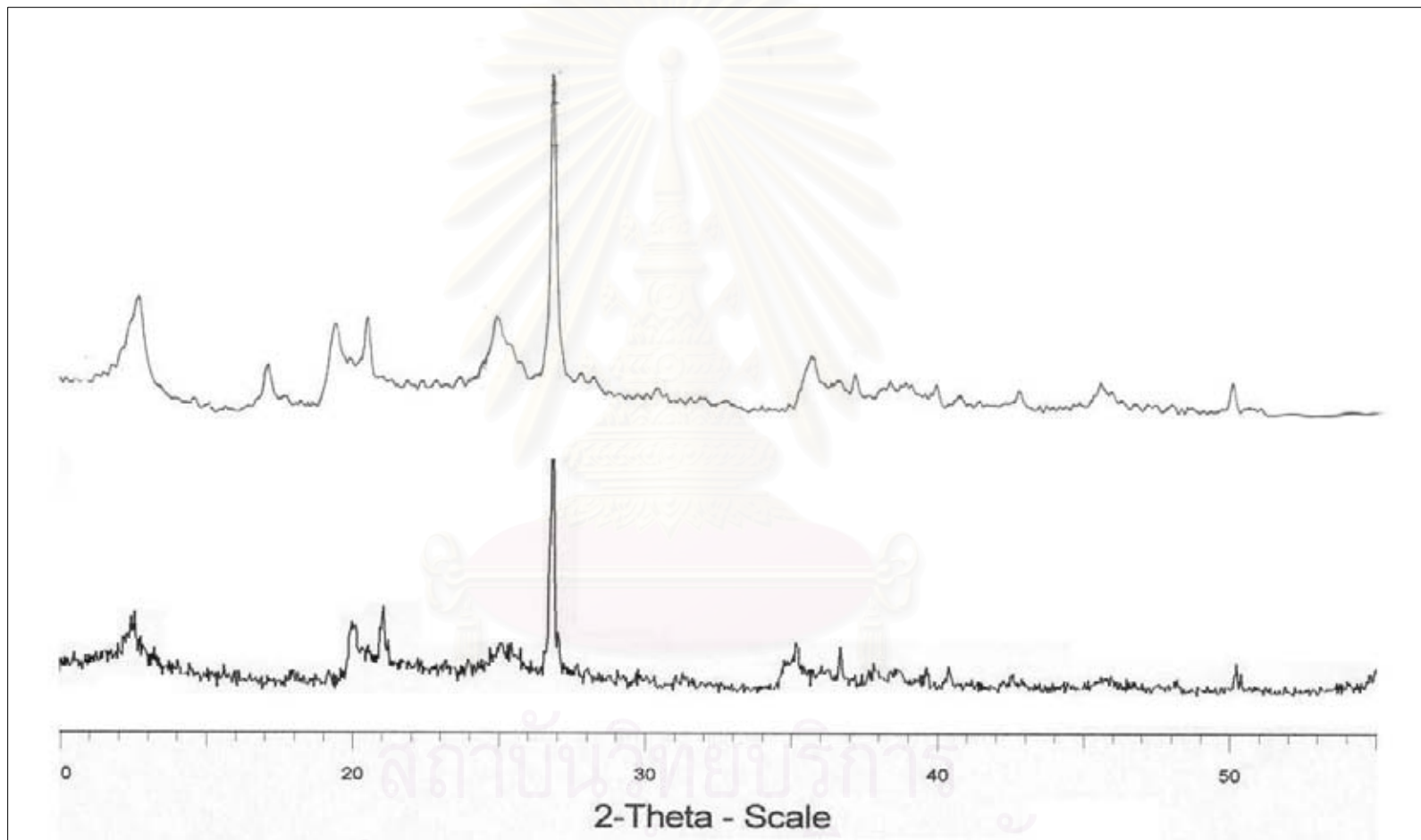


Figure A18 XRD patterns of ball (a) non-acid activated (b) acid activated with H<sub>2</sub>SO<sub>4</sub>.

FEED

26074504

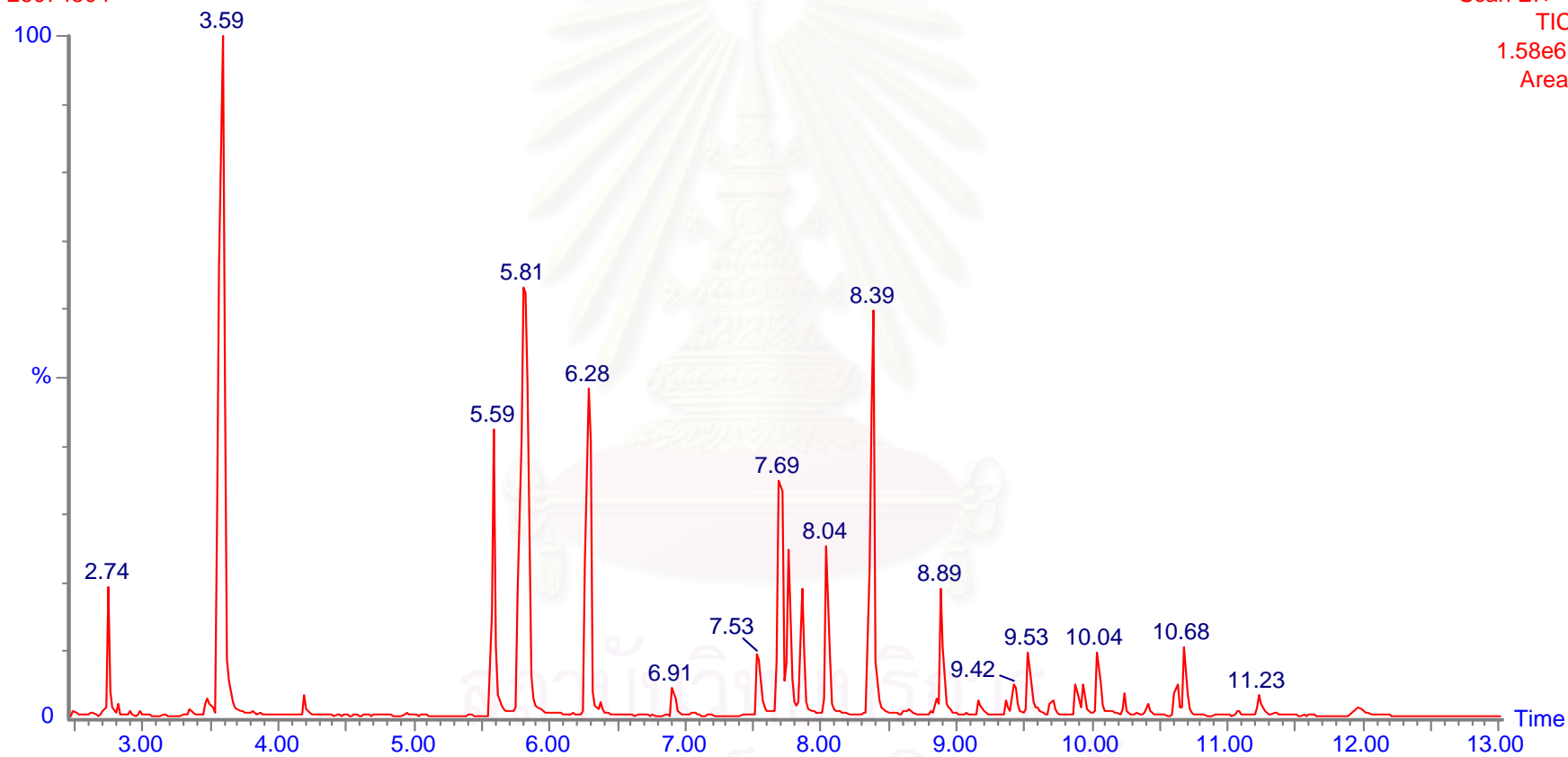


Figure A19 GC-MS Chromatogram of BTX feedstock.

616 GSE

26074506

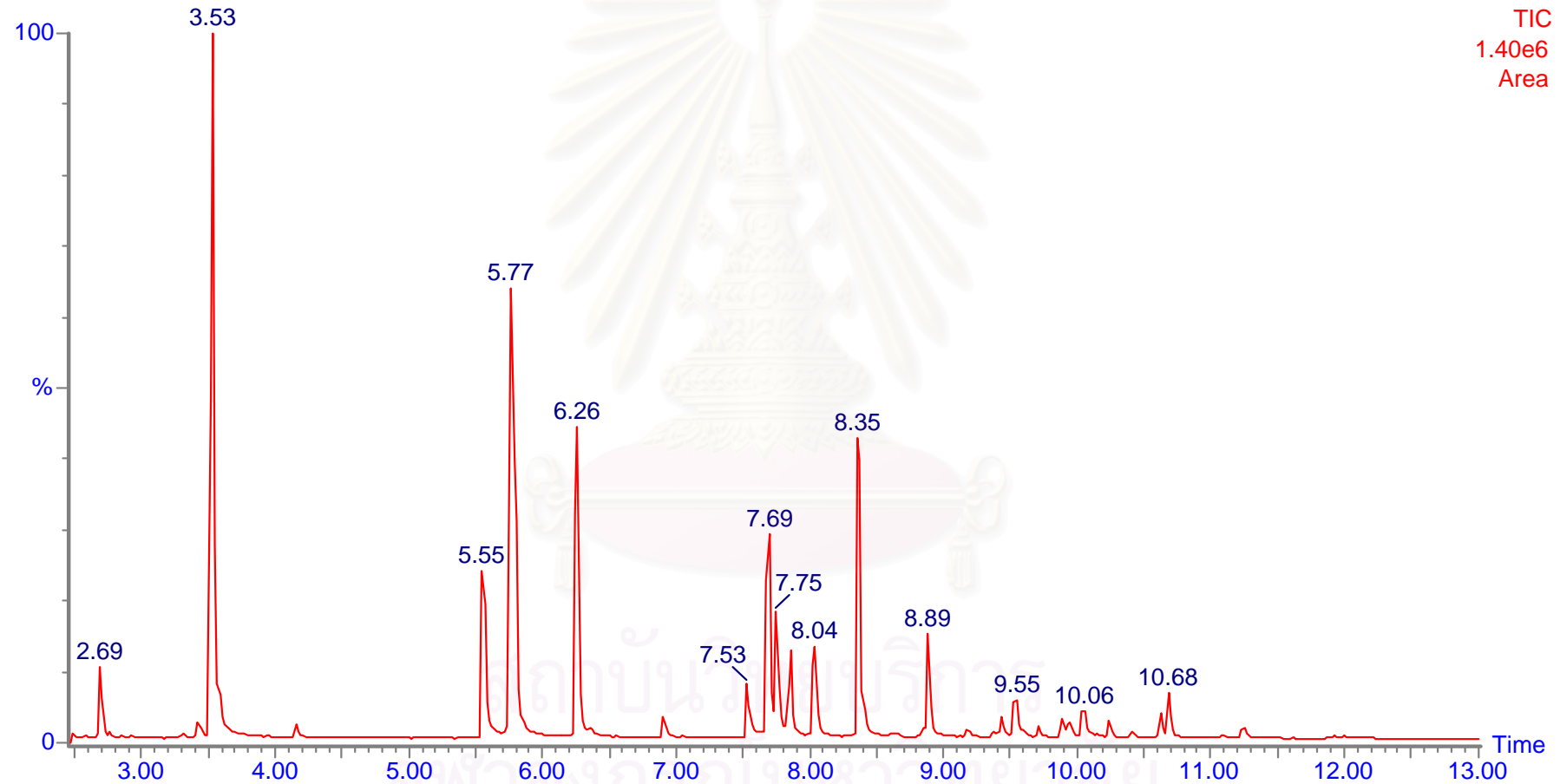


Figure A20 GC-MS Chromatogram of BTX feedstock refluxed with Tonsil 616GSE.

**BEN**

26074505

Scan EI+  
TIC  
1.01e6  
Area

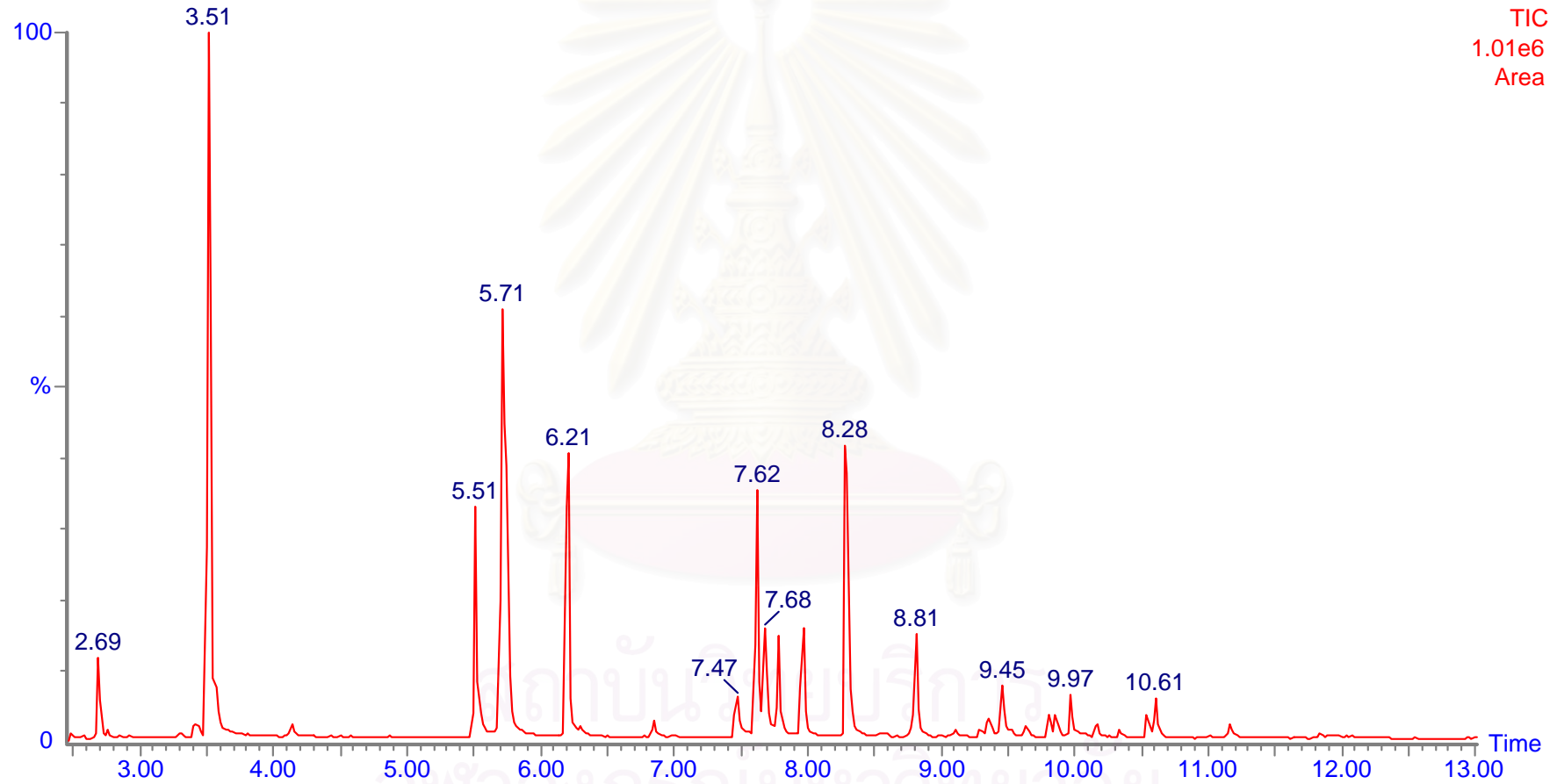


Figure A21 GC-MS Chromatogram of BTX feedstock refluxed with bentonite.

TALC

26074507

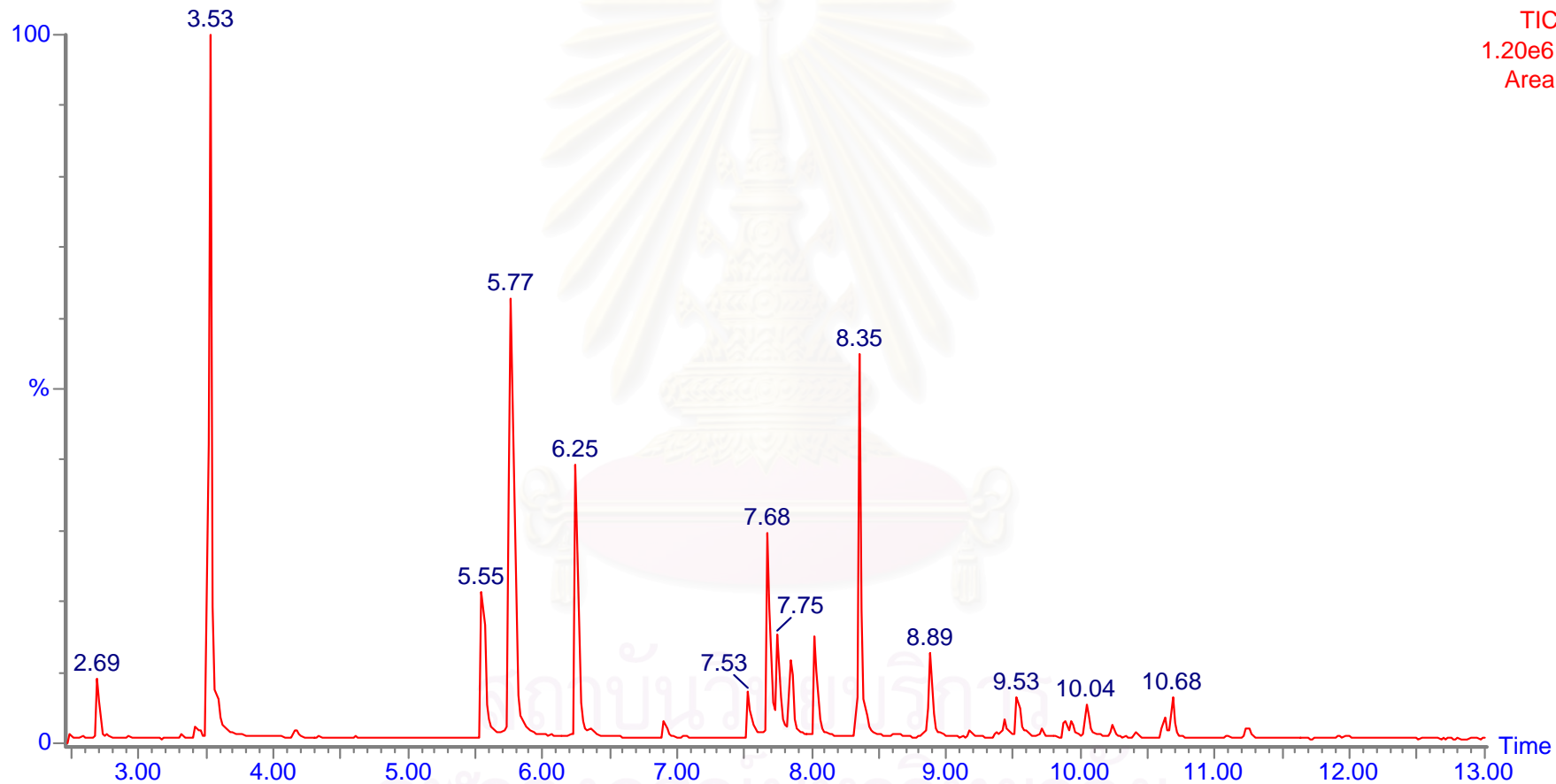


Figure A22 GC-MS Chromatogram of BTX feedstock refluxed with talcum.

RES 616GSE

26074503

Scan EI+  
TIC  
1.63e5  
Area

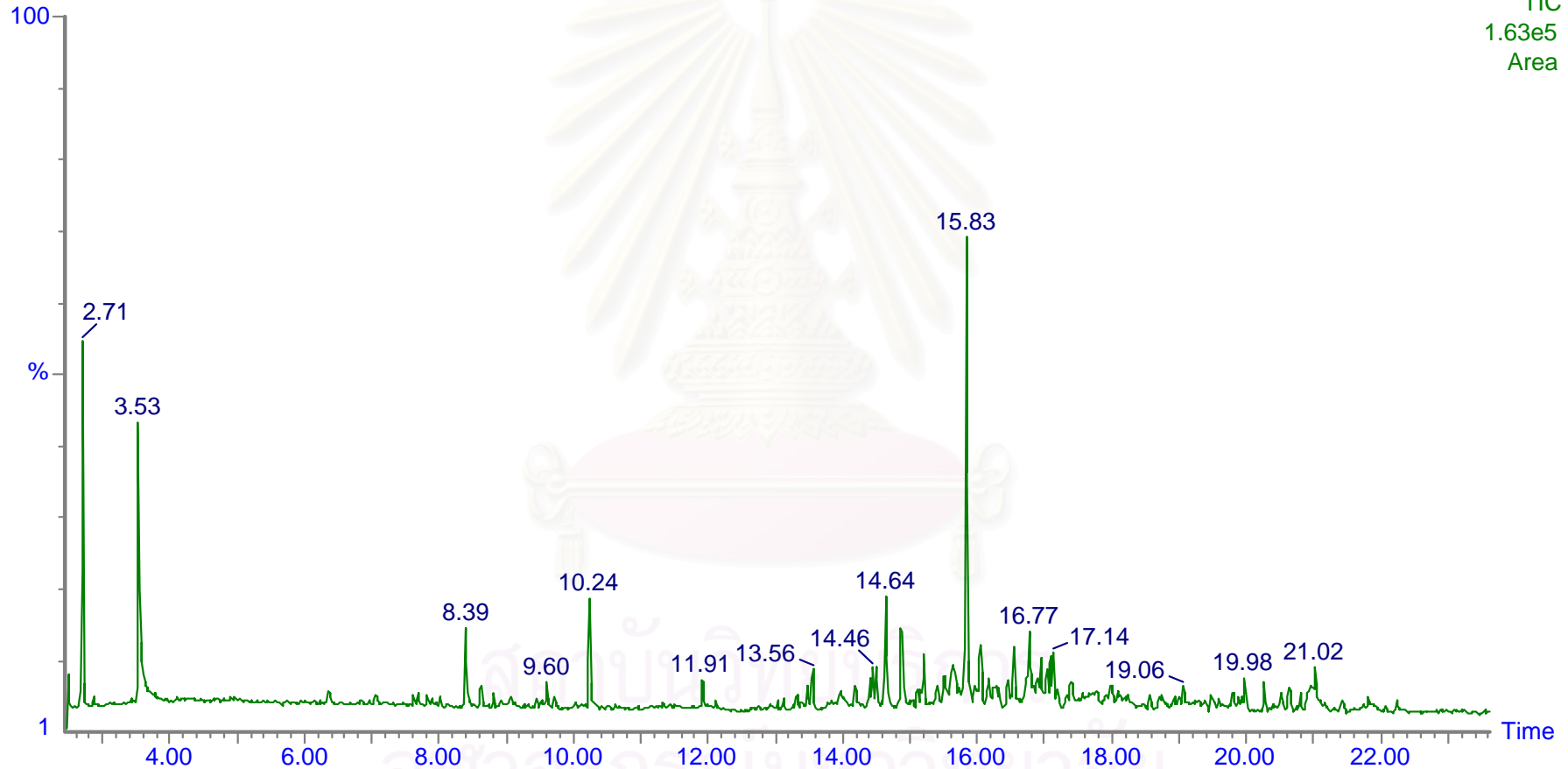


Figure A23 GC-MS Chromatogram of residue BTX feedstock in Tonsil 616GSE.



**RES BEN**

26074508

Scan EI+  
TIC  
2.05e5  
Area

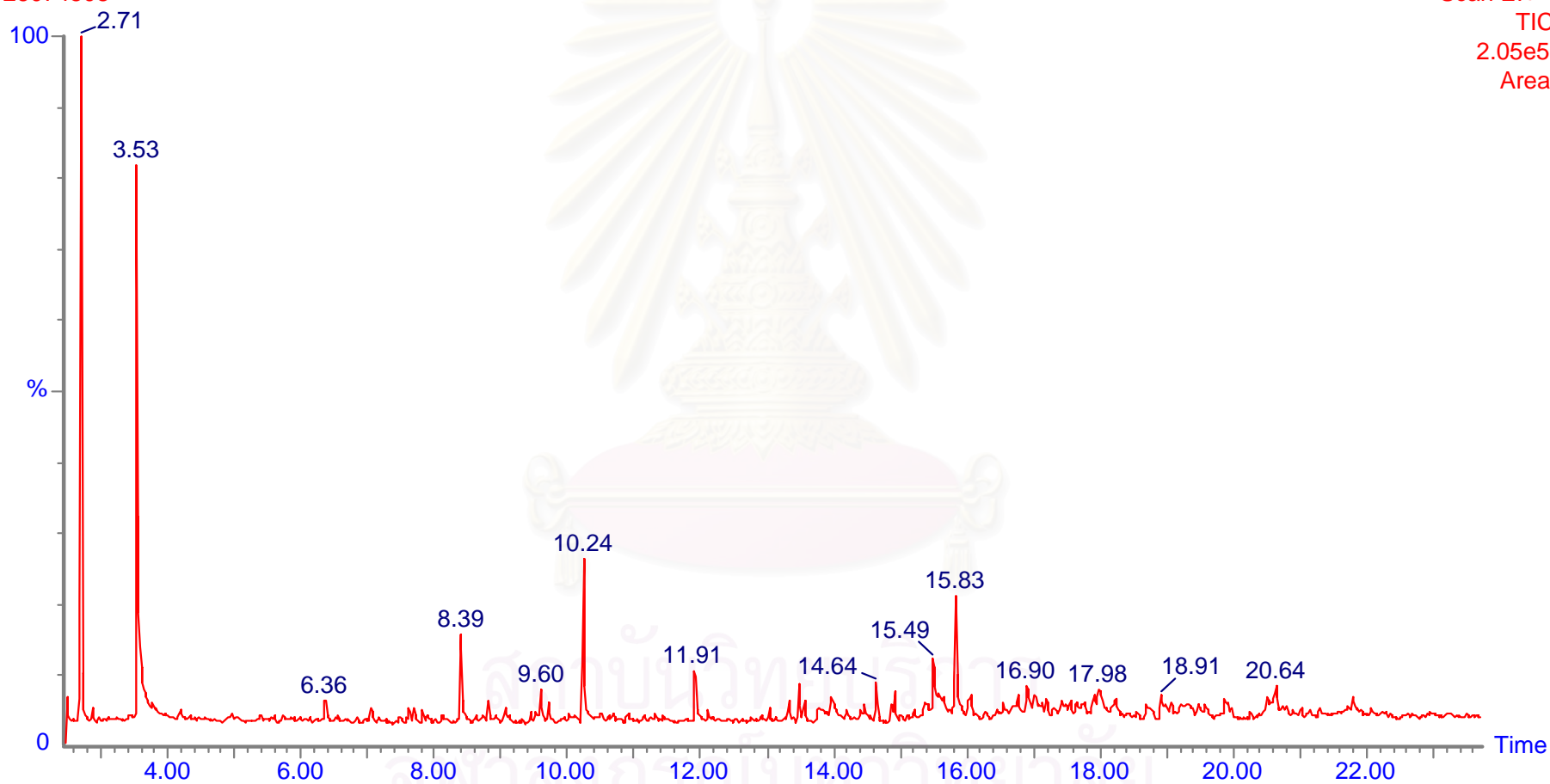


Figure A24 GC-MS Chromatogram of residue BTX feedstock in bentonite.

**RES TALC**

26074509

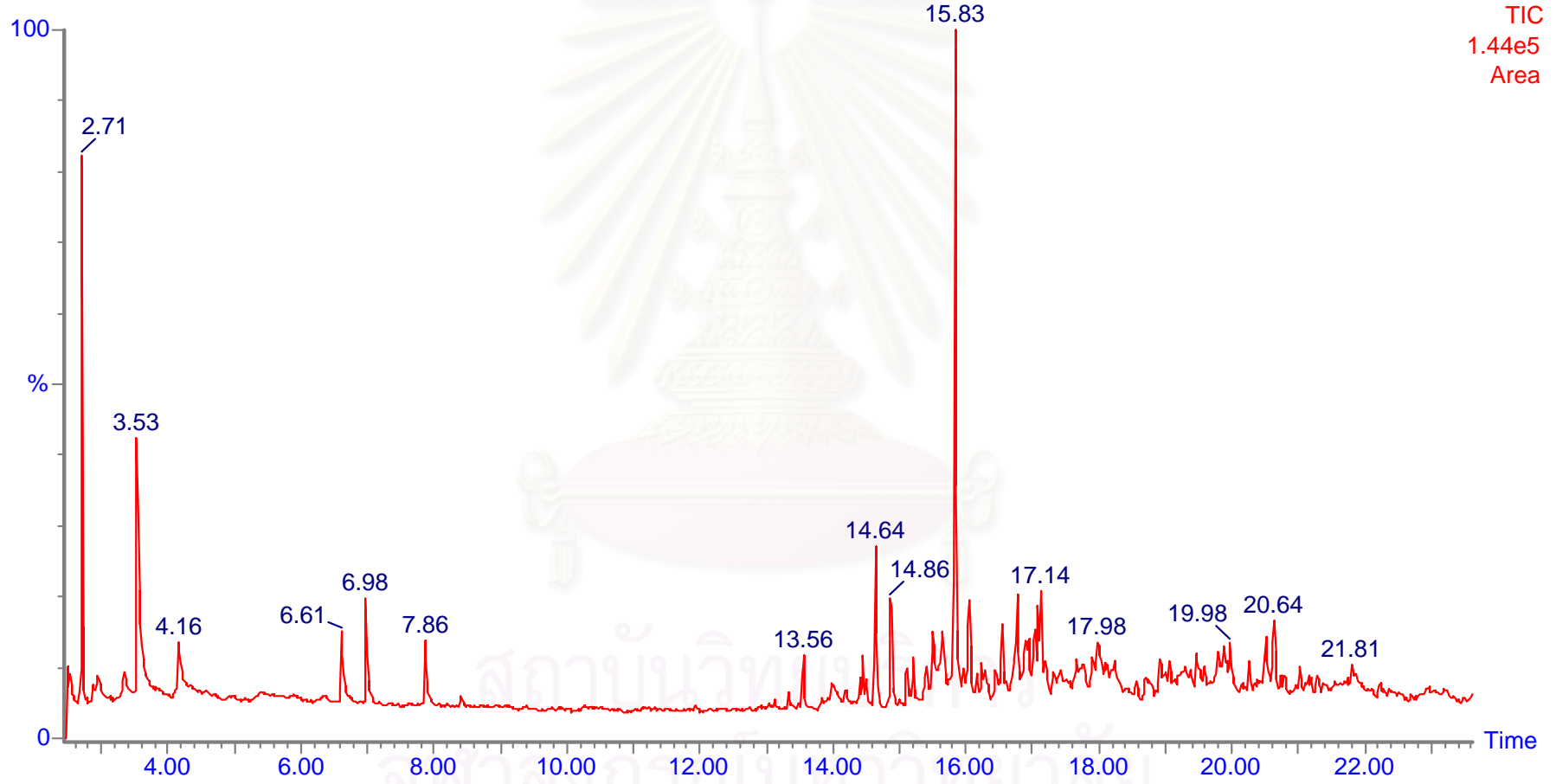


Figure A25 GC-MS Chromatogram of residue BTX feedstock in talcum.



APPENDIX B

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

# JAPANESE INDUSTRIAL STANDARD

JIS K 0070 - 1966

## 1. Scope

This standard specifies testing methods for acid value, ester value, iodine value, and hydroxyl value of chemical products.

## 2. Method of test

Iodine value : the iodine value is defined by the amount of halogen (calculated to the number of grams of iodine) absorbed by 100 g of the sample under the prescribed conditions.

## 3. Reagents

- a) Wijs' solution: Weigh 7.9 g of iodine trichloride and 8.7 g of iodine into separate flasks. Dissolve them in acetic acid, mix well and dilute with acetic acid into 1000 ml.

This solution should be stored in a brown bottle, in a dark place. When it might freeze at winter, it should be heated to a temperature not higher than 40°C prior to use.

- 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 24.6 g of sodium thiosulfate in water and dilute with water to 100 ml. This solution should be standardized as follows.
- d) Starch solution: weight 1 g of soluble starch with a small amount of water and pour slowly with constant stirring, into 200 ml of boiling water. Allow cooling to room temperature and supernatant liquid or the filtrate should be for test.
- e) N/10 Potassium dichromate solution (primary standard substance): Pulverize potassium dichromate specified in JIS K 8005 and heat at 100 to 110°C for 3-4 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 diluted with water to mark.

### Standardization

Take 10 ml of potassium iodide solution (10% w/v) into a glass-stoppered Erlenmeyer flask and 5 ml of hydrochloric acid and shake well. And exactly 25 ml of N/10 potassium dichromate solution (primary standard 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-starch changes to green. Run the blank titration and calculate the factor of N/10 sodium thiosulfate solution, f, by the following formula:

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

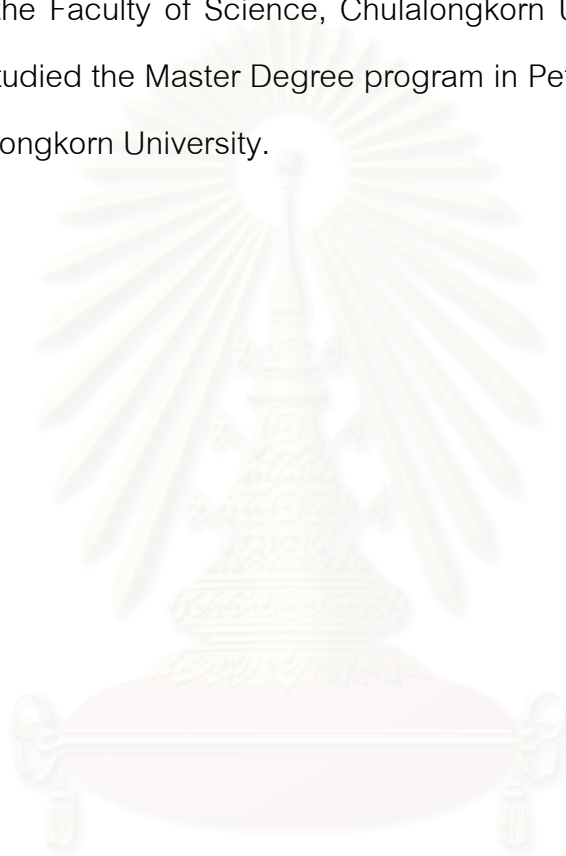
Where: A = volume of N/10 sodium thiosulfate solution consumed in actual titration (cm<sup>3</sup>)  
B = volume of N/10 sodium thiosulfate solution consumed in blank titration (cm<sup>3</sup>)



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## VITAE

Miss Pennapa Klurvudtikul was born on November 14, 1978, in Bangkok Province, Thailand. She graduated with a Bachelor's Degree of Science in Chemistry, from the Faculty of Science, Chulalongkorn University in 1999. In the same year, she studied the Master Degree program in Petrochemistry and Polymer Science at Chulalongkorn University.



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