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**REGENERATION OF SPENT BENTONITE CLAY
FOR TREATMENT OF BTX FEEDSTOCK**



Miss Kittirat Laohaledsakda

**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**

Graduate School

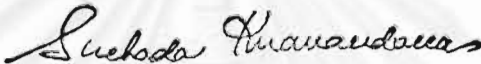
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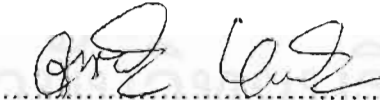
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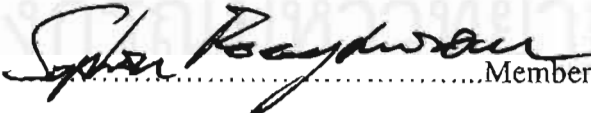
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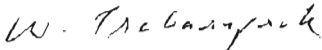
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งานวิจัยนี้ได้ศึกษาการฟื้นฟูดินฟอกสีเบนโทไนต์ที่ใช้แล้วเพื่อนำกลับมาใช้ใหม่ในการบำบัดสารป้อนบีทีเอ็กซ์ โดยการใช้ความร้อนเผาเพื่อกำจัดคาร์บอนที่เกาะบนพื้นผิว หรืออุดตันรูพรุน ซึ่งกระทำโดยการแปรค่าอุณหภูมิและเวลาดังนี้ 650 องศาเซลเซียส เป็นเวลา 6-8 ชั่วโมง 700 และ 750 องศาเซลเซียส เป็นเวลา 3-5 ชั่วโมง จากนั้นทำการบำบัดด้วยแอมโมเนียมฟลูออไรด์ ที่ความเข้มข้น 1-5 เปอร์เซ็นต์เพื่อเพิ่มแหล่งของกรด ดินฟอกสีเบนโทไนต์ที่ถูกฟื้นฟูมีประสิทธิภาพประมาณ 91 เปอร์เซ็นต์ เนื่องจากการใช้ความร้อนเผาโดยตรงมีผลทำให้โครงสร้างของดินฟอกสีเบนโทไนต์บางส่วนเปลี่ยนแปลงไป และพื้นที่ผิวลดลง



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KITTRAT LAOHALEDSAKDA : REGENERATION OF SPENT BENTONITE CLAY FOR TREATMENT OF BTX FEEDSTOCK. THESIS ADVISOR : ASSOC. PROF. AMORN PETSOM, Ph.D. THESIS CO-ADVISOR : CHATURONG BOONTUNJAL, Ph. D. 67 pp. ISBN 974-332-992-7.

In this research, regeneration of spent bentonite clay for treatment of BTX feedstock was studied using combustion process to remove carbon deposits on the surface or blockage of pores. The combustion temperatures and time were varied as follows: 650°C for 6-8 hrs; 700°C and 750°C for 3-5 hrs. Then, the product was treated with ammonium fluoride at 1-5% concentration in order to increase acid site. The efficiency of regeneration clay was approximately 91% because direct combustion partially changed bentonite clay structure and decreased surface area.

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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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CONTENTS

	Page
ABSTRACTS IN THAI.....	iv
ABSTRACTS IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LISTS OF TABLES.....	x
LISTS OF FIGURES.....	xi
ABBREVIATIONS.....	xiii
CHAPTER	
I INTRODUCTION	
Objective and scope of the research.....	2
II THEORETICAL CONSIDERATION	
2.1 Basic of BTX plant.....	3
2.2 Introduction of bentonite clay.....	5
2.3 Bentonite clay for treatment of BTX feedstock.....	6
2.4 Reactions occurring on bentonite clay treatment of BTX.....	10
2.5 Cause of deactivation.....	12
2.6 Regeneration of spent clay.....	12
2.7 Literature reviews.....	14

	Page
III EXPERIMENTAL	
3.1 Materials.....	17
3.2 Apparatus and instruments.....	18
3.3 Procedure.....	19
3.3.1 Regeneration of spent clay.....	19
3.3.2 Treatment of C_8^+ stream with regenerated clay.....	19
3.4 Analysis of C_8^+ stream.....	21
3.5 Determination of clay properties.....	21
IV RESULTS AND DISCUSSION	
4.1 Selection of the optimum regeneration condition.....	24
(1) Studies of various temperature and time for combustion of spent clay.....	24
(2) Studies of various NH_4F concentration on impregnation of clay.....	26
4.2 Characterization of C_8^+ stream.....	32
4.3 Determination of clay properties.....	35
(1) Study of clay structure.....	35
(2) Surface area and pore size analysis.....	35
V CONCLUSIONS	
Suggestions for future work.....	40

	Page
REFERENCES.....	41
APPENDICES.....	43
Appendix A.....	44
Appendix B.....	64
VITA.....	67



LIST OF TABLES

TABLE	Page
3.1 Conditions of regeneration procedure.....	20
4.1 Weight loss through TGA of fresh clay, spent clay and regenerated clay.....	31
4.2 Identification of C_8^+ compositions.....	33
4.3 Surface area and pore size analysis of clay.....	37
A1 BI of C_8^+ stream blank and after refluxed with clay.....	44
A2 Surface acidity of fresh clay and regenerated clay.....	45
A3 Weight loss of fresh clay, spent clay and regenerated clay.....	46
A4 Identification of C_8^+ compositions blank and after refluxed with F-24 and BSC-65-65F5.....	48
A5 XRF analyses of fresh clay, spent clay and regenerated clay.....	50

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

FIGURE	Page
2.1 Typical BTX Plant simplified block diagram.....	4
2.2 Structure of montmorillonite (sodium form).....	7
2.3 Acid activated bentonite clay process.....	10
4.1 BI curve of C_8^+ stream refluxed with clay at 650-750°C.....	25
4.2 BI curve of C_8^+ stream refluxed with regenerated clay at 650°C for 6-8 hrs, treated with NH_4F concentration 1-5%. BI of C_8^+ blank and fresh clay are 523.8 and 120.9 mg Br/100g.....	27
4.3 Surface acidity data of various fluoride-treated clays at 650°C for 6-8 hrs.....	28
4.4 BI curve of C_8^+ stream refluxed with clay regenerated at 700°C for 3-5 hrs, treated with NH_4F concentration 1-5%. BI of C_8^+ blank and fresh clay are 523.8 and 120.9 mgBr/100g.....	29
4.5 Surface acidity data of various fluoride- treated clays at 700°C for 3-5 hrs	30
4.6 XRD patterns of fresh clay, spent clay and regenerated clay	36
A1 TG and DTG curves of fresh clay	51
A2 TG and DTG curves of spent clay	52
A3 TG and DTG curves of clay regenerated at 650°C for 6.5 hrs.....	53
A4 TG and DTG curves of clay regenerated at 650°C for 6.5 hrs and treated with 1% NH_4F	54

	Page
A5 TG and DTG curves of clay regenerated at 650°C for 6.5 hrs and treated with 3% NH ₄ F.....	55
A6 TG and DTG curves of clay regenerated at 650°C for 6.5 hrs and treated with 5% NH ₄ F.....	56
A7 TG and DTG curves of clay regenerated at 700°C for 4 hrs	57
A8 TG and DTG curves of clay regenerated at 700°C for 4 hrs and treated with 1% NH ₄ F.....	58
A9 TG and DTG curves of clay regenerated at 700°C for 4 hrs and treated with 3% NH ₄ F.....	59
A10 TG and DTG curves of clay regenerated at 700°C for 4 hrs and treated with 5% NH ₄ F.....	60
A11 GC chromatogram of C ₈ ⁺ blank.....	61
A12 GC chromatogram of C ₈ ⁺ refluxed with fresh clay	62
A13 GC chromatogram of C ₈ ⁺ refluxed with regenerated clay	63

ABBREVIATIONS

BTX	=	Benzene, Toluene, and Xylene
C ₈ ⁺	=	C ₈ and heavier hydrocarbon
GC	=	Gas chromatograph
VOC	=	Volatile organic carbon
°C	=	degree of Celsius
g	=	gramme
ml	=	millilitre
min	=	minute
hrs	=	hours
BSC	=	Combustion of spent clay
BSC-65-65F5	=	Combustion of spent clay at 650 °C for 6.5 hrs and impregnated with 5% NH ₄ F
BSC-70-4F5	=	Combustion of spent clay at 700 °C for 4 hrs and impregnated with 5% NH ₄ F
F-24	=	Fresh clay F-24
BF-24	=	Combustion of fresh clay F-24
BF-24F5	=	Combustion of fresh clay F-24 at 650 °C for 6.5 hrs and impregnated with 5% NH ₄ F
MTG	=	Transformation of methanol into hydrocarbons of boiling point range within that of gasoline
HZSM-5	=	High silica Zeolite

FTIR	=	Fourier transform infrared
TGA	=	Thermogravimetric analysis
BI	=	Bromine index
BET method	=	Brunauer, Emmett and Teller method.



CHAPTER I

INTRODUCTION

BTX is an acronym for benzene-toluene-xylene. Petroleum sources BTX is produced by catalytic reforming and pyrolysis. BTX are the aromatic hydrocarbons of most value and widely used as petrochemicals. They are important precursors for plastics, such as nylon, polyurethane, polyesters and alkyd resins. The demand for aromatics in Thailand and SEA is increasing constantly, especially in Thailand which has a 10-15 % average expansion up until 2002 [1].

Bentonite clays sorbent [2], produced in granular form to facilitate its use in fixed bed applications. This sorbent is used for treatment of BTX feedstock, for removal of unsaturated compounds especially naphthene and olefin. The olefin content of BTX as measured by bromine index is reduced [3]. In Thailand about 500 metric tons of wastes clay is generated annually. These wastes have to be disposed of in an environmentally responsible manner and at minimum cost such as mixing in cement slurry, brick partly and glass raw material. The regeneration of spent bentonite clays is not known in Thailand.

The potential causes of clays deactivation are (1) reversible deactivation by carbon deposits and pore plugging by carbon or polymer buildup, this carbon deposition can be removed by combustion with air, and (2) irreversible deactivation by loss of acidity due to operation condition and combustion step. Acid sites were regenerated by impregnation with ammonium fluoride.

Objective and scope of the research

The objectives of this study were to regenerate spent bentonite clay and to study the properties and performance of regenerated clay. The scopes were the following: (1) to find regeneration conditions for spent clay used in the treatment of BTX feedstock, and (2) to compare physical properties, chemical properties and structure of regenerated clay with fresh clay.





CHAPTER II

THEORETICAL CONSIDERATION

2.1 Basic of BTX plant [2].

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, for example, using 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 useful form, particularly for nitration-grade aromatics.

Figure 2.1 illustrates typical BTX plant. In general, BTX is separated from hydrocarbon mixture by fractionation distillation and extractive distillation. The C_8^+ bottoms stream from the C7/C8 splitter is fed to clay treater (bentonite clay grade F-24) for removal of unsaturated compounds especially naphthene and olefin, and color producing materials. **Performance on treated BTX** is usually measured by the Bromine index (ASTM D-1492) for olefin content.

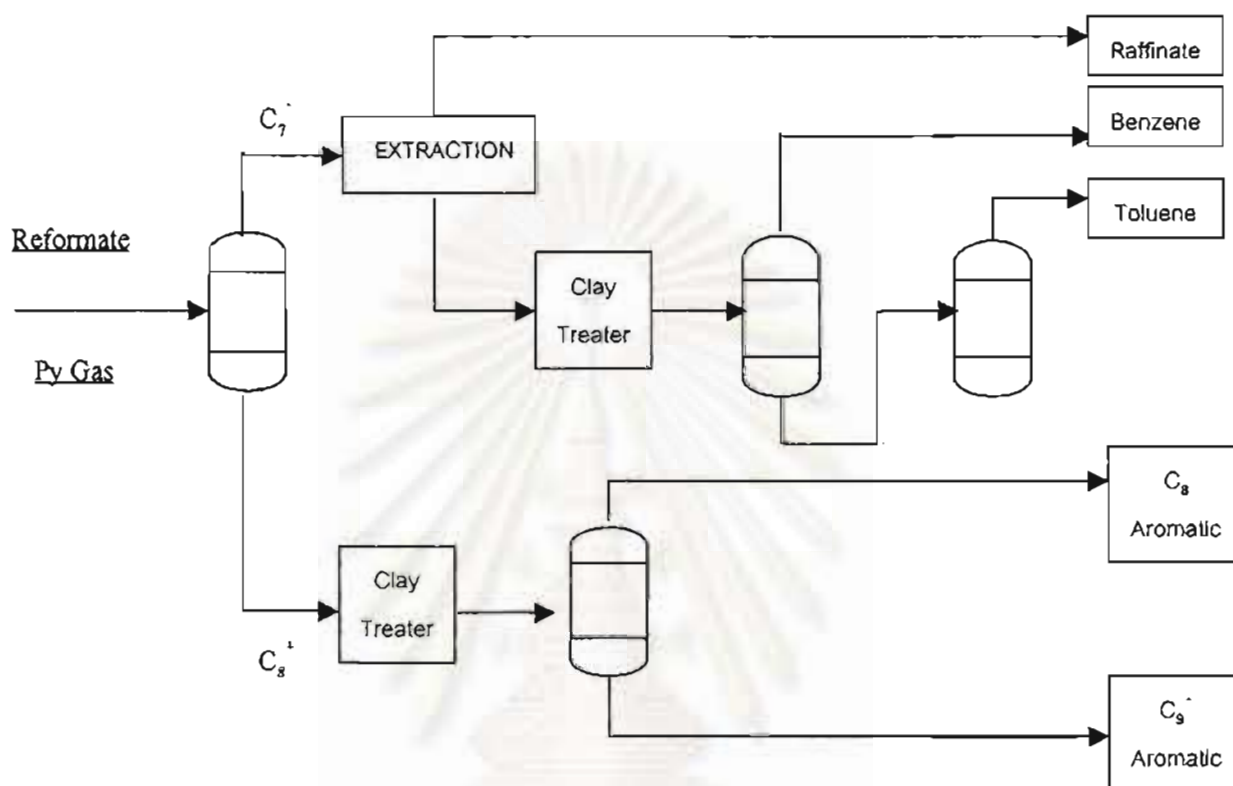


Figure 2.1 Typical BTX Plant simplified block diagram [2].

Olefins are objectionable in aromatic hydrocarbon, e.g., BTX, because of the following reasons: they are reactive and produce undesirable co-products in downstream 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 bromine index of BTX prior to treatment is usually greater than 200. After percolation through a fixed bed of grade F-24, the bromine index will be decreasing. As a charge of grade F-24 approaches the end of its life, the bromine index will begin to rise. 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 [4].

The term “bleaching earths” refers to clays that their natural state or after chemical or physical activation, have the capacity to adsorb coloring matters from oil. The term “bleaching” is reserved for treatment designed solely to reduce the color of the oil. Very little material is removed from the oil by bleaching, and bleaching treatment is commonly applied to oil after purification has been largely accomplished by refining.

Bleaching earths are finely crystalline silicates of aluminium 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.

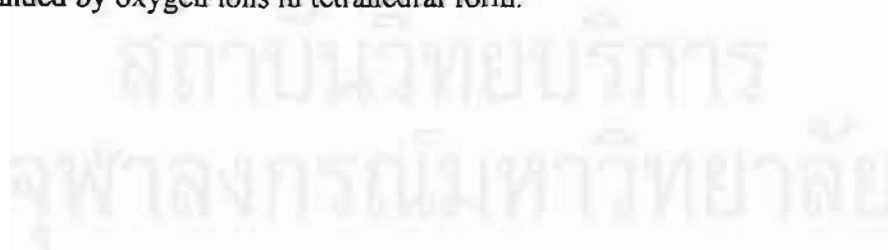
The geologically term “bentonites” refer to any clays produced by the devitrification of volcanic ash. Such clays are characterized by their power to adsorb water to a greater extent than other plastic clays. Two main types of bentonites are recognized. The first are those that absorb large quantities of water, “swelling” greatly in process, and remaining in suspension in thin water dispersions (Wyoming type); these gel have pronounced thixotropic properties. The second type are those

that absorb only slightly more water than ordinary plastic clays, and are characterized by rapid slaking and slight swelling when placed in water. Usually bentonites of the lesser swelling type exhibit high decolorizing ability after acid treatment.

Bentonite usually composed mainly of montmorillonite, although some may consist of the rare clay Minerals beidellite, saponite, hectorite and nontronite. Mineralogically, bentonites are 75 percent or more of montmorillonites with fragment of kaolinite, illite feldspar and traces of other minerals.

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 aluminium, iron and magnesium. The most important bentonite clays is the montmorillonite group of minerals. Figure 2.2 at the atomic level, montmorillonite possesses the layered sheet structure that is typical of most minerals. Each sheet consists of a three-layer sandwich of ions. The central layer consists of aluminium ions surrounded by oxygen ions in octahedral form. The outer layers are silicon ions surrounded by oxygen ions in tetrahedral form.



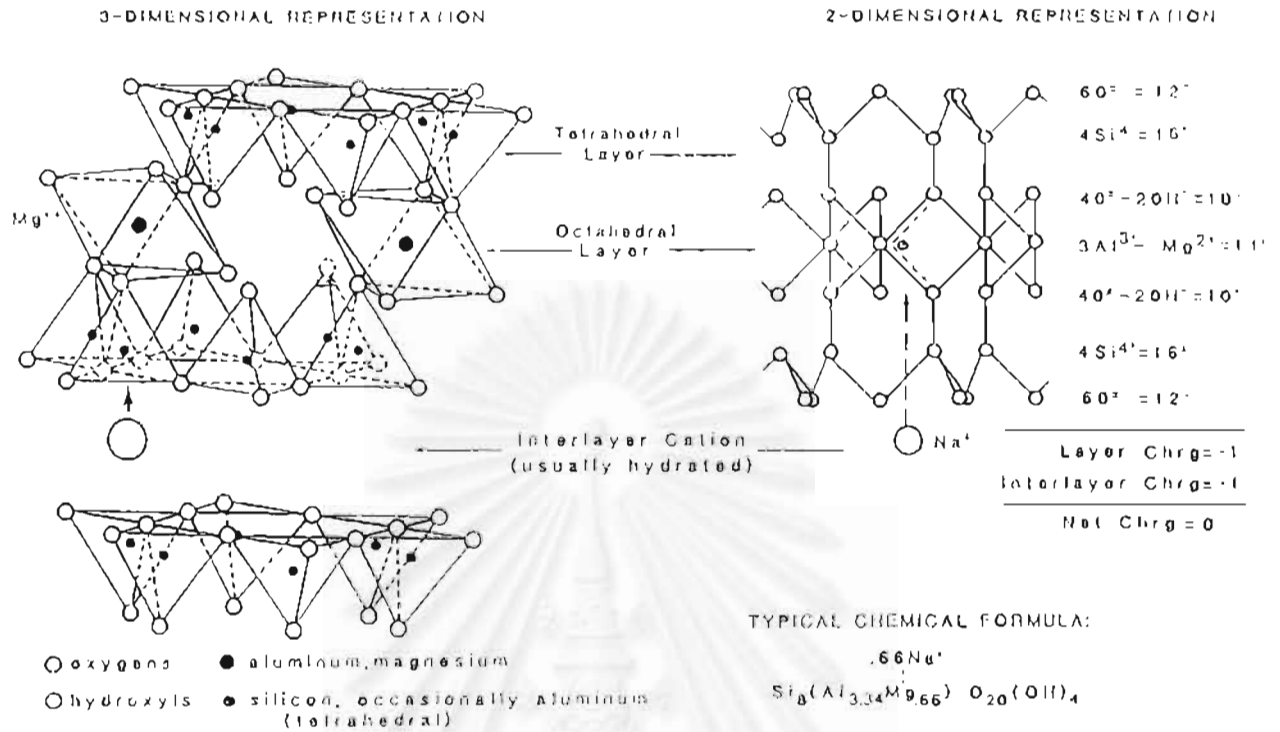
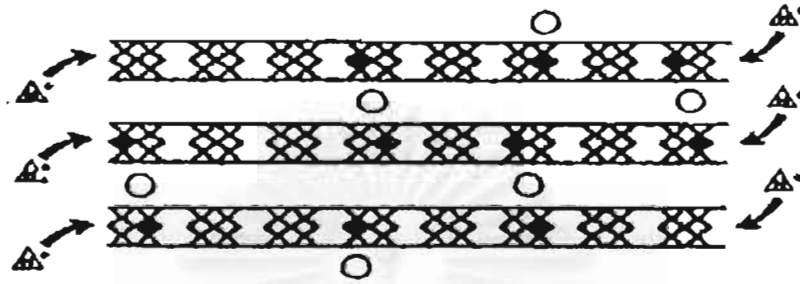


Figure 2.2 Structure of montmorillonite (sodium form)[2].

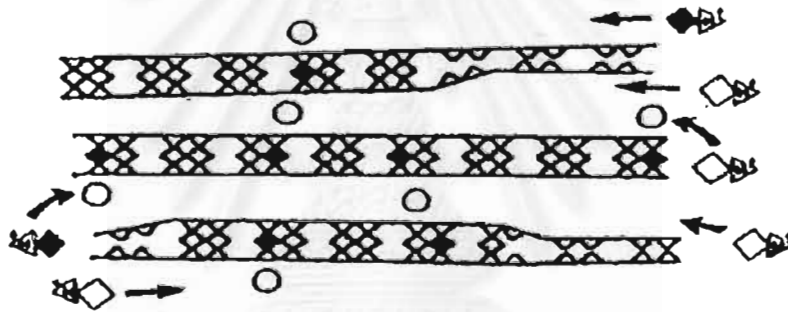
Acid activation enhances the natural ability of Montmorillonites to adsorb polar molecules. The naturally occurring substitution of magnesium (+2) ions for aluminium (+3) ions in certain clay deposits leaves a negative charge, which thus requires a positive charge to achieve electroneutrality. This positive 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

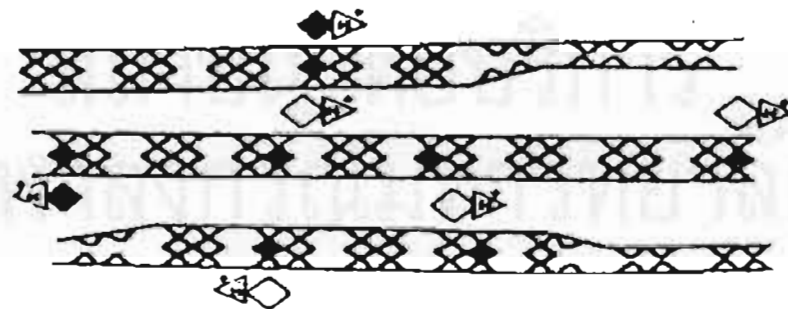


2. Structure disrupted surface area increases



3. Acid cations released from structure exchanged for calcium cations

4. Acid activated clay with acid cations in exchange sites



It is important to start with the right kind of montmorillonite because subtle differences in cation and lattice substitution pattern within the montmorillonite structure can cause significant differences in performance. Calcium montmorillonite are noted for their superior response to the acid activation process and are, therefore, the raw materials of choice in the manufacture of activated clay adsorbents and catalysts. Natural sodium montmorillonites, although noted for their unique swelling characteristics and used widely as drilling muds, generally do not respond to acid activation.

A well-controlled process has been developed to activate calcium montmorillonites, exploiting the natural characteristics of its structure. The principle is to render soluble the structural 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 (calcium) cations originally present in the space between the sheets, thus increasing its characteristic acidic adsorption and catalytic nature.

There is considerable evidence that these acidic (active) cations serve as the active sites in the activated clay. When a pigment molecule (polar impurity) approaches one of these 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.

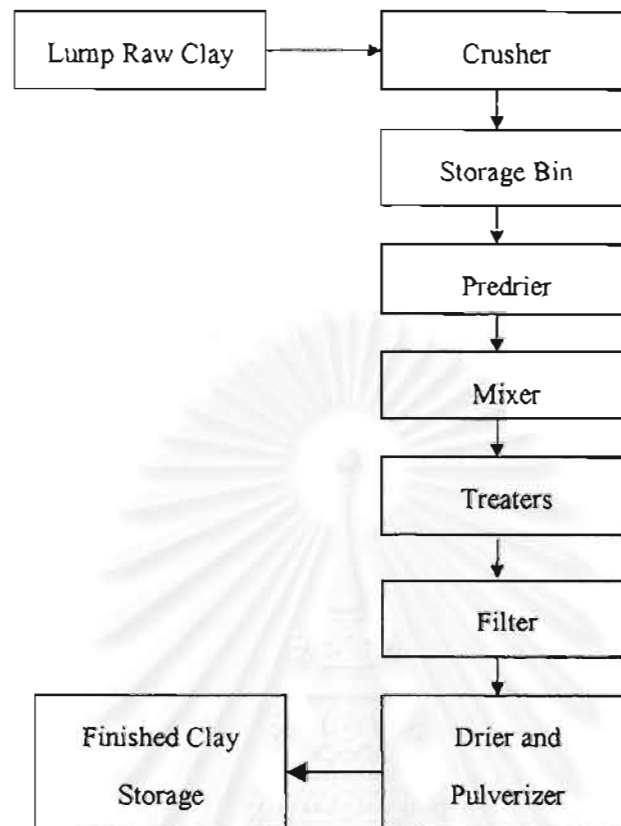


Figure 2.3 Acid activated bentonite clay process [2].

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

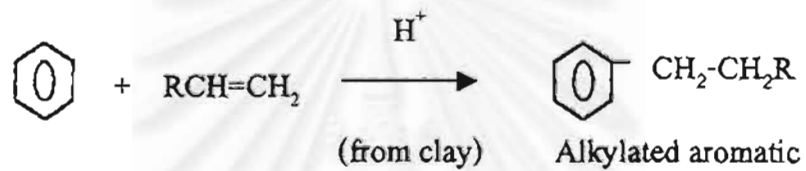
2.4 Reactions occurring on bentonite clays treatment of BTX.

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.

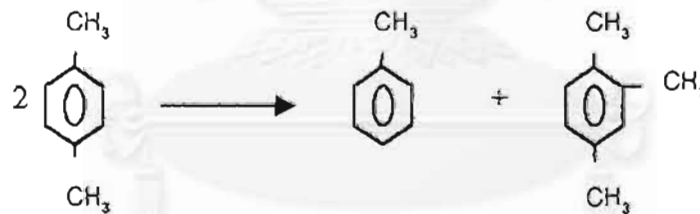
1. Adsorption of olefinic materials on active surface.
2. Polymerization and alkylation, by catalytic reaction with acid catalyst of the impurities to high boiling compounds that can be more easily removed downstream.

Alkylation



Side reaction occurring at higher temperature :

Disproportionation



Isomerization



2.5 Cause of deactivation [3].

Potential clay deactivation mechanisms include deactivation of active sites by poisoning or carbon deposits and plugging pore by carbon or polymer buildup, by catalytic reaction of the unsaturated compounds. Ishiguro et al. [5] studied the effect of heavy aromatics on clay life by a model system of heptene-2-spiked benzene with various components at the 2 %wt. Anthracene was found to significantly deactivate the clay. They suggested that deactivation with anthracene occurred by adsorption on Lewis acid sites with a concurrent reduction in the activity of neighboring Bronsted sites due to steric hindrance.

2.6 Regeneration of spent clay.

In many hydrocarbon reactions, such as catalytic cracking and BTX treater, carbonaceous deposits are formed on the surface of catalyst. The continuing accumulation of these deposits reduces the activity of the catalyst to the point that it must be regenerated. This is accomplished by burning off the carbon deposits, usually with air. In various regeneration studies in air at atmospheric pressure, it indicates that on a silica-alumina bead clay with large pores [6] (e.g., half-exceeding 2000 Å in diameter), rate diffusion is not rate controlling even between from 1200 °F to 1290°F (650 °C to 700°C).

In fact recent careful studies on the reaction of zeolites [7] with moderate acid molarities demonstrate that the first stage is that of a cation exchange whereby

hydronium ions (H_3O^+) replace the indigenous cations. This can be carried out even in zeolites and can be linked to the hydrolysis phenomenon, which includes the same exchange process.

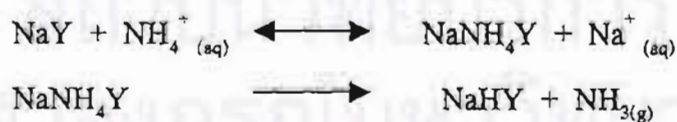
If the hydronium form of a catalyst is heated, water is lost and a 'hydrogen zeolites' is formed, viz.:



When the catalyst Si : Al ratio is high these 'hydrogen zeolites' are stable and are desirable catalyst.

A complication to this phenomenon is that, during cation exchanges involving the introduction of polyvalent transition elements into a zeolite, localized acid conditions prevail, creating the simultaneous hydronium exchanges previously mentioned, with the adjunct possibility of creating acid sites on subsequent calcination.

Yet another way to introduce the H^+ species is via a route described originally as 'decationization' or "deamination". This involves a partial exchange with ammonium ions followed by a careful calcination to decompose the ammonium species, viz.:



This proved to be a route to a very stable acid-cracking catalyst, able to resist temperatures to over 1000 °C.

2.7 Literature reviews

Majorities of catalytic reactions are affected by a deactivation phenomenon. The fundamental causes of this phenomenon involve carbonaceous deposits. As a result of the many facets of this problem, there have been a number of experimental and theoretical investigations of catalyst deactivation. This literature review will emphasize the above topics.

Ortega et al. [8] have studied the effect on combustion in air of the coke deposited in HZSM5 zeolites used in the MTG process in the range of 300 to 400°C. This coke was highly hydrogenated and unstable, and its H/C ratio decreased during combustion or when a previous thermal treatment was carried out. The HZSM5 zeolite has been subjected to an agglomeration process with bentonite. Si/Al ratio of HZSM5 is 24. The zeolite properties are particle size between 0.3 – 0.5 mm, pore volume 0.43 ccg⁻¹ and BET area 124 m² g⁻¹.

Kumar et al. [9] have 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 was measured by Benesi's technique of nonaqueous titration. Nitrogen adsorption-desorption hysteresis data indicated the transformation of pores from slit-shaped to spheroid or ink bottle type as the acid concentration was increased from 1 to 8 N. These observations were explained in terms of structural modifications of clay on treatment with acid by X-ray diffraction and FTIR.



Belzunce et al.[10] have studied an application of natural silicates and various F⁻ treatment have been applied to sepiolite to increase its acidic properties for use as a catalyst in reactions occurring via carbonium ions. Two types of treatments including hydrofluoric acid (HF) at different concentrations and 2 N NH₄F have been utilized and the physicochemical characteristics of the resulting materials were studied using standard techniques. The X-ray diffractogram (XRD) patterns indicated a reduction the crystallinity of the original material as well as the appearance of amorphous silica. Fourier transform infrared (FTIR), thermogravimetric analysis/differential thermal analysis (TGA/DTA), and N₂ adsorption-desorption isotherms were used to study the changes occurring in the structure. Additionally, structural changes induced by acid treatments modified the Bronsted and Lewis acidities. Mild treatments with ammonium fluoride are more effective than HF treatments in acidity generation.

Gayubo et al. [11] have studied the skeletal isomerization of butenes over a chlorinated alumina catalyst by operating under reaction-regeneration cycles in isothermal fixed-bed integral reactor. The limiting values of the reaction and regeneration temperatures for avoiding irreversible deactivation by loss of chlorine have been determined. Reversible deactivation by deposition of coke, which was completely removable by combustion, was unavoidable. The effect of the operating conditions upon the deposition of coke and the deterioration of the porous structure as consequences of the deposition have been analyzed.

Nebegall et al. [12] have studied process for regenerating spent acid-activated bentonite clays and smectite catalysts in the form of finely ground powders, which were used to adsorb colored pigments in fat and oil applications. Three regeneration steps were as follows: (1) an extraction step to remove a majority of entrained oil,

preferably about 75% to about 95% by weight of the entrained oil, when regenerating bleaching clays; (2) an oxidation step to remove the majority of remaining carbonaceous adsorbates which are not removed by the preceding extraction step, and (3) an acid wash step to restore the acidity normally associated with fresh acid-activated bleaching clays.

Hynes et al. [13] have studied a bentonite clay-based polymerization catalyst. This clay was manufactured by adhering together a plurality of smaller acid-activated bentonite clay particle, using a strong mineral acid, such as H_2SO_4 , as a binder. An acid-activated bentonite clay having a particle size below about 60 mesh, U.S. Sieve Series, preferably calcium bentonite, having calcium as a predominant exchangeable cation, was mixed with a strong mineral acid, preferably H_2SO_4 , and water to form the catalyst. The mixture was subjected to intensive mixing, curing and drying to form strong particles capable of grinding to a desired particle size distribution, e.g., -6 mesh to +60 mesh, to form the catalyst. Fine particles resulting from the grinding step were completely recycled to the intensive mixing stage of the process to achieve 100% yield.

CHAPTER III

EXPERIMENTAL

3.1 Materials

- (1) Bentonite clay grade Filtrol 24 was a commercial catalytic sorbent from Engelhard cooperation (Chemical Catalysts Group), produced in granular form (White solid). Typical properties and characteristics were :

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

- (2) Spent clays were obtained from a plant in Rayong. It was dark solid after being used in BTX process. The properties of spent clay were black granule, total weight loss 21.64%, and surface area (BET method) 122.5 m²g⁻¹.

(3) BTX feedstocks were supplied from a plant in Rayong. All studies of C_8^+ stream in this research separated from C7/C8 splitter of BTX process are shown in Figure 2.3. The chemical composition consists of aromatic (95%) and non-aromatic (5%), density 0.85 to 0.87, distillation range 130 to 210°C and bromine index 523.8 mgBr/100g.

(4) Ammonium fluoride (NH_4F) is obtained from Merck.

3.2 Apparatus and instruments

(1) Furnace

Carbolite furnace model CWF 1100.

(2) Instrument for Bromine Index Standard ASTM method D1492.

Electrometric titration Metrohm Automatic Titroprocessor 716.

(3) Instrument for P.I.A.N.O.* Analysis.

Perkin-Elmer Autosystem GC model Series 9000.

* P.I.A.N.O. is a commercial name of one type of GC Instrument which P. stands for paraffins, I. stands for isoparaffins, A. stands for aromatics, N. stands for naphthenes, and O. stands for olefins.

3.3 Procedure

3.3.1 Regeneration of spent clay.

(1) Burning off the carbonaceous deposits on the surface of spent clay in a furnace with air flow. This process parameters were monitored by total weight loss, and the appearance was compared to that of fresh clay. The variation conditions were shown in Table 3.1.

(2) Impregnation of Fluoride on regenerated clay.

An aqueous impregnating solution was prepared by dissolving appropriate amount of NH_4F in deionized water (the volume of aqueous equivalent to pore volume of clay) and left at room temperature for one hour, dried at $110\text{ }^\circ\text{C}$ for 16 hrs to obtain the fluoride doped clay. NH_4F concentration was varied from 1 to 5%F. This fluoride doped clay was calcined in air flow at $500\text{ }^\circ\text{C}$ for 3 hrs.

3.3.2 Treatment of C_8^+ stream with regenerated clay.

One gram of clay was refluxed with 100 ml of C_8^+ stream at $150 - 155\text{ }^\circ\text{C}$ for 3 hrs in a round-bottom flask. After treatment, C_8^+ stream was measured by using bromine index (the basis for evaluating clay performance). The bromine index data are shown in Table A1 in Appendix A.

Table 3.1 Conditions of regeneration procedure.

Sample no.	Temperature (°C)	Time (hrs)	NH ₄ F impregnation concentration (wt. %)
BSC-65-6	650	6	1, 3, 5
BSC-65-65	650	6.5	1, 3, 5
BSC-65-7	650	7	1, 3, 5
BSC-65-75	650	7.5	1, 3, 5
BSC-65-8	650	8	1, 3, 5
BSC-70-3	700	3	1, 3, 5
BSC-70-35	700	3.5	1, 3, 5
BSC-70-4	700	4	1, 3, 5
BSC-70-45	700	4.5	1, 3, 5
BSC-70-5	700	5	1, 3, 5
BSC-75-3	750	3	-
BSC-75-35	750	3.5	-
BSC-75-4	750	4	-
BSC-75-45	750	4.5	-
BSC-75-5	750	5	-

3.4 Analysis of C_8^+ stream.

The C_8^+ hydrocarbons before and after treatment with fresh clays and regenerated clays were characterized by P.I.A.N.O. autosystem GC. Their hydrocarbon composition were identified by this instrument with the library search program. The ability of olefin removal performance of clays in the treatment of BTX feedstocks was measured by bromine index (ASTM method D1492).

3.5 Determination of clay properties.

(1) Thermogravimetric analysis

The weight loss of clay was determined by thermogravimetric analyzer with temperature gradient at 100°C per minute. The thermograms were shown in Appendix Figures A1-A10.

(2) Acidity

NH_4F contribution in the treatment generates active site[11]. The acidity was determined as following: clay (0.5 g) was dried at 120°C for 6 hours. The clay was then treated with 15 ml 0.1N NaOH for 10 min. Excess NaOH was titrated with 0.1N H_2SO_4 . The acidity of clay was calculated according to the following equation.

$$\text{Acidity of clay (meq/100g clay)} = \frac{(V1 - V2) \times [\text{H}_2\text{SO}_4] \times 100}{\text{amount of clay}}$$

V1	=	Volume of NaOH
V2	=	Volume of H ₂ SO ₄
[H ₂ SO ₄]	=	H ₂ SO ₄ concentration

(3) Structure of clay.

The structure of clay was characterized by X-Ray diffractometer using Cu K α line ($\lambda = 1.5406 \text{ \AA}$) and X-Ray fluorescence using a Phillips model PW 2400 equipment.

(4) Surface area and pore volume.

The porous structure and the surface area (BET method) of the clay were characterized from isotherms of N₂ adsorption-desorption carried out in Autosorb-1, equipment from micrometric. Surface area was calculated using BET isotherm. Pore size distribution was determined from nitrogen desorption data $p/p_0 = 0.3$ and above.

CHAPTER IV

RESULTS AND DISCUSSION

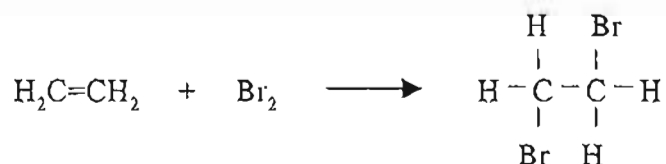
All trials for the regeneration of spent clay from BTX process took into account the appearance, weight loss of regenerated clay, and bromine index (BI) of C_8^+ stream after refluxing with clays. The first attempt to regenerate spent clay by extraction with toluene, oxidation with H_2O_2 and washing with 10% sulfuric acid did not give good results. The appearance of regenerated clay using the method mentioned above was nearly the same as spent clay, i.e., dark color solid, total weight loss at 10.2% and BI at 300 mgBr/100g. This result demonstrated that this process could not remove carbon deposition on clay. The second attempt was carried out by burning spent clay in air at $650^\circ C$ for 6.5 hrs and washing with 10% H_2SO_4 . After H_2SO_4 treatment, clay particle size was smaller and appeared to be grey. The weight loss of regenerated clay was 22.5%, and BI was 170.9 mgBr/100g. The efficiency of clay after acid treatment appeared to be approximately 70% of unused clay. It indicated that this process could remove carbon deposits on clay but H_2SO_4 treatment may not be suitable. The acidity modification of catalysts could be carried out using NH_4F . Therefore, the third attempt was performed using the same condition of the second trial but impregnated with 5% NH_4F instead of H_2SO_4 . It showed that the fluoride treated clay gave better performance than the one treated with sulfuric acid. Therefore, all studies in this research used combustion in air to remove carbon deposits and followed by impregnation with NH_4F to enhance the clay acidity.

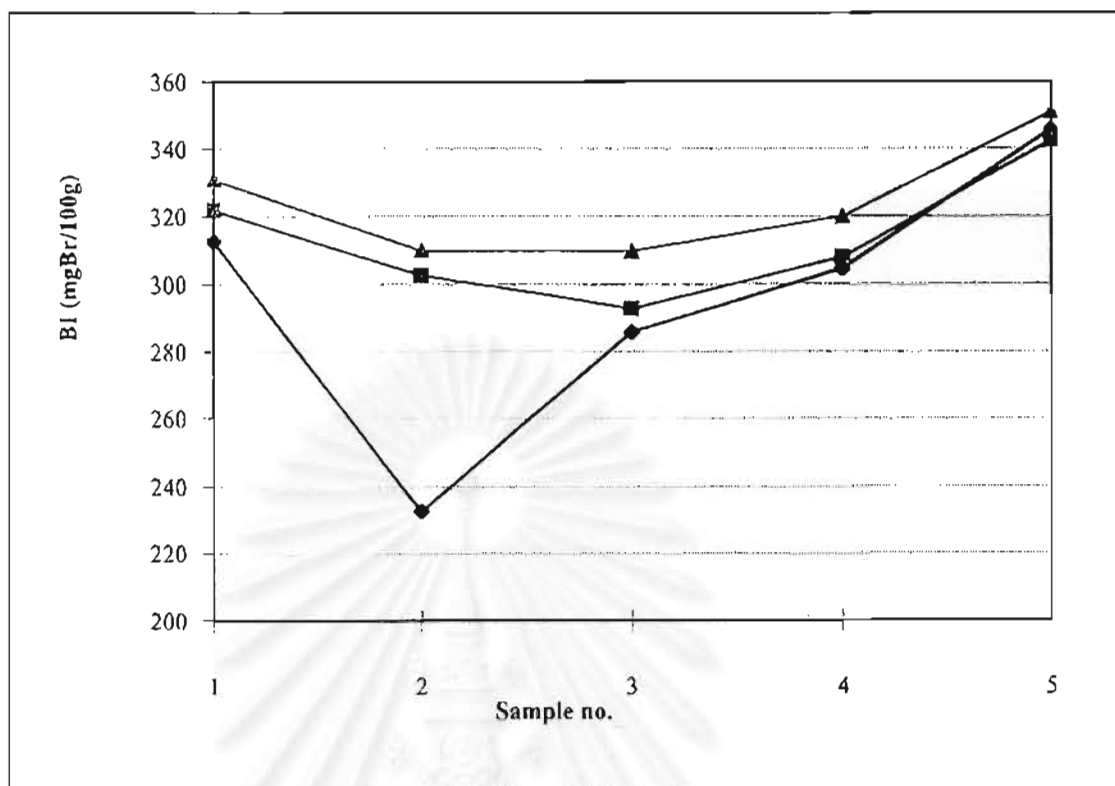
4.1 Selection of the optimum regeneration condition.

(1) Studies of various temperature and time for combustion of spent clay.

Thermogravimetric analyses in Figures A1 and A2 show how much weight was lost in air as temperature was raised at 100°C per minute of fresh clay and spent clay, respectively. Fresh clay appeared as white solid. The weight loss observed between 100 and 300°C was due to the loss of water. Spent clay appeared as dark solid. The weight loss between 100 and 300°C was also due to the loss of water and some volatile hydrocarbons. Above 300°C, there was some cracking and combustion of non-volatile organics. These materials were oligomers, catalytic reaction of unsaturated compounds were normally presented in feedstocks. These oligomers were cracked and volatilized. Therefore, the temperature between 650 and 750°C indicated total weight loss close to 21.64% and the combustion clay appeared to be white.

All studies of the bromine index on C_8^* stream as a function of various regeneration conditions, form the basis for evaluating clay performance. The bromine index was a broad indication of olefin content. The reaction of olefins with bromine was an electrophilic addition to the carbon-carbon double bond as shown below.





	Sample no. (Time,hrs)				
Temp	1	2	3	4	5
◆ 650	6	6.5	7	7.5	8
■ 700	3	3.5	4	4.5	5
▲ 750	3	3.5	4	4.5	5

Figure 4.1 BI curve of C_8^+ stream refluxed with clay regenerated at 650 to 750 °C.

The bromine index data of C_8^+ stream before and after refluxing with clay were presented in Appendix A. Figure 4.1 illustrated bromine index of C_8^+ stream after refluxing with clay regenerated at 650 to 750 °C. The bromine index on C_8^+ hydrocarbon refluxing with clay regenerated at 650 < 700 < 750 °C, and the one at 650 °C for 6.5 hrs was the lowest.

(2) Studies of various NH_4F concentration on impregnation of clay.

Figure 4.2 illustrated the performance of clay regenerated at 650 °C for 6 to 8 hrs and impregnated with NH_4F , as a plot of bromine index versus NH_4F concentration which varied from 1 to 5 %. The bromine index on C_8^+ stream refluxing with clay regenerated at 650 °C was decreased when NH_4F concentration was increased, especially bromine index of clay regenerated at 650 °C for 6.5 hrs (BSC-65-65F5) was the lowest. Figure 4.3 illustrated acidity of clay regenerated at 650 °C for 6 to 8 hrs and impregnated with NH_4F . The acidity increased when NH_4F concentration increased.

Figure 4.4 illustrated the performance of regenerated clay at 700 °C for 3 to 5 hrs and impregnated with NH_4F , as a plot of bromine index versus NH_4F concentration varies from 1 to 5 %. The bromine index on C_8^+ stream refluxing with regenerated clay at 700 °C is decreased when NH_4F concentration was increased, especially bromine index of clay regenerated at 700 °C for 4 hrs (BSC-70-4F5) was the lowest. Figure 4.5 illustrated the acidity of regenerated clay at 700 °C for 3 to 5 hrs and impregnation with NH_4F . It showed that acidity was increased when NH_4F concentration was increased. Comparing with the performance of regenerated clay BSC-65-65F5 and BSC-70-4F5, BSC-65-65F5 has performance closed to that of fresh clay F-24.

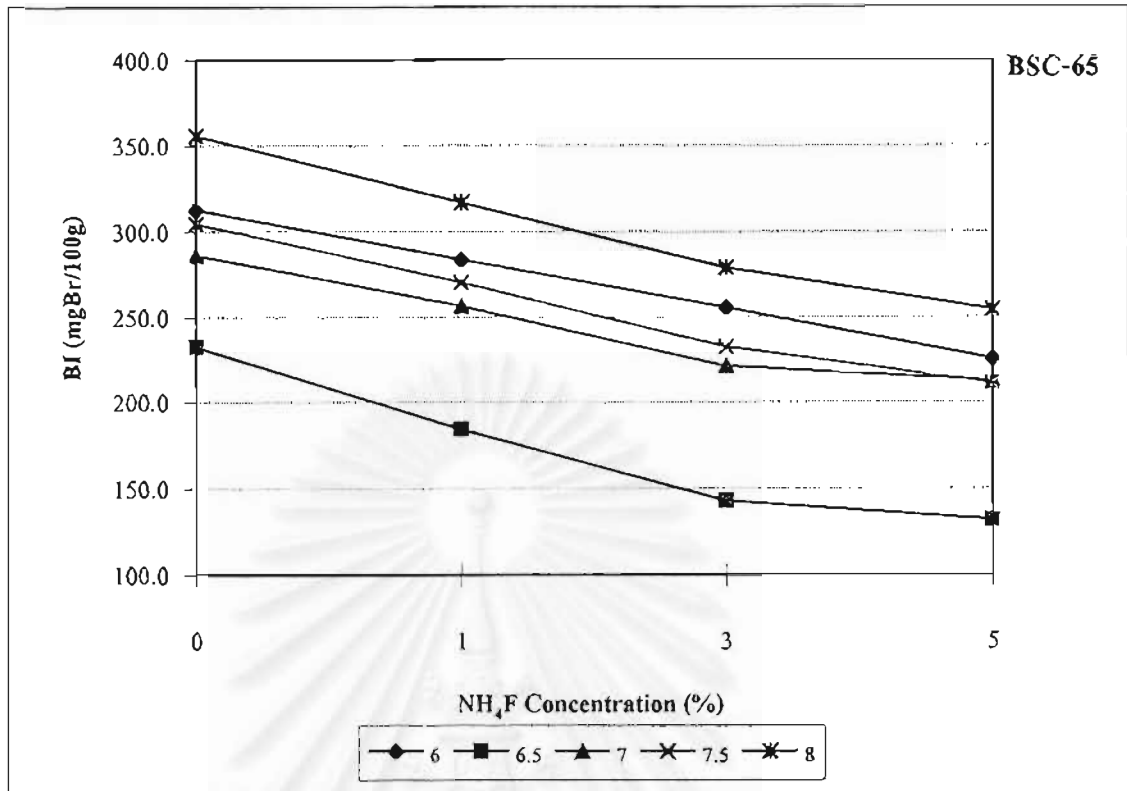


Figure 4.2 BI curve of C_8^+ stream refluxed with regenerated clay at 650°C for 6 - 8 hrs, treated with NH_4F concentration 1 - 5 %. BI of C_8^+ blank and fresh clay F-24 are 523.8 and 120.9 mgBr/100g respectively.

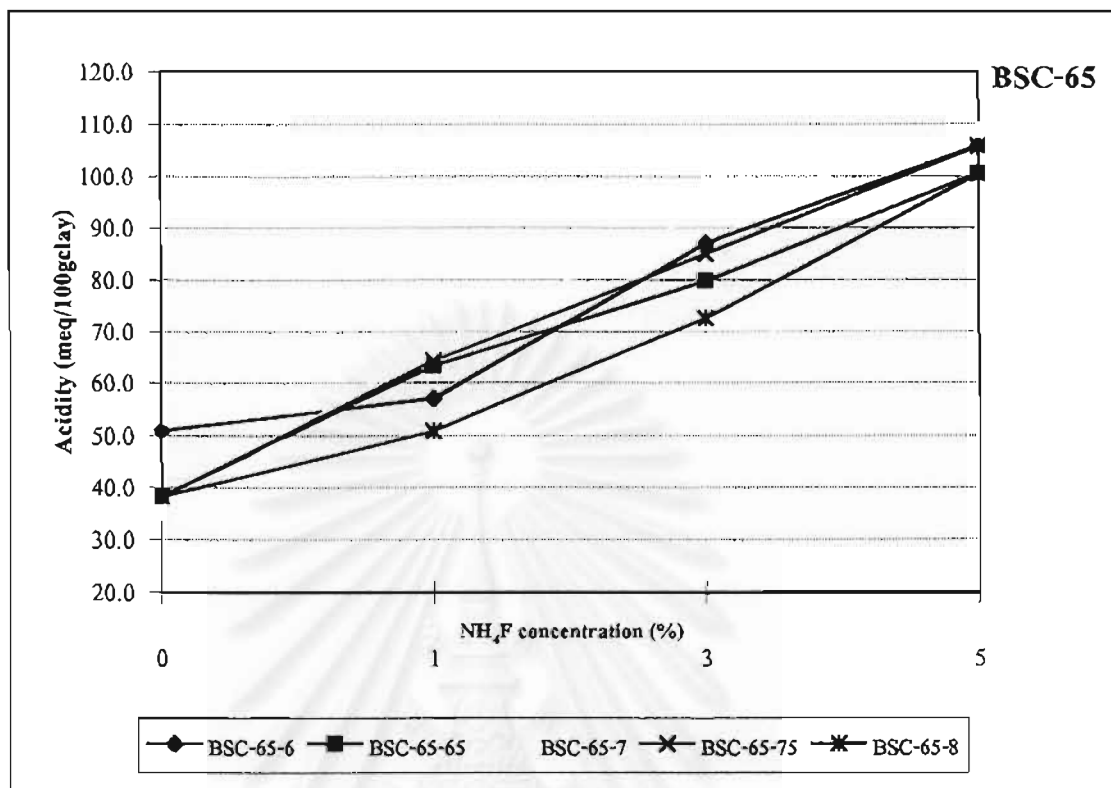


Figure 4.3 Surface acidity data of various fluoride-treated clays at 650 °C for 6 - 8 hrs.

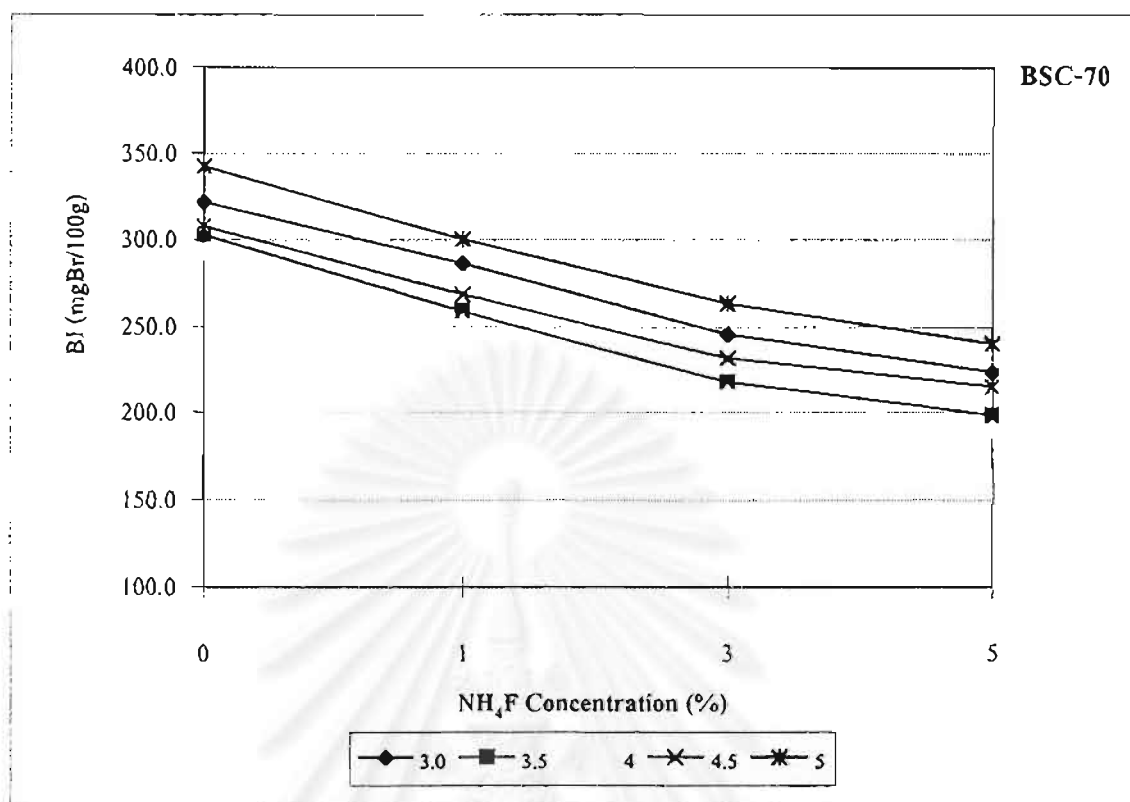


Figure 4.4 BI curve of C_8^+ stream refluxed with clay regenerated at 700°C for 3 - 5 hrs, treated with NH_4F concentration 1 - 5 %. BI of C_8^+ blank and fresh clay F-24 are 523.8 and 120.9 mgBr/100g respectively.

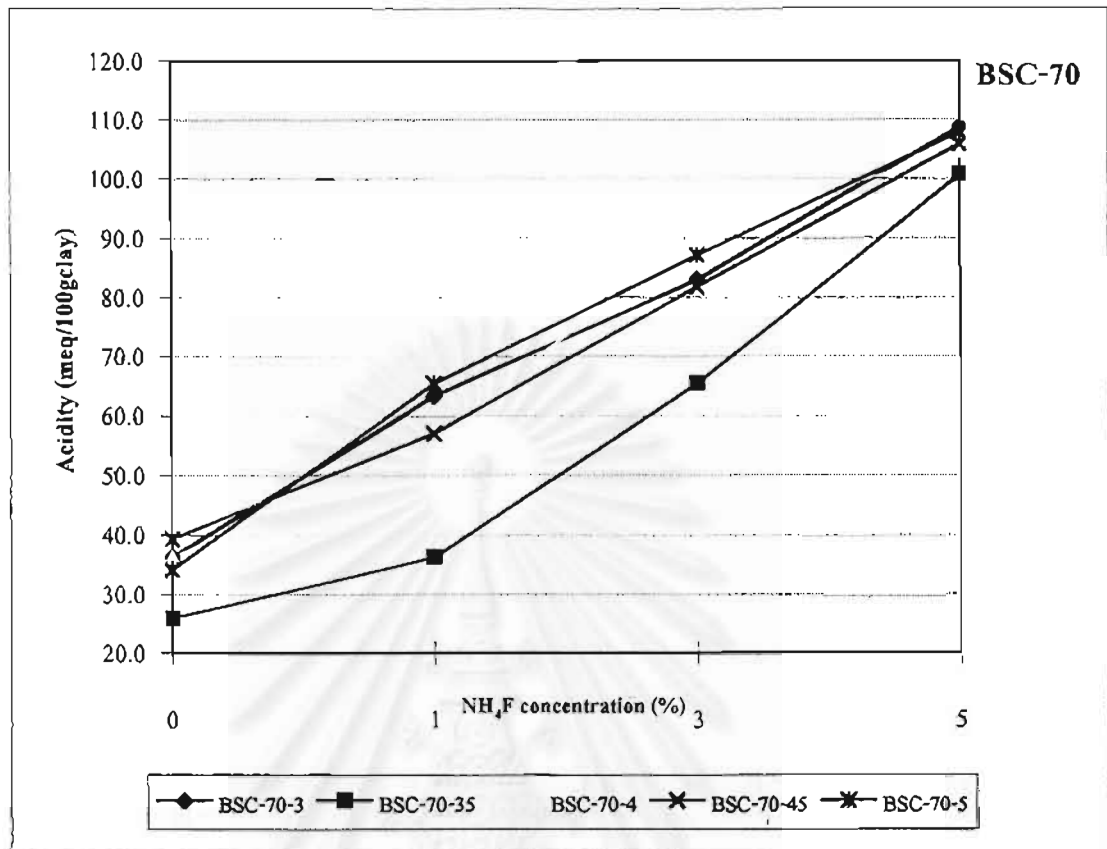


Figure 4.5 Surface acidity data of various fluoride-treated clays at 700 °C for 3 - 5 hrs.

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Table 4.1 summarized the temperature intervals and the weight losses corresponding to the different dehydration and dehydroxylation obtained from DTG. The TGA curves were shown in Appendix A.

Table 4.1 Weight loss through thermogravimetric analysis of fresh clay, spent clay and regenerated clay

Sample name	Steps of dehydration				Total loss
	I < 300 °C	II 300-600 °C	III 600-770 °C	New phase	
F-24	19.7	2.28	1.57	0.73	24.28
BSC-65-65F5	15.70	2.05	1.27	0.82	19.84
BSC-70-4F5	6.60	1.51	0.88	1.10	10.09

Remark : I : zeolitic water, II : coordination water, III : structural water [10]

The DTG curves between 300 and 600 °C range must be ascribed to additional water loss caused by proton migration inside the clay structure, with subsequent interaction with -OH groups within the octahedral sheet [10]. Weight loss of regenerated clay BSC-65-65F5 between 300 and 600 °C range was 2.05%. It was much more than regenerated clay BSC-70-4F5 and close to that of fresh clay F-24. This indicated that heating temperature at 700 °C in combustion step has affected the change of the clay structure more than combustion at 650 °C.

4.2 Characterization of C_8^+ stream.

The C_8^+ stream obtained from BTX process was identified for its composition by P.I.A.N.O. autosystem GC with its library search program. The percentage compositions of C_8^+ stream was shown in Figure A11, and its percentages and retention times were presented in Table 4.2. These data indicated that there were many types of hydrocarbons in C_8^+ , i.e., branched-chain paraffins, cycloparaffins and aromatics. However, GC library could not specify the type of C_{13} and heavier hydrocarbons. Some chromatograms of C_8^+ stream after refluxing with clay from the chosen regeneration condition were presented in Appendix A, and their composition were similar to C_8^+ before refluxing.

The GC Chromatogram of C_8^+ stream after refluxing with clay indicated some alkylation reaction of olefin. The amount of toluene in C_8^+ stream after treatment with clay was increased. It indicated that the disproportionation reaction of clay was occurred.

Composition	Blank	F-24	BSC-65-65F5
Toluene	0.015	0.075	0.051
m-Xylene	23.419	23.519	23.782
p-Xylene	7.220	6.947	7.014
o-Xylene	14.405	14.254	14.362
i-Propylbenzene	0.673	0.677	0.678
C_9^+ hydrocarbon	46.681	47.209	46.863

Table 4.2 Identification of C₈⁺ compositions.

Peak no.	Retention time (min)	Area	%Area (%composition)	Name	Group
1	10.20	516	0.002	n-Pentane	P5
2	13.40	492	0.001	2-Methylpentane	I6
3	20.44	1120	0.003	Benzene	A6
4	22.63	846	0.002	2-Methylhexane	I7
5	22.85	559	0.002	2,3-Dimethylpentane	I7
6	23.72	868	0.002	3-Methylhexane	I7
7	27.02	837	0.002	n-Heptane	I7
8	35.11	5786	0.015	Toluene	A7
9	43.67	8107	0.023	n-Octane	P8
10	47.16	3025	0.009	2,3,4-Trimethylhexane	I9
11	47.96	6510	0.019	2,2-Dimethylheptane	I9
12	48.91	10547	0.030	1c,2-Dimethylcyclohexane	N8
13	50.05	2105	0.006	2,3-Dimethylheptane	I9
14	50.50	3555	0.009	2,4-Dimethylheptane	I9
15	52.14	13469	0.039	1,1,4-Trimethylcyclohexane	N9
16	52.55	8180	0.024	3,5-Dimethylheptane	I9
17	54.85	2413783	6.624	Ethylbenzene	A8
18	57.60	8479850	23.419	m-Xylene	A8
19	57.81	2614391	7.22	p-Xylene	A8
20	58.22	15654	0.045	1c,2t,4-Trimethylcyclohexane	N9
21	59.72	29438	0.086	2-Methyloctane	I9
22	61.21	14887	0.043	3-Ethylheptane	I9
23	61.62	72894	0.114	1,1,2,-Trimethylcyclohexane	N9
24	62.75	5161687	14.405	o-Xylene	A8
25	67.47	46940	0.134	n-Nonane	P9
26	69.25	282093	0.673	1-Propylbenzene	A9
27	70.98	4413	0.013	2,2-Dimethyloctane	I10
28	72.91	1817	0.005	n-Butylcyclopentane	N9
29	74.44	814515	2.088	n-Propylbenzene	A9
30	75.83	2714945	7.261	1-Methyl-3-ethylbenzene	A9

Table 4.2 Identification of C_8^+ compositions (continued)

Peak no.	Retention time (min)	Area	%Area (%composition)	Name	Group
31	76.11	1236054	3.144	1-Methyl-4-ethylbenzene	A9
32	76.29	1243767	3.008	1,3,5-Trimethylbenzene	A9
33	78.38	1288695	3.282	1-Methyl-2-ethylbenzene	A9
34	79.57	2152	0.032	3-Methylnonane	I10
35	80.77	5406751	13.832	1,2,4-Trimethylbenzene	A9
36	82.69	28219	0.082	Methyl-2-n-propylcyclohexane	N10
37	84.29	1405288	3.595	1,2,3-Trimethylbenzene	A9
38	-	2017163	5.136	Total	A10
39	-	439240	1.903	Total	A11
40	-	57624	0.118	Total	A12
41	-	1182509	3.546	Total	C13+
	Total	37041291	100.00		

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4.3 Determination of clay properties.

(1) Study of clay structure

BSC-65- 65F5 was a regenerated clay with the performance as close as those of fresh clay. Figure 4.6 showed the X-ray diffractograms of fresh clay; spent clay and regenerated clay. The structure from X-ray diffractograms indicated that the main bentonite clay structure persisted except BSC-65-65F5 sample, the intensity of line $2\theta = 6.4$ decreased and changed. X-ray diffraction showed a decrease in crystallinity of BSC-65-65F5 and BF-24F5. The loss of crystallinity increased with extension of the regeneration. X-ray fluorescence showed the decreasing of Al but increasing of Si of spent clay. The reason of these observations was that the regeneration step changed the structure of clay. It was similar to that found by Belzunce et al.[10] who observed the sepiolite structure persists after the NH_4F treatment. A broadening characteristic of sepiolite peaks indicated that free silica might be contributed to the reaggregation.

(2) Surface area and pore size analysis

The N_2 adsorption isotherms at 77 K of sample, specified the determination of the amount of N_2 gas required to cover the external and the accessible internal pore surfaces of a solid with complete monolayer of adsorbate. This monolayer capacity was used to calculate from the adsorption isotherm by BET equation. Table 4.2 showed BET surface area, total pore volume and average pore radius.

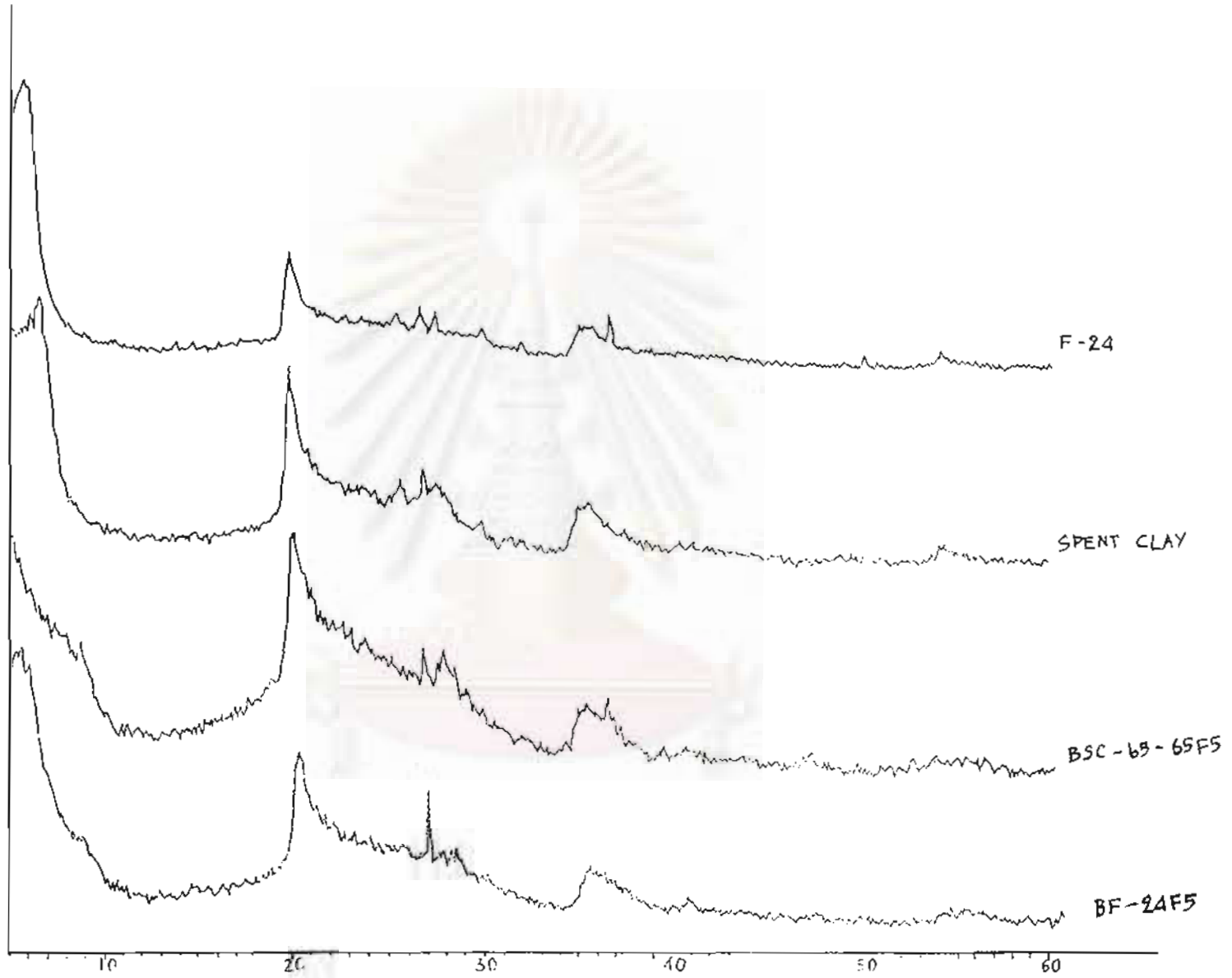


Figure 4.6 XRD patterns of fresh clay, spent clay and regenerated clay.

Table 4.3 Surface area and pore size analysis of clay.

Clay	Surface area (BET, m ² /g)	Total pore volume (cc/g)	Average pore radius (Å)	%Carbon
F-24	347.3	3.87 E-01	22.26	< 0.1
Spent clay	122.5	1.80 E-01	29.30	3.32
BSC-65-65F5	228.0	3.42 E-01	30.01	0.15
BF-24F5	202.2	2.98 E-01	25.09	< 0.1

Surface area and total pore volume of spent clay was decreased due to the presence of the carbonaceous material adsorbed and plugged in pore. This observation was similar to that found by Gayubo et al.[11] who observed that carbon deposition caused a reduction in surface area and pore volume. The reduction in surface area of catalyst depended on the amount of coke. It could thus be considered that coke deposition took place mainly in a monolayer and that deactivation occurred by active site coverage and not by pore blockage.

Regeneration of spent clay could remove the carbon deposits on clay, as shown by reduction of the carbon content. The pore volume of BSC-65-65F5 was slightly lower than that of fresh clay, but higher than that of BF-24F5 which was regenerated from fresh clay at 650°C for 6.5 hrs and impregnated with 5% NH₄F. Surface area of BF-24F5 was close to that of BSC-65-65F5. It indicated that heating in the regeneration step changed the texture of clay surface, therefore surface area was decreased. This observation was similar to that found by Belzunce et al. [10] who observed that the treatment of sepiolite with mild NH₄F led to change in the

morphological-structural-textural characteristics as well as in the acid properties of the sample. NH_4F treatment caused cationic (NH_4^+) as well as anionic (F^-) surface exchange and a partial dissolution of the octahedral sheet with the release of octahedral Mg^{2+} and the formation of amorphous silica.





CHAPTER V

CONCLUSIONS

The regeneration of spent bentonite clay was studied using combustion process to remove carbon deposition on clay. There were two significant conditions, combustion temperature and impregnation of fluoride on regenerated clay. The regeneration step by determining bromine index of C_8^+ stream before and after refluxing with clay indicated that the regeneration occurred well at temperature of $650\text{ }^\circ\text{C}$ for 6.5 hrs and impregnation with 5% NH_4F (BSC-65-65F5).

The fresh clay (F-24) was compared with regenerated clay (BSC-65-65F5) under this condition and it was found that bromine index of C_8^+ stream after treatment with F-24 and BSC-65-65F5 were 120.9 and 131.5 mgBr/100g clay, respectively. The efficiency of regenerated clay appeared to be approximately 91% of fresh clay. This indicated that the reaction of olefin on fresh clay was more active than that on regenerated clay.

The structure of regenerated clay from XRD investigation indicated that the main bentonite clay structure persisted but crystallinity was decreased. Free Si occurred and the clay lost its crystallinity with the extension of regeneration time and temperature.

Surface area and pore volume of spent clay were $122.5\text{ m}^2\text{g}^{-1}$ and $1.80\text{E-}01\text{ ccg}^{-1}$, respectively. After regeneration, surface area and pore volume of BSC-65-65F5 were $228.0\text{ m}^2\text{g}^{-1}$ and $3.42\text{E-}01\text{ ccg}^{-1}$, respectively, which were lower than those of

fresh clay. It indicated that this process could be used to regenerate spent clay although heating temperature has affected some changed in the clay structure.

This regeneration of spent bentonite clay could remove carbon deposition on clay and improved the acid site with ammonium fluoride. Thus, the regenerating clay was able reused in BTX process.

Suggestions for future works

1. In these studies, the structure of clay has been changed because of direct heating in combustion step. The further study should be done using direct heating applied by fluidized bed method or indirect heating using high pressure steam to remove carbon deposition that might reserve the structure of clay.
2. Investigation of the use of regenerated clay under reaction -regeneration cycles by determining BTX in aging test.
3. Investigation of the economic feasibility.

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APPENDICES

Table A1 Bromine index of C_8^+ stream blank and refluxed with clay.

Temperature (°C)	Time (hrs)	NH ₄ F concentration (%F)											
		0			1			3			5		
		1	2	Average	1	2	Average	1	2	Average	1	2	Average
650	6	315.2	310.5	312.8	293.4	273.2	283.3	269.6	241.1	255.3	235.1	216.0	225.5
	6.5	230.1	235.2	232.7	192.7	175.6	184.2	151.8	133.6	142.7	129.9	133.0	131.5
	7	288.8	283.2	286.0	258.7	254.1	256.4	232.5	210.1	221.3	220.0	204.3	212.2
	7.5	308.5	300.7	304.6	274.8	265.4	270.1	245.0	220.2	232.6	222.4	200.0	211.2
	8	341.4	350.2	345.8	318.2	315.4	316.8	281.9	275.5	278.7	257.3	251.1	254.2
700	3	320.0	324.1	322.1	285.9	287.0	286.5	247.3	244.5	245.9	222.6	225.3	224.0
	3.5	300.6	304.3	302.5	257.0	260.1	258.6	215.8	220.0	217.9	194.2	202.2	198.2
	4	289.6	295.7	292.7	251.7	253.0	252.4	212.4	210.7	211.6	189.4	191.9	190.7
	4.5	306.3	309.7	308.0	266.8	270.5	268.7	233.3	230.2	231.8	220.3	210.3	215.3
	5	336.4	348.1	342.3	296.1	304.6	300.4	257.0	270.0	263.5	236.7	244.3	240.5

Remark : C_8^+ blank is 523.8 mgBr/100g

C_8^+ refluxed with F-24 is 120.9 mgBr/100g

Table A2 Acidity of fresh clay and regenerated clay.

Temperature (°C)	Time (hrs)	NH ₄ F concentration (%F)	Amount of clay (g)	Volume of H ₂ SO ₄ (ml)	Acidity (meq/100g clay)	Temperature (°C)	Time (hrs)	NH ₄ F concentration (%F)	Amount of clay (g)	Volume of H ₂ SO ₄ (ml)	Acidity (meq/100g clay)
650	6	0	0.5000	12.55	50.9	700	3	0	0.5000	13.25	36.3
		1	0.5005	12.25	57.0			1	0.5009	11.95	63.2
		3	0.5007	10.80	87.1			3	0.5003	11.00	83.0
		5	0.5003	9.90	105.8			5	0.5012	9.75	108.7
	6.5	0	0.5003	13.15	38.4		3.5	0	0.5013	13.75	25.9
		1	0.5005	11.95	63.3			1	0.5002	13.25	36.3
		3	0.5007	11.15	79.8			3	0.5000	11.85	65.4
		5	0.5008	10.15	100.5			5	0.5003	10.15	100.6
	7	0	0.5002	13.30	35.3		4	0	0.5006	13.25	36.3
		1	0.5006	11.75	67.4			1	0.5002	12.30	56.0
		3	0.5012	10.50	93.2			3	0.5006	10.60	91.2
		5	0.5009	9.75	108.8			5	0.5007	9.95	104.7
	7.5	0	0.5009	13.15	38.3		4.5	0	0.5010	13.10	39.4
		1	0.5001	11.90	64.3			1	0.5006	12.25	57.0
		3	0.5002	10.90	85.1			3	0.5011	11.05	81.8
		5	0.5009	9.90	105.7			5	0.5005	9.90	105.8
	8	0	0.5011	13.15	38.3		5	0	0.5010	13.35	34.2
		1	0.5002	12.55	50.8			1	0.5000	11.85	65.4
		3	0.5002	11.50	72.6			3	0.5002	10.80	87.2
		5	0.5012	10.15	100.4			5	0.5006	9.80	107.8

Remark : Acidity of fresh clay F-24 is 91.8 meq/100g clay.

Table A3 Weight loss of fresh clay, spent clay and regenerated clay.

Temperature (°C)	Time (hrs)	NH ₄ F concentration (%)	Steps of dehydration				Total loss
			< 300 °C	300-600 °C	600-770 °C	New phase	
650	6	0	1.69	0.78	0.18	0.21	2.86
		1	5.11	1.51	0.59	0.35	7.56
		3	5.11	1.52	0.80	0.63	8.06
		5	6.76	1.38	0.82	0.91	9.87
	6.5	0	4.24	1.05	0.27	0.27	5.83
		1	5.19	0.96	0.53	0.67	7.35
		3	8.55	1.10	0.61	1.22	11.48
		5	15.70	2.05	1.27	0.82	19.84
	7	0	5.91	1.13	0.25	0.25	7.54
		1	6.69	1.38	0.71	0.4	9.18
		3	6.43	1.31	0.76	0.54	9.04
		5	5.89	1.27	0.90	1	9.06
	7.5	0	5.41	1.06	0.24	0.23	6.94
		1	6.97	1.30	0.49	0.31	9.07
		3	6.89	1.41	0.69	0.53	9.52
		5	6.33	1.43	0.79	0.87	9.42
	8	0	5.84	1.18	0.25	0.27	7.54
		1	7.95	1.54	0.58	0.39	10.46
		3	7.37	1.41	0.76	0.49	10.03
		5	7.31	1.48	0.82	0.77	10.38
700	3	0	5.47	1.14	0.23	0.2	7.04
		1	7.01	1.56	0.56	0.36	9.49
		3	6.85	1.50	0.75	0.54	9.64
		5	6.14	1.46	0.89	1.1	9.59
	3.5	0	5.50	1.13	0.25	0.21	7.09
		1	7.08	1.40	0.52	0.34	9.34
		3	7.05	1.42	0.76	0.63	9.86
		5	6.64	1.40	0.85	0.98	9.87

Table A3 Weight loss of fresh clay, spent clay and regenerated clay (continued).

Temperature (°C)	Time (hrs)	NH ₄ F concentration (%)	Steps of dehydration				Total loss	
			< 300 °C	300-600 °C	600-770 °C	New phase		
700	4	0	5.07	1.04	0.19	0.18	6.48	
		1	6.89	1.48	0.54	0.37	9.28	
		3	6.88	1.45	0.75	0.65	9.73	
		5	6.60	1.51	0.88	1.1	10.09	
	4.5	0	4.82	1.00	0.19	0.16	6.17	
		1	6.92	1.52	0.61	0.38	9.43	
		3	6.89	1.43	0.78	0.57	9.67	
		5	6.36	1.44	0.90	0.89	9.59	
	5	0	5.69	1.14	0.22	0.18	7.23	
		1	7.07	1.44	0.55	0.37	9.43	
		3	7.38	1.42	0.76	0.56	10.12	
		5	5.13	1.45	0.99	1.1	8.67	
			F-24	19.70	2.28	1.57	0.73	24.28
			Spent Clay	7.71	5.30	5.88	2.75	21.64

Table A4 Identification of C_8^+ composition blank and refluxed with F-24 and BSC-65-65F5.

Item	Group	Name	%composition of C_8^+		
			Blank	After reflux with	
				F-24	BSC-65-65F5
1	P5	n-Pentane	0.002	0.000	0.000
2	I6	2-Methylpentane	0.001	0.000	0.000
3	A6	Benzene	0.003	0.004	0.003
4	I7	2-Methylhexane	0.002	0.000	0.000
5	I7	2,3-Dimethylpentane	0.002	0.000	0.000
6	I7	3-Methylhexane	0.002	0.000	0.000
7	I7	n-Heptane	0.002	0.000	0.000
8	A7	Toluene	0.015	0.075	0.051
9	P8	n-Octane	0.023	0.021	0.024
10	I9	2,3,4-Trimethylhexane	0.009	0.009	0.004
11	I9	2,2-Dimethylheptane	0.019	0.021	0.019
12	N8	1c,2-Dimethylcyclohexane	0.030	0.024	0.026
13	I9	2,3-Dimethylheptane	0.006	0.006	0.006
14	I9	2,4-Dimethylheptane	0.009	0.010	0.010
15	N9	1,1,4-Trimethylcyclohexane	0.039	0.022	0.042
16	I9	3,5-Dimethylheptane	0.024	0.027	0.023
17	A8	Ethylbenzene	6.624	6.555	6.614
18	A8	m-Xylene	23.419	23.519	23.782
19	A8	p-Xylene	7.220	6.947	7.014
20	N9	1c,2t,4-Trimethylcyclohexane	0.045	0.008	0.022
21	I9	2-Methyloctane	0.158	0.088	0.096
22	I9	3-Ethylheptane	0.047	0.023	0.026
23	N9	1,1,2,-Trimethylcyclohexane	0.114	0.179	0.203
24	A8	o-Xylene	14.405	14.254	14.362
25	P9	n-Nonane	0.120	0.127	0.123
26	A9	1-Propylbenzene	0.673	0.677	0.678
27	I10	2,2-Dimethyloctane	0.011	0.008	0.009
28	N9	n-Butylcyclopentane	0.002	0.003	0.002
29	A9	n-Propylbenzene	2.088	2.371	2.103

Table A4 Identification of C_8^+ composition blank and refluxed with F-24 and BSC-65-65F5 (continued).

Item	Group	Name	%composition of C_8^+		
			Blank	After reflux with	
				F-24	BSC-65-65F5
30	A9	1-Methyl-3-ethylbenzene	7.261	7.235	7.332
31	A9	1-Methyl-4-ethylbenzene	3.144	3.099	3.145
32	A9	1,3,5-Trimethylbenzene	3.008	3.022	3.043
33	A9	1-Methyl-2-ethylbenzene	3.282	3.685	3.260
34	I10	3-Methylnonane	0.032	0.102	0.096
35	A9	1,2,4-Trimethylbenzene	13.832	13.769	13.931
36	N10	1t-Methyl-2-n-propylcyclohexane	0.082	0.082	0.084
37	A9	1,2,3-Trimethylbenzene	3.595	3.552	3.568
38	A10	Total	5.136	3.916	3.871
39	A11	Total	1.903	1.795	1.869
40	A12	Total	0.118	0.135	0.127
41	C13+	Total	3.493	4.630	4.432
		Total	100.00	100.00	100.00

Table A5 XRF analyses of fresh clay, spent clay and regenerated clay.

Component	Spent clay	Fresh clay	BSC-65-65F5	BF-24F5
1. MgO	2.86	2.77	3.07	3.14
2. Al ₂ O ₃	10.67	13.51	11.44	12.00
3. SiO ₂	65.30	57.79	69.23	67.71
4. SO ₃	0.93	1.05	0.32	1.25
5. K ₂ O	0.13	0.17	0.18	0.19
6. CaO	0.68	0.99	0.71	0.78
7. TiO ₂	0.23	0.24	0.27	0.27
8. Fe ₂ O ₃	1.09	1.05	1.15	1.18
9. MnO ₂	0.10	0.09	0.00	0.09
10. Other (moisture+VOC+trace element)	18.02	22.34	13.63	13.39
Total	100.00	100.00	100.00	100.00

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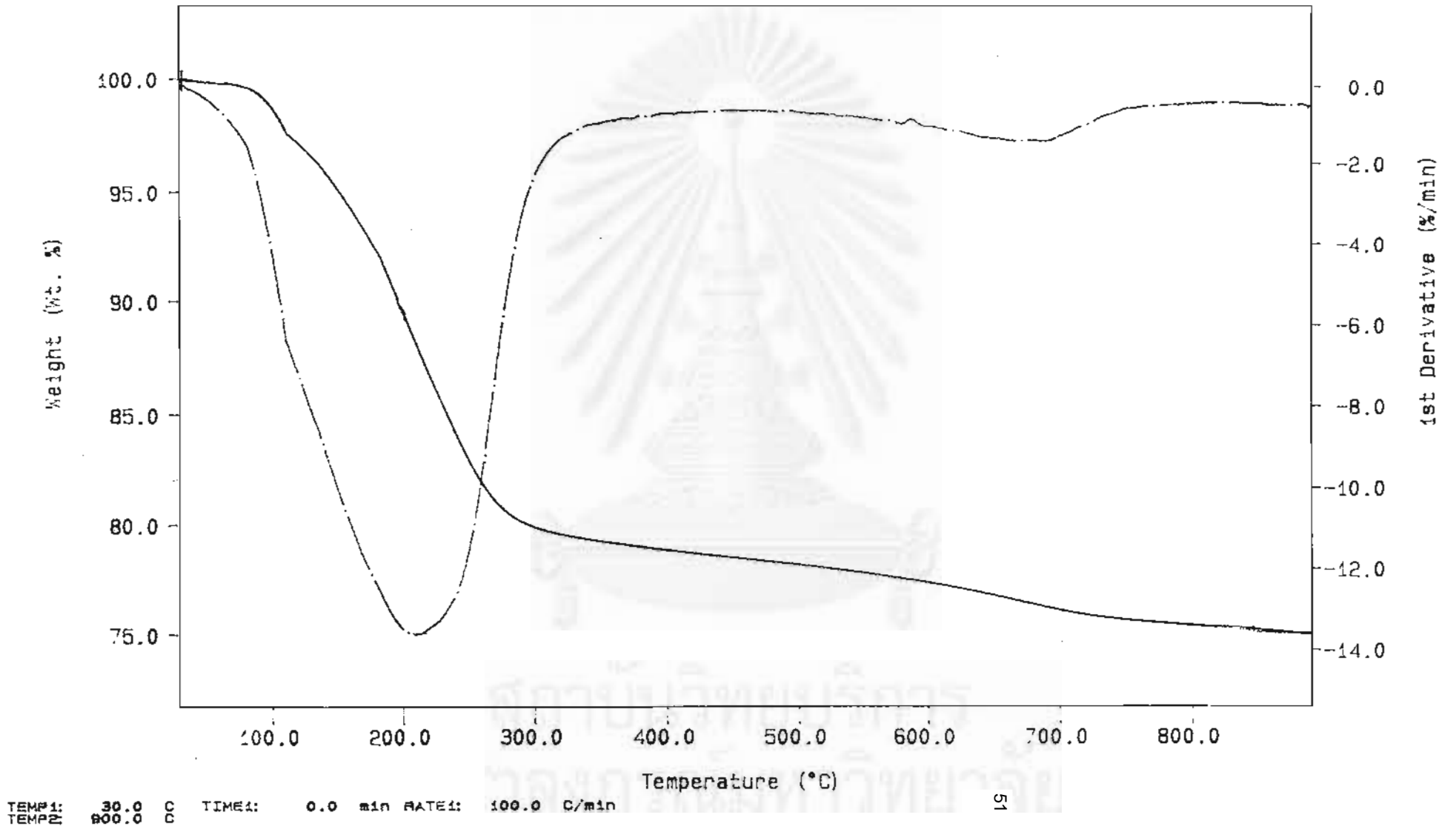
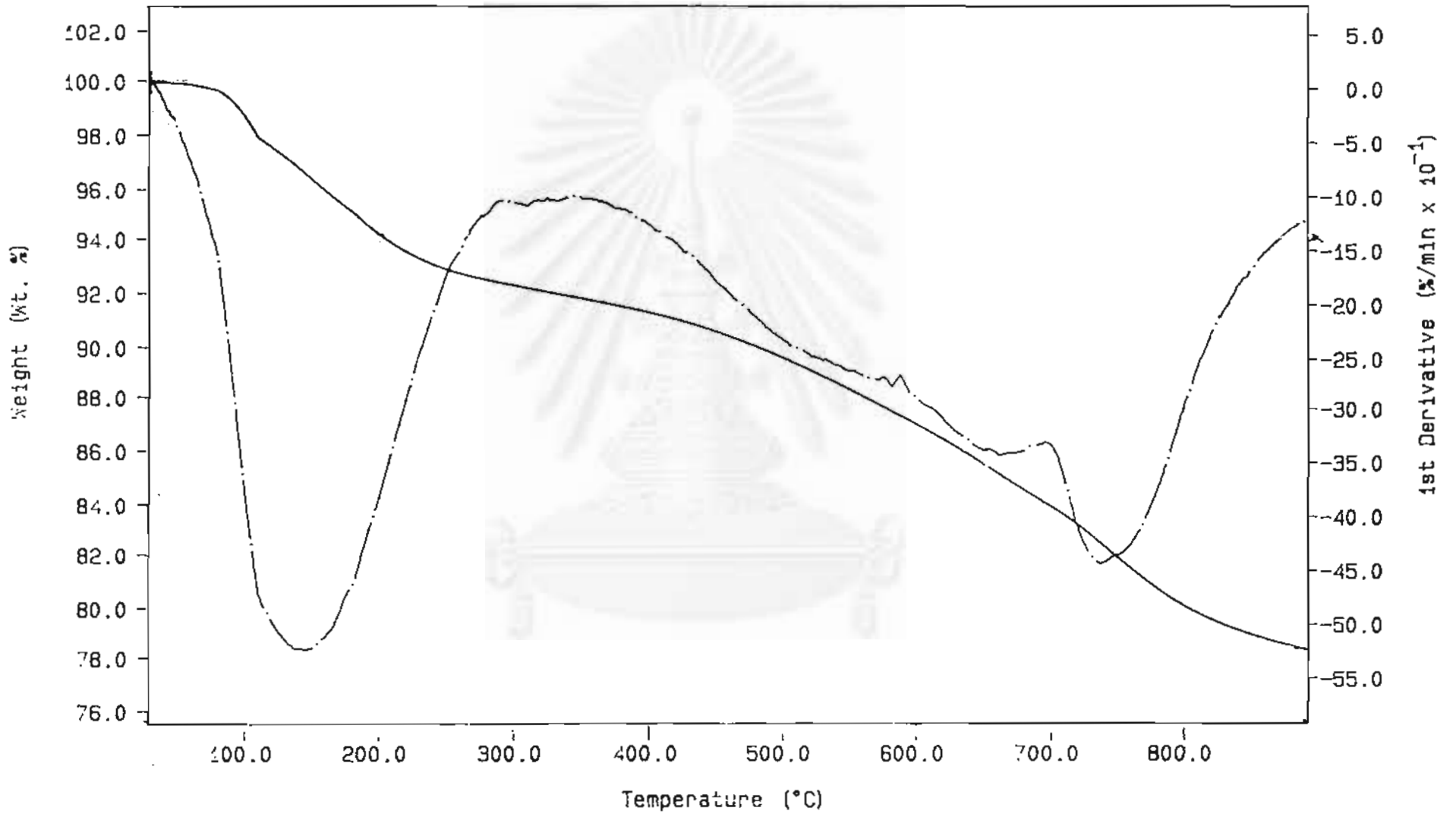
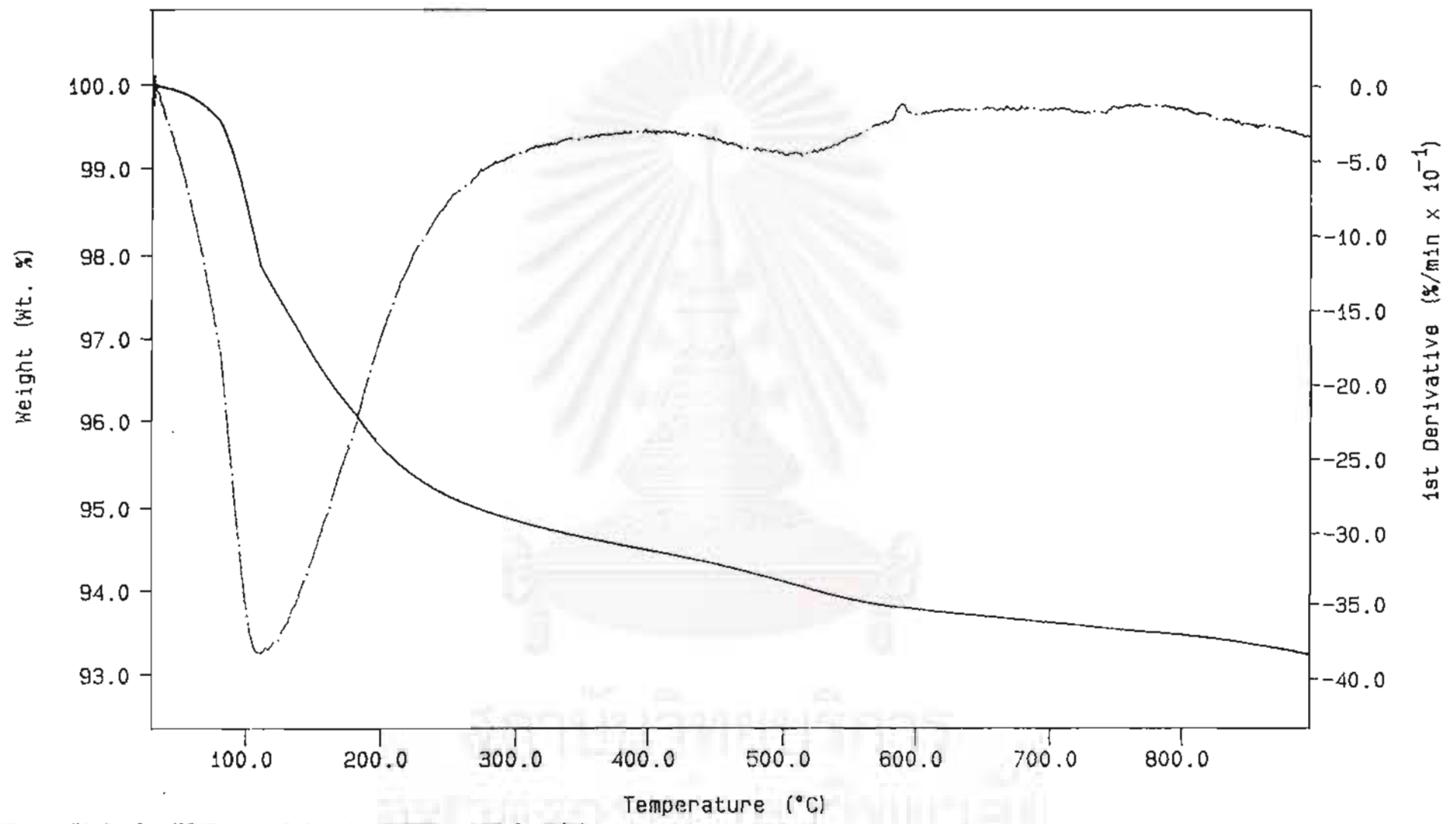


Figure A1 TG and DTG curves of fresh clay.



TEMP1: 30.0 C TIME: 0.0 min RATE: 100.0 C/min
TEMP2: 900.0 C

Figure A2 TG and DTG curves of spent clay⁵²



TEMP1: 50.0 C TIME1: 0.0 min RATE1: 100.0 C/min
TEMP2: 900.0 C

Figure A3 TG and DTG curves of clay regenerated at 650 °C for 6.5 hrs.

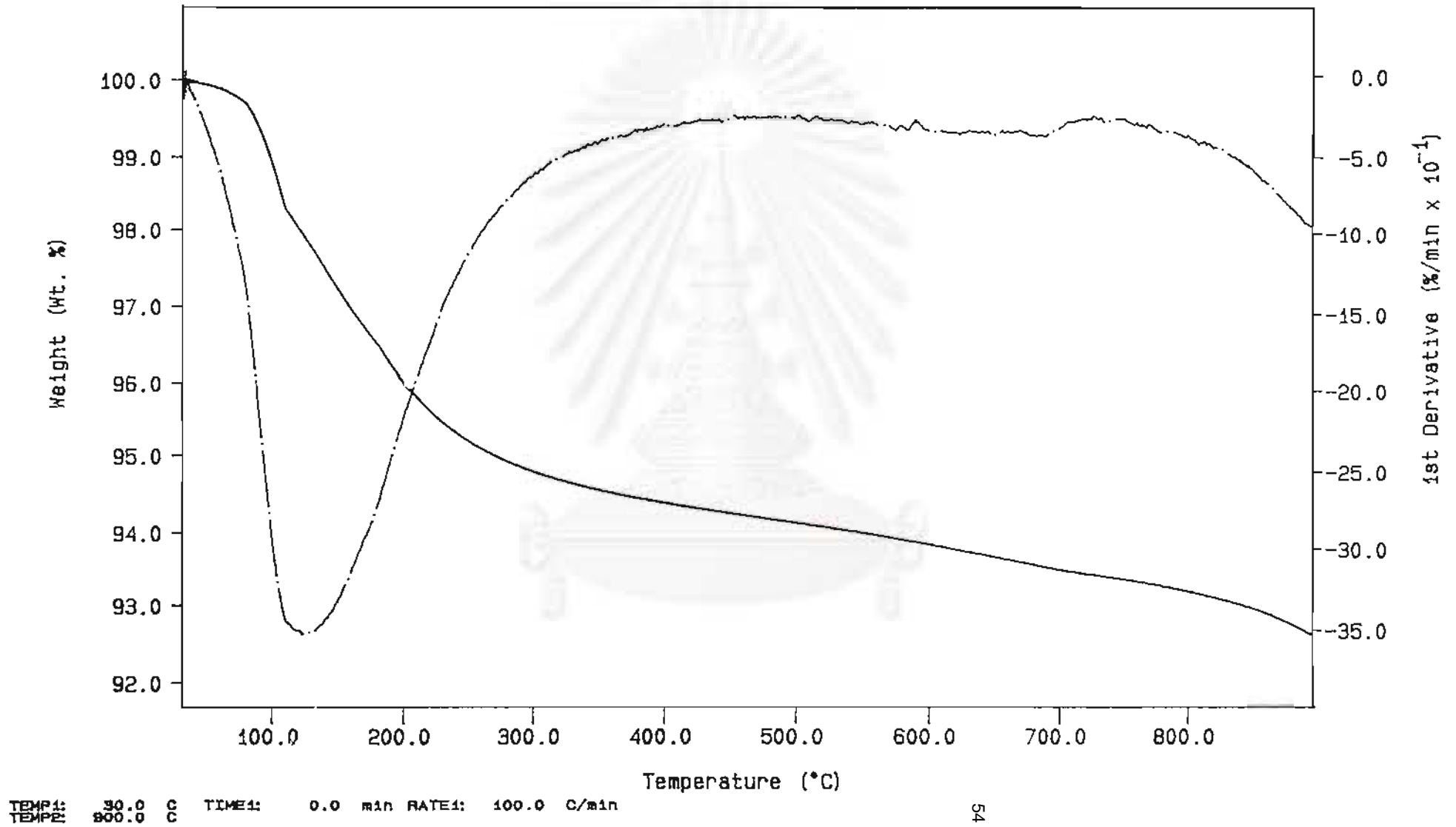


Figure A4 TG and DTG curves of clay regenerated at 650 °C for 6.5 hrs and treated with 1% NH₄F.

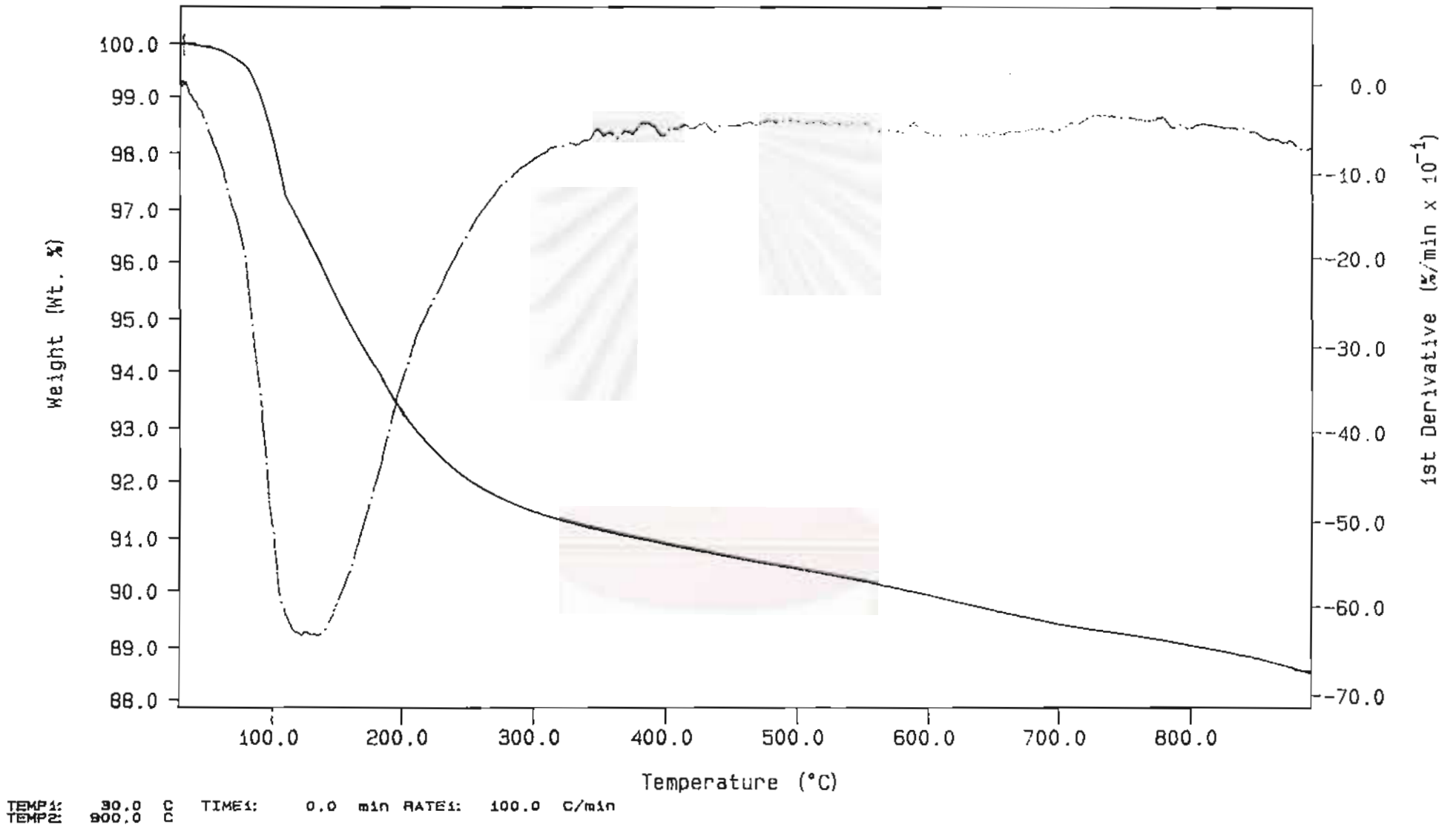


Figure A5 TG and DTG curves of clay regenerated at 650 °C for 6.5 hrs and treated with 3% NH₄F.

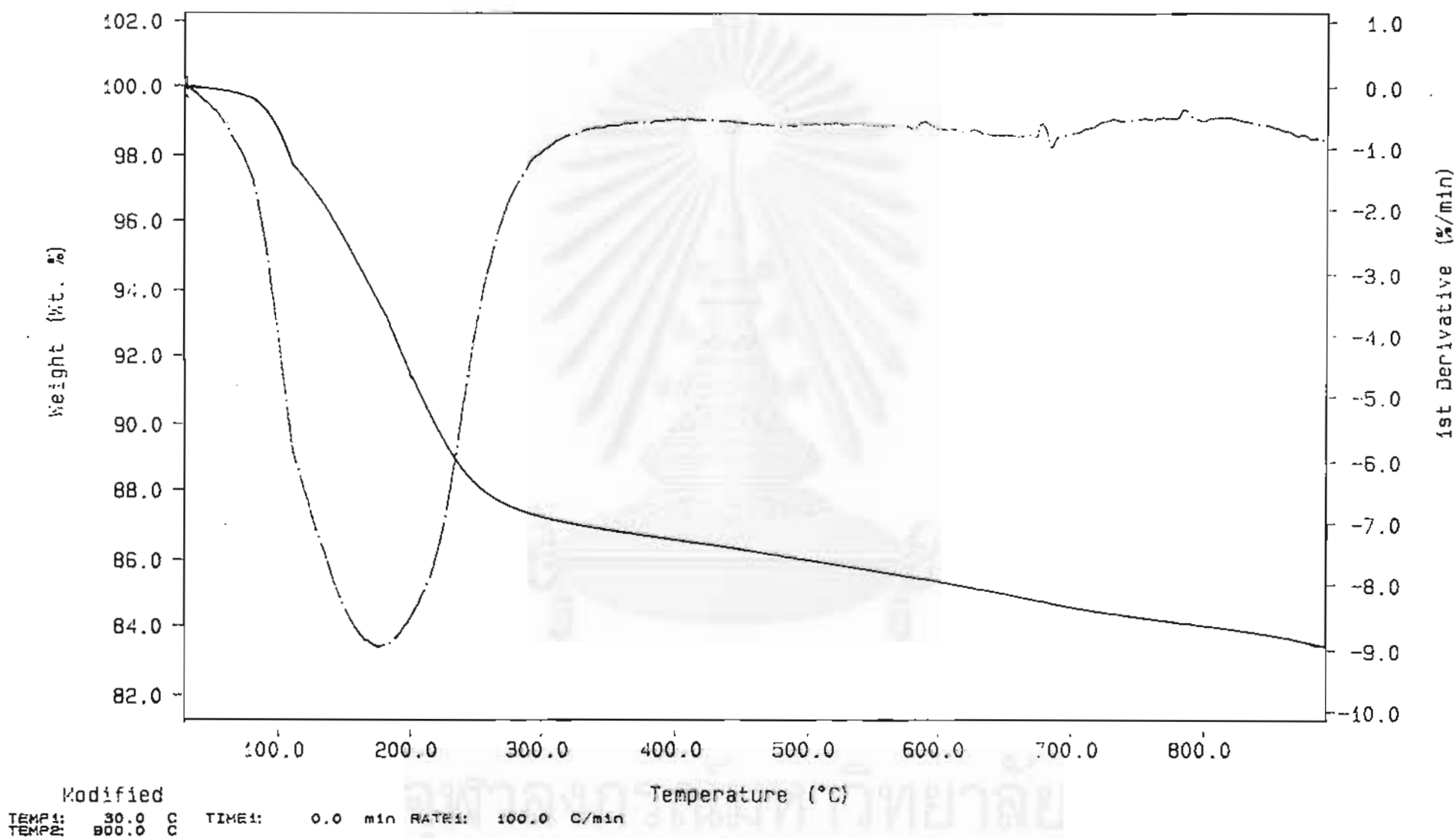
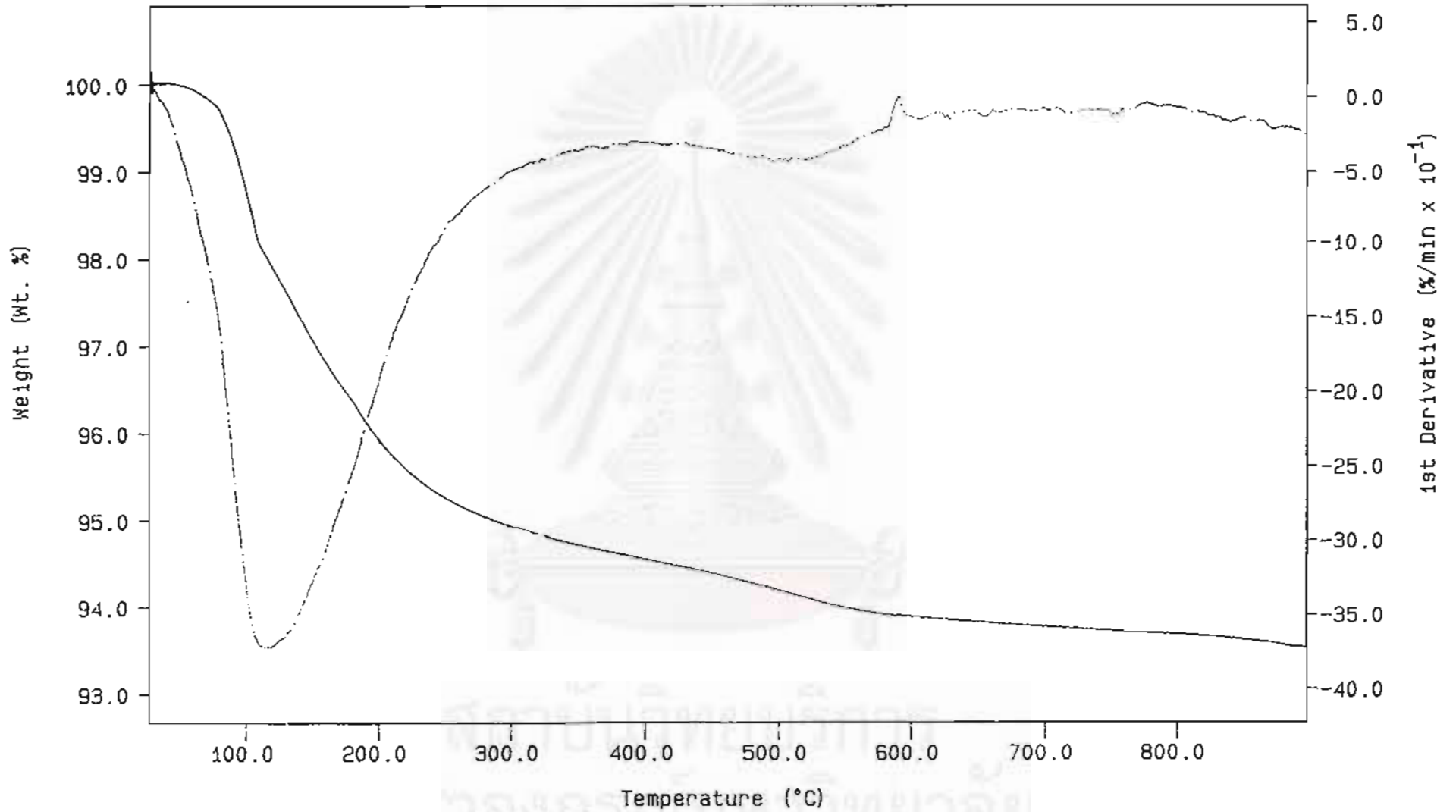
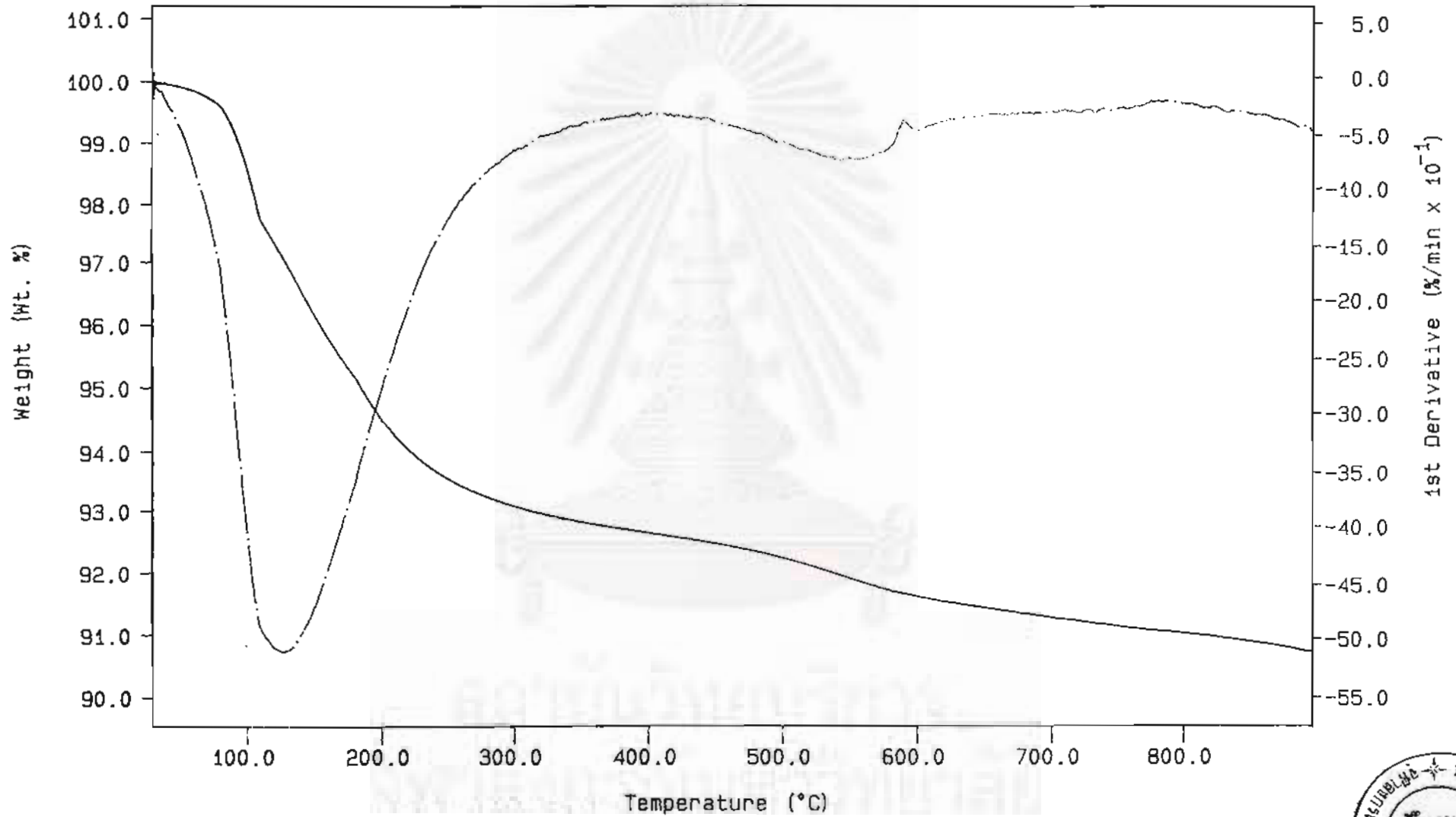


Figure A6 TG and DTG curves of clay regenerated at 650 °C for 6.5 hrs and treated with 5% NH₄F.



TEMP1: 30.0 C TIME1: 0.0 min RATE1: 100.0 C/min
TEMP2: 900.0 C

Figure A7 TG and DTG curves of clay regenerated at 700 °C for 4 hrs.



TEMP1: 30.0 C
 TEMP2: 900.0 C
 TIME1: 0.0 min RATE1: 100.0 C/min

Figure A8 TG and DTG curves of clay regenerated at 700 $^{\circ}\text{C}$ for 4 hrs and treated with 1% NH_4F .



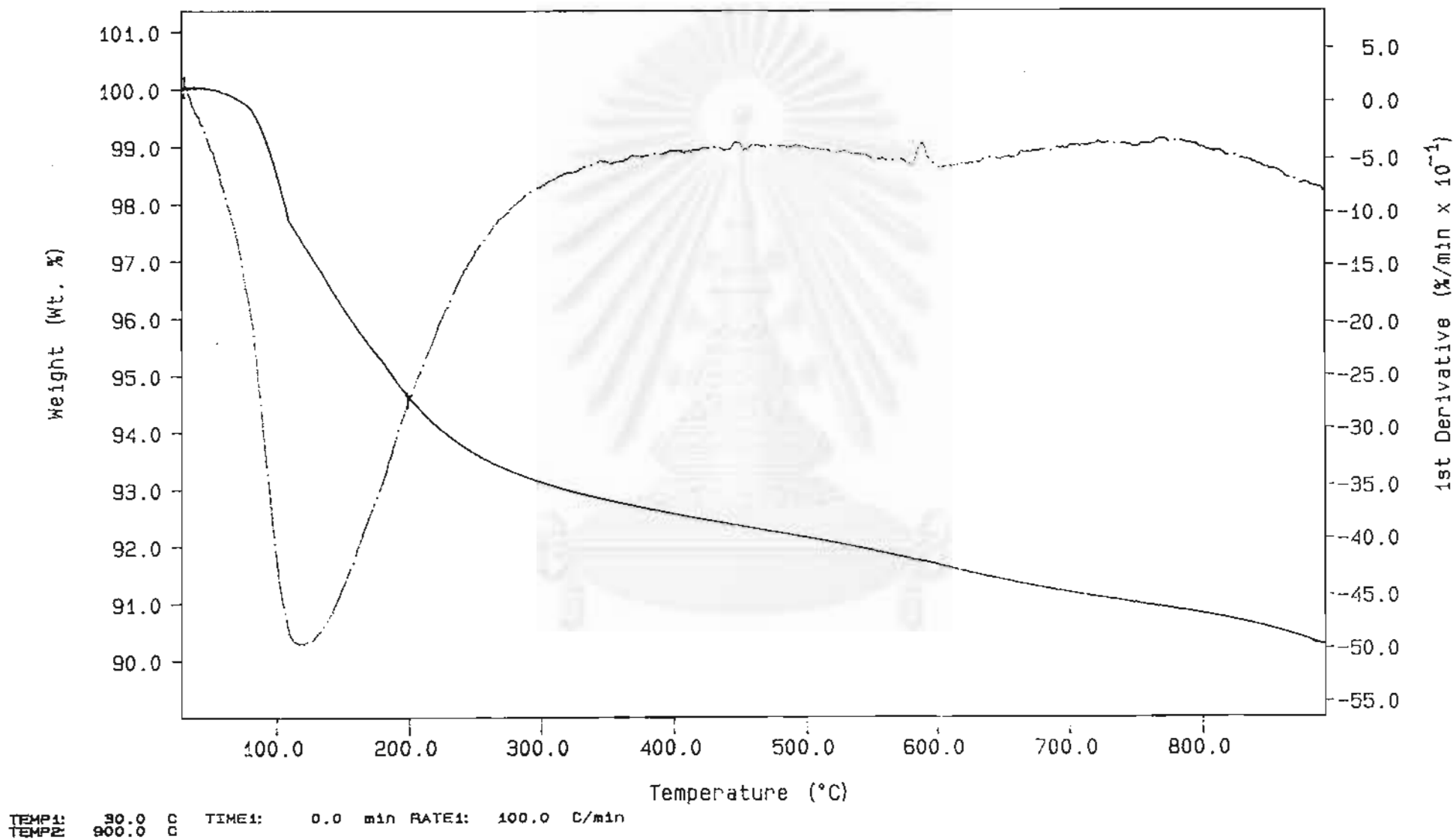


Figure A9 TG and DTG curves of clay regenerated at 700 °C for 4 hrs and treated with 3% NH₄F.

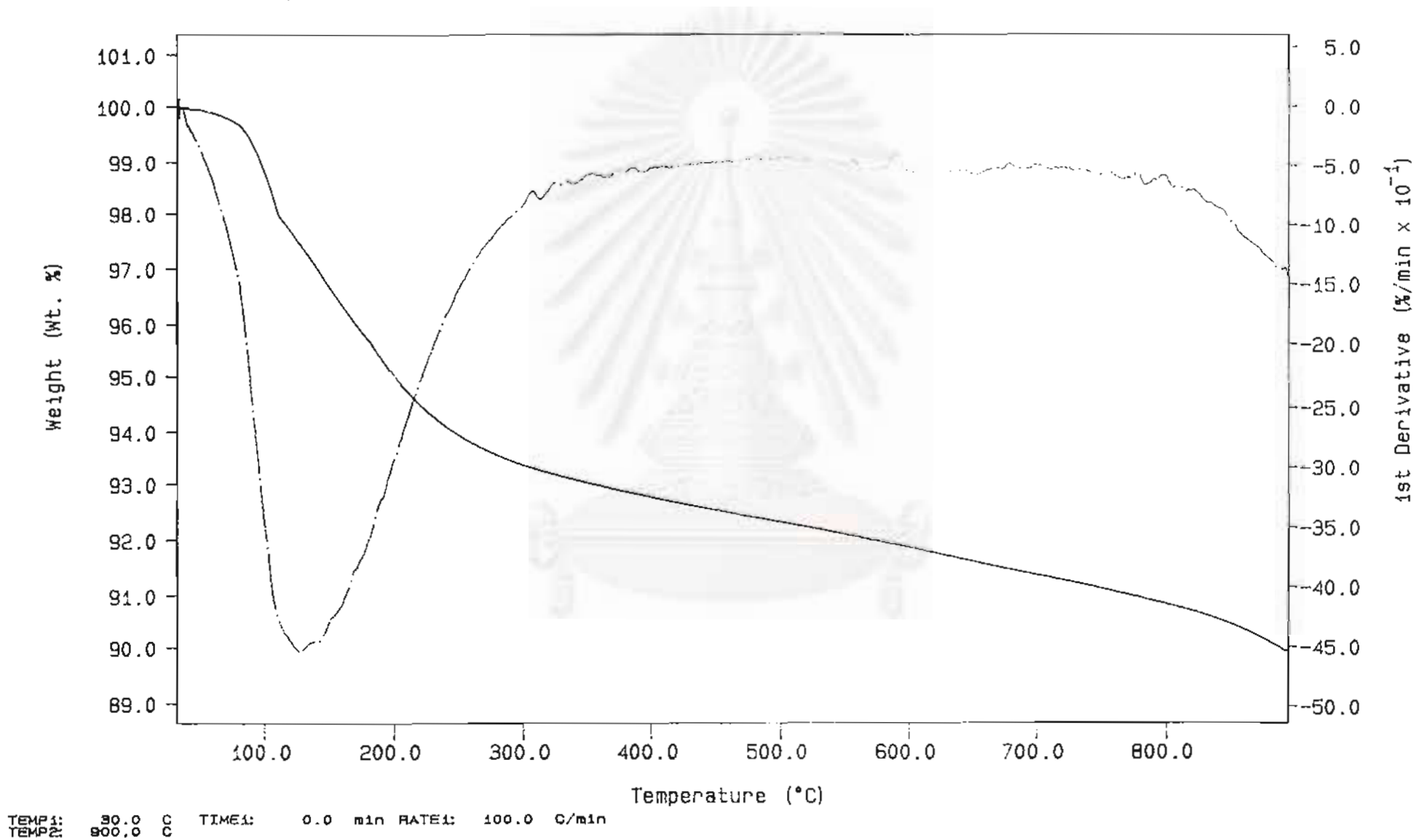


Figure A10 TG and DTG curves of clay regenerated at 700 °C for 4 hrs and treated with 5% NH₄F.

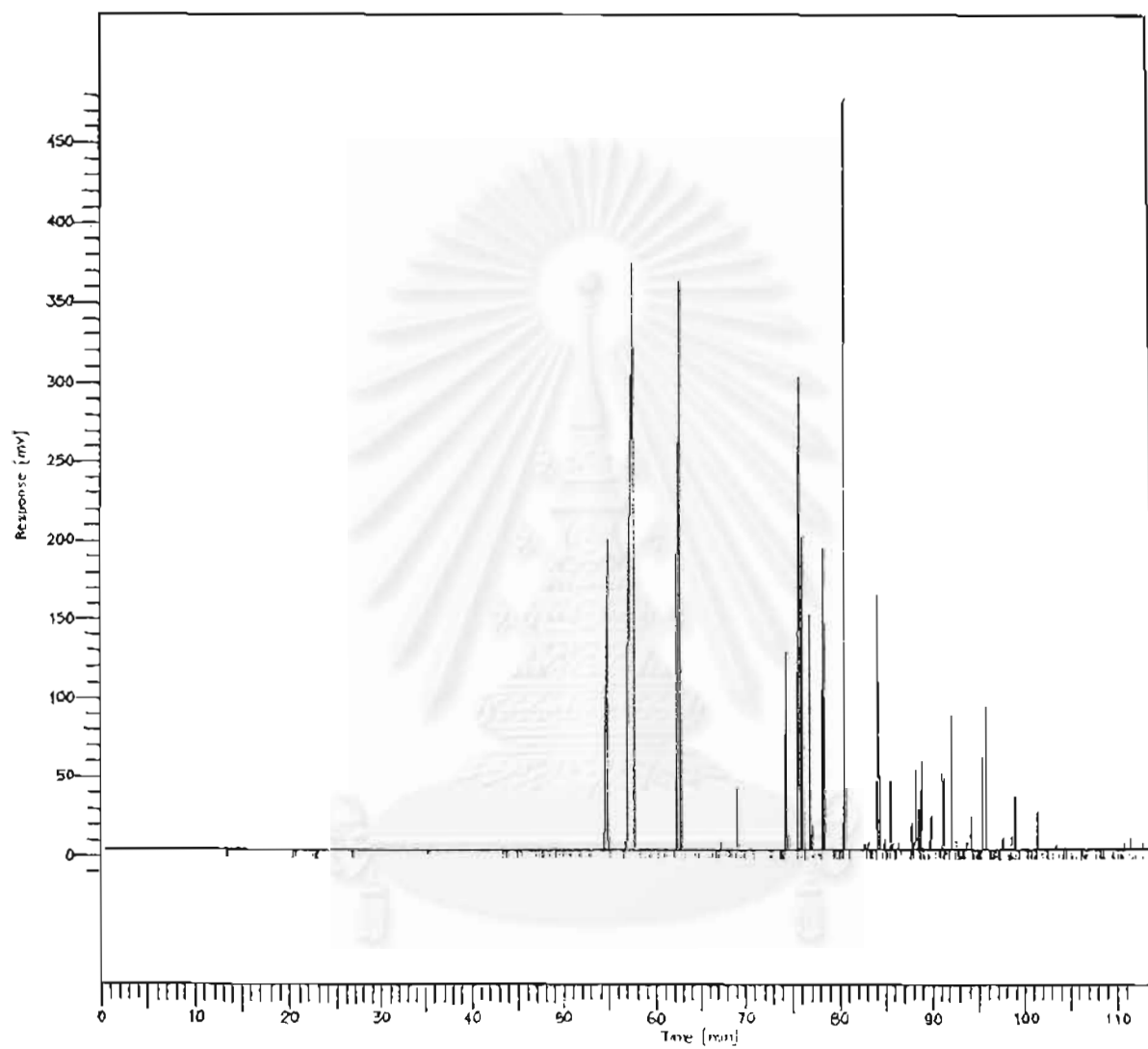


Figure A11 GC Chromatogram of C_g^+ blank

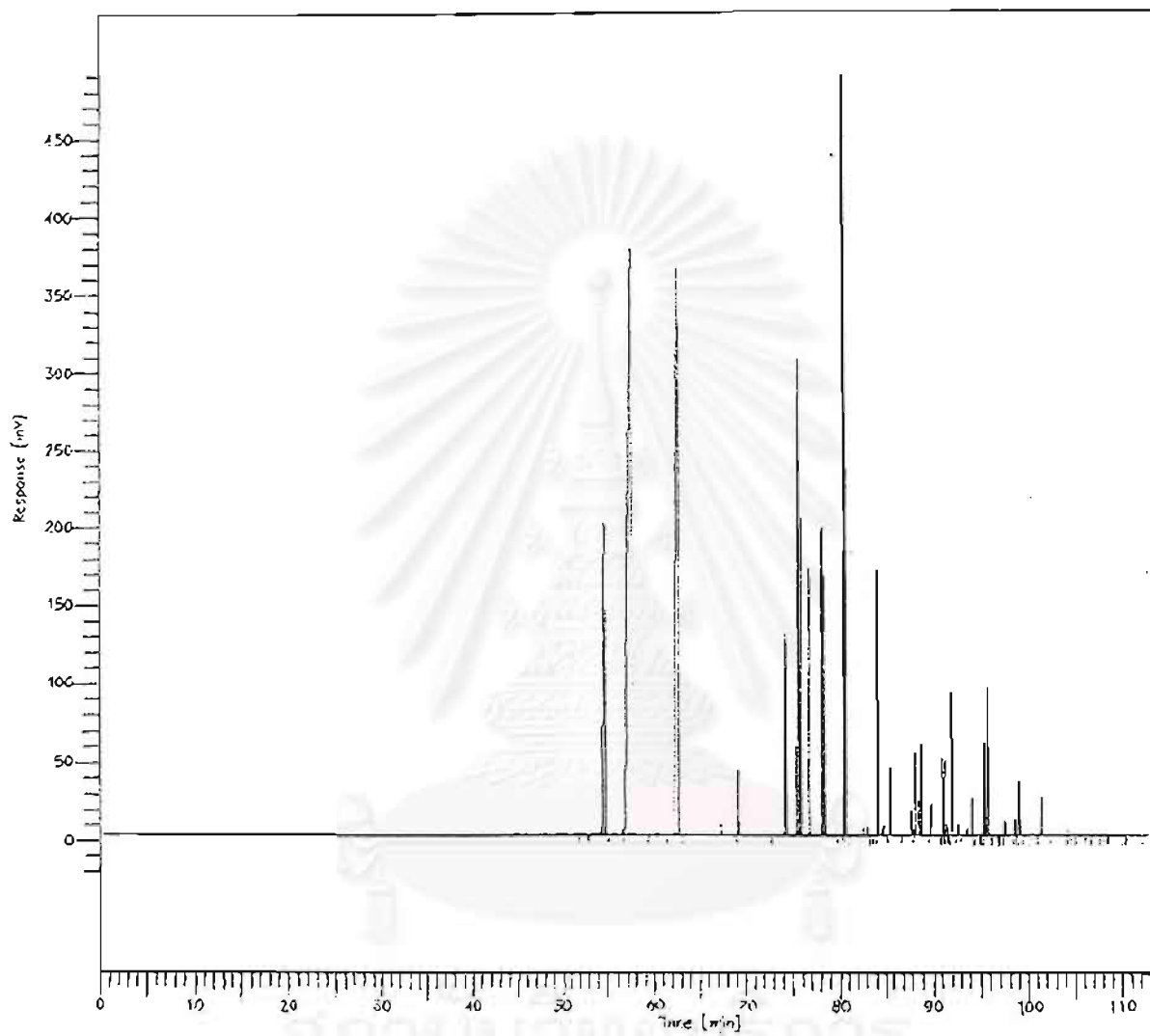


Figure A12 GC Chromatogram of C_8^+ refluxed with fresh clay.

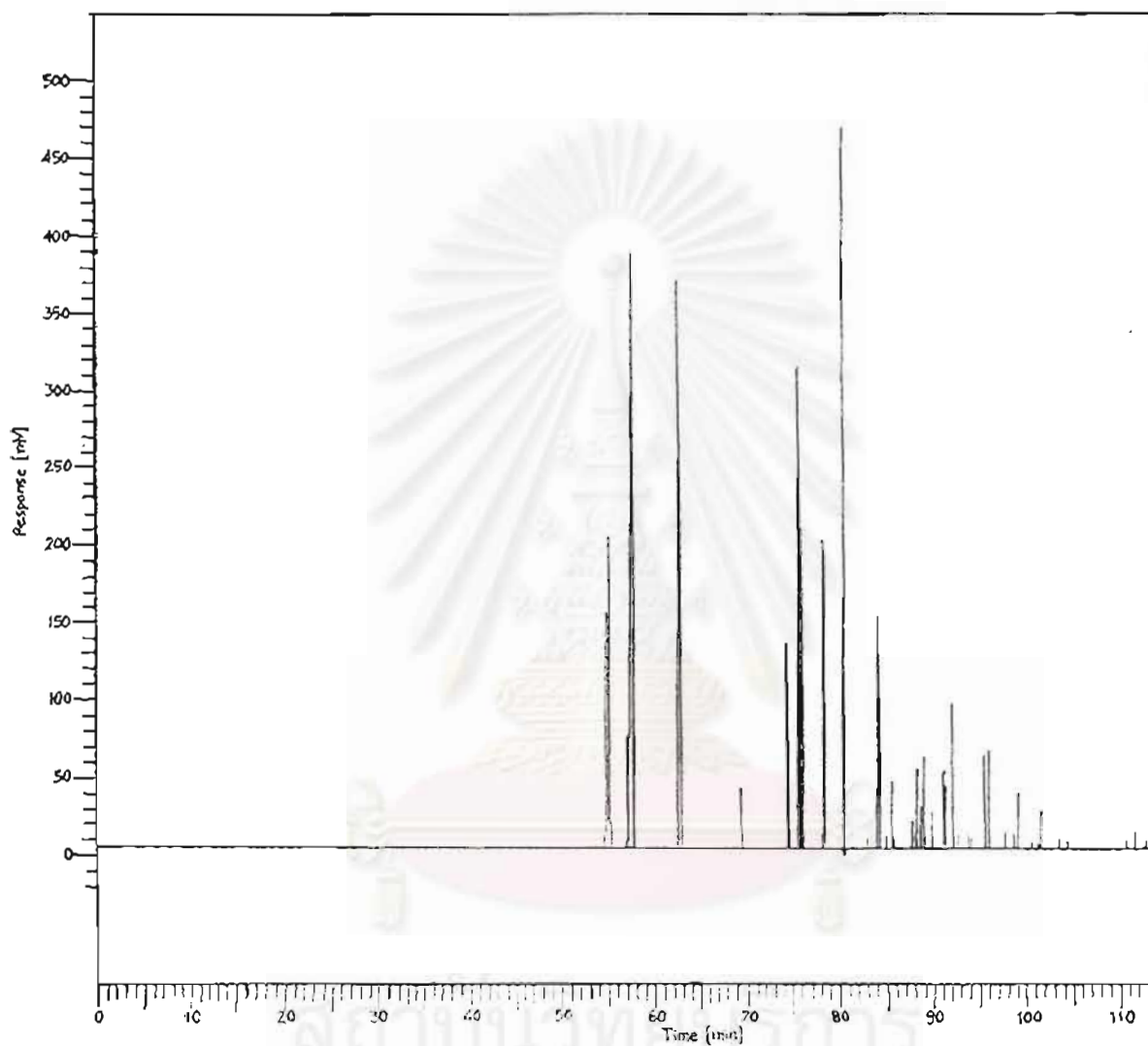


Figure A13 GC Chromatogram of C_8^+ refluxed with clay regenerated at 650°C for 6.5 hrs and treated with 5% NH_4F .

APPENDIX B

BET surface area calculation.

From BET equation :

$$\frac{X}{V(1-X)} = \frac{1}{V_m C} + \frac{(C-1)X}{V_m C} \quad (\text{A. 1})$$

- where :
- X = relative partial pressure of N_2 , P/P_0
 - P_0 = saturated vapour pressure of N_2 (or adsorbed gas) at the experimental temperature
 - P = equilibrium vapour pressure of N_2
 - V = volume of gas adsorbed at pressure P , ml. at the NTP/gram of sample
 - V_m = volume of gas adsorbed in monolayer, ml. at the NTP/gram of sample
 - C = $\exp(E_1 - E_2/RT)$
 - where : E_1 = heat of adsorption on the first layer
 - E_2 = heat of condensation of adsorbed gas on all the Layers

assume $C \rightarrow \infty$, then

$$\frac{X}{V(1-X)} = \frac{1(X)}{V_m C} \quad (\text{A. 2})$$

let : $V_m = V_m'$

V_m' = mean the volume of gas adsorbed to form the N_2 complete monolayer

V = volume of gas adsorbed measured by GC

$X = P/P_o$

$$\frac{P_b V}{273} = \frac{P_t V}{T} \quad (\text{A. 3})$$

where : $V =$ constant volume

$P_b =$ pressure at 0°C

$P_t =$ pressure at $t^\circ \text{C}$

$T = 273.15 + t, \text{K}$

$P_b = (273.15/T) \cdot P_t = 1 \text{ atm}$

partial pressure

$$P = \frac{[\text{Flow of } (\text{He} + \text{N}_2) - \text{Flow of He}] \cdot P_b}{\text{Flow of } (\text{He} + \text{N}_2)} \quad (\text{A. 4})$$

$= 0.3 \text{ atm}$

N_2 saturated vapour pressure, $P_o = 1.1 \text{ atm} = 836 \text{ mm. Hg}$

$$X = P/P_o = P/1.1$$

How to measure v



Desorption of N_2 area	S_2	S_1		
	N_2 calibration area			
V	$=$	$\frac{S_2 \cdot 1}{S_1 \cdot w} \cdot \frac{273.15}{T}$	ml/g of clay	(A. 5)

where : w = weight of sample

$$V_m' = \frac{v[1 - (\text{flow of He} + N_2 - \text{flow of He})/1.1]}{\text{Flow of He} + N_2} \quad \text{ml NTP/g of clay}$$

$$S_b = S \cdot V_m' \quad \text{(A. 6)}$$

where : S = surface area from literature of N_2

$$= 4.373 \text{ m}^2/\text{ml. Of } N_2$$

$$\text{so that : } S_b = 4.373 V_m' \text{ m}^2/\text{g. of catalyst} \quad \text{(A.3.7)}$$

VITA



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