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SYNTHESIS OF GLYPHOSATE FROM GLYCINE USING ZEOLITES AS CATALYSTS

Mr. Pichate Hublee

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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Thesis Title	SYNTHESIS OF GLYPHOSATE FROM GLYCINE USING ZEOLITES AS CATALYSTS
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Field of Study	Petrochemistry and Polymer Science
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พิเชษฐ์ ยับหลี : การสังเคราะห์ไกลโฟเสตจากไกลซีนโดยใช้ซีโอไลต์เป็นตัวเร่งปฏิกิริยา. (SYNTHESIS OF GLYPHOSATE FROM GLYCINE USING ZEOLITES AS CATALYSTS) อ. ที่ปรึกษา: รศ. ดร. อมร เพชรสม, อ. ที่ปรึกษาร่วม: ดร. จรรยา ชัยเจริญพงศ์, 108 หน้า.

ไกลโฟเสต (เอ็นฟอสโฟโนเมทธิลไกลซีน) เป็นสารกำจัดวัชพืชที่ใช้กันทั่วโลกมีการนำมาใช้ในการควบคุมและกำจัดวัชพืชอย่างต่อเนื่อง ไกลโฟเสตที่นำมาใช้ในการกำจัดวัชพืชนั้นจะใช้ในรูปของสารละลายเกลือไอโซโพรพิลามีน ซึ่งจะไม่เป็นพิษต่อสิ่งมีชีวิตจำพวกสัตว์เลี้ยงลูกด้วยนม ในปัจจุบันการเตรียมไกลโฟเสตในอุตสาหกรรมมี 2 ขั้นตอน ขั้นแรกคือ การเตรียมกรดเอ็นฟอสโฟโนเมทิลอิมิโนไดอะซิติกจากกรดอิมิโนไดอะซิติก ขั้นที่สองคือ การออกซิไดซ์กรดเอ็นฟอสโฟโนเมทิลอิมิโนไดอะซิติกเป็นไกลโฟเสตโดยใช้โคบอลต์(II)คลอไรด์เป็นตัวเร่งปฏิกิริยา ในงานวิจัยนี้ได้สังเคราะห์ไกลโฟเสตจากฟอร์มัลดีไฮด์ ไกลซีนและกรดฟอสฟอรัสในปฏิกิริยาแบบภาชนะเดียว พบว่าภาวะที่ดีที่สุด 2 ภาวะ ภาวะแรก คือการใช้อัตราส่วนโมลเป็น 2:1:1 ของฟอร์มัลดีไฮด์:ไกลซีน:กรดฟอสฟอรัส ที่อุณหภูมิ 70 °C เป็นเวลา 2 ชั่วโมงได้ไกลโฟเสต 35 เปอร์เซ็นต์ และภาวะที่สอง คือการใช้อัตราส่วนโมลเป็น 2:1:0.5 ของฟอร์มัลดีไฮด์:ไกลซีน:กรดฟอสฟอรัส ที่อุณหภูมิและเวลาที่ทำปฏิกิริยาเดียวกัน ร่วมกับตัวเร่งปฏิกิริยาโมเลกุลาร์ซีพ 3เอ ที่กระตุ้นด้วยกรด (137 มิลลิสมมูล/100 กรัม; 4 กรัม ต่อไกลซีน 1 โมล) ได้ 39 เปอร์เซ็นต์ อย่างไรก็ตามถ้าใช้กรดไฮโดรคลอริกในการสังเคราะห์ไกลโฟเสตจะให้ปริมาณไกลโฟเสตมากกว่าการใช้กรดซัลฟูริก ได้ติดตามและวิเคราะห์ผลิตภัณฑ์ที่ได้จากการสังเคราะห์นี้โดยเทคนิคโปรตอนนิวเคลียร์แมกนีติกเรโซแนนซ์สเปกโทรสโกปีโดยใช้โซเดียมอะซิเตตเป็นสารมาตรฐานภายใน

สาขาวิชา.....ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต .....

ปีการศึกษา ..... 2550..... ลายมือชื่ออาจารย์ที่ปรึกษา .....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

487 23899 23: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: GLYPHOSATE / *N*-PHOSPHONOMETHYLGLYCINE / SYNTHESIS / GLYCINE / ZEOLITE

PICHATE HUBLEE: SYNTHESIS OF GLYPHOSATE FROM GLYCINE USING ZEOLITES AS CATALYSTS. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., THESIS COADVISOR: CHANYA CHAICHAROENPONG, Ph.D., 108 pp.

Glyphosate (*N*-phosphonomethylglycine) is the most frequently used herbicide in the world. It is used to control a wide variety of annual and perennial weeds. Glyphosate is used worldwide in the form of an aqueous solution of isopropylamine salt and this organic phosphorous herbicide is considered as a non-toxic herbicide for mammals when used normally. At present, preparation of glyphosate in the industry comprises of two steps; (1) preparation of *N*-phosphonomethyliminodiacetic acid from iminodiacetic acid and (2) oxidation of *N*-phosphonomethyliminodiacetic to glyphosate using cobalt(II)chloride as a catalyst. In this research, we synthesized glyphosate from formaldehyde, glycine and phosphorous acid as one-pot reaction. Two optimum conditions were found: (1) The use of 2:1:1 formaldehyde:glycine: phosphorous acid mole ratio at 70 °C for 2 hours giving 35% yield; (2) The use of 2:1:0.5 formaldehyde:glycine:phosphorous acid mole ratio with the catalysis of acid activated molecular sieve 3A (137 meq/100 g; 4 g per 1 mole glycine) at the same temperature and reaction time, leading to 39% yield. However, using hydrochloric acid as a catalyst gave higher yield of glyphosate than using sulfuric acid as a catalyst. The resulting product mixtures were monitored and quantitatively determined by proton nuclear magnetic resonance spectroscopy using sodium acetate as an internal standard.

Field of Study:...Petrochemistry and Polymer Science...Student's Signature:.....Pichate Hublee

Academic Year:.....2007.....

Advisor's Signature:.....

Co-advisor's Signature:.....Chanya Chaicharoenpong

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LIST OF ABBREVIATIONS

Å	angstrom
δ	chemical shift
^{13}C NMR	carbon-13 nuclear magnetic resonance
^{1}H NMR	proton nuclear magnetic resonance
°C	degree celsius
FT-IR	fourier transform infrared spectrophotometer
kg	kilogram (s)
g	gram (s)
meq	milliequivalent
ml	milliliter (s)
mg	milligram (s)
min	minute (s)
mmol	millimole
M	mole per liter
MS	molecular sieve
N	normality
nm	nanometer
ppm	part per million
XRF	X-ray fluorescence
% wt	percent weight by weight
% w/v	percent weight by volume
% yield	percent yield

CHAPTER I

INTRODUCTION

1.1 Background

Herbicides are widely used by farmers to destroy or inhibit plant growth, especially of weeds or other undesirable vegetation and help to increase crop yields for such staple crops as corn, soybean and rice. In addition herbicides can be obtained from natural sources or by chemical synthesis. Commercial herbicides are shown in Table 1.1 and as shown in the table glyphosate is the most popular herbicide.

Table 1.1 Importation of herbicides in 2003

Rank	Compound	Weight (ton)	Cost (millionbaht)
1	Glyphosate isopropylammonium	24,812	1,824
2	Paraquat dichloride	8,366	1,385
3	Ametryn	2,374	488
4	2,4-D	5,114	392
5	Atarazine	2,364	310
6	Diuron	984	179
7	Bromacil	304	173
8	Fenoxaprop-P-ethyl	210	151
9	Butachlor	1,309	126
10	Propanil	827	118
	total	**73,027**	**10,036**

Table 1.2 Importation of herbicide in 2000-2007

Year	Weight (ton)	Cost (millionbaht)
2000	51,344	6,418
2001	55,471	8,560
2002	70,158	9,202
2003	73,027	10,035
2004	99,839	10,372
2005	78,593	10,571
2006	101,854	12,966
2007	122,337	14,643

Table 1.1 shows that glyphosate the biggest part of the herbicide importation in Thailand, based on the record for year 2003. Moreover, the trend of herbicide importation from 2000-2007 indicates the increasing need of herbicides as shown in Table 1.2. One of the strategic to reduce national expense spent for agricultural production is to investigate the synthesis of glyphosate that is practical and economically suitable. Therefore, the aim of this research is to synthesize glyphosate from simple raw materials with convenient route.

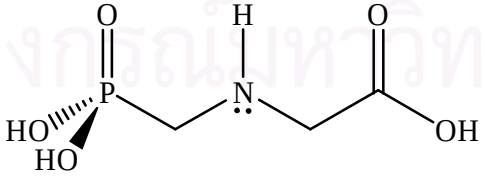

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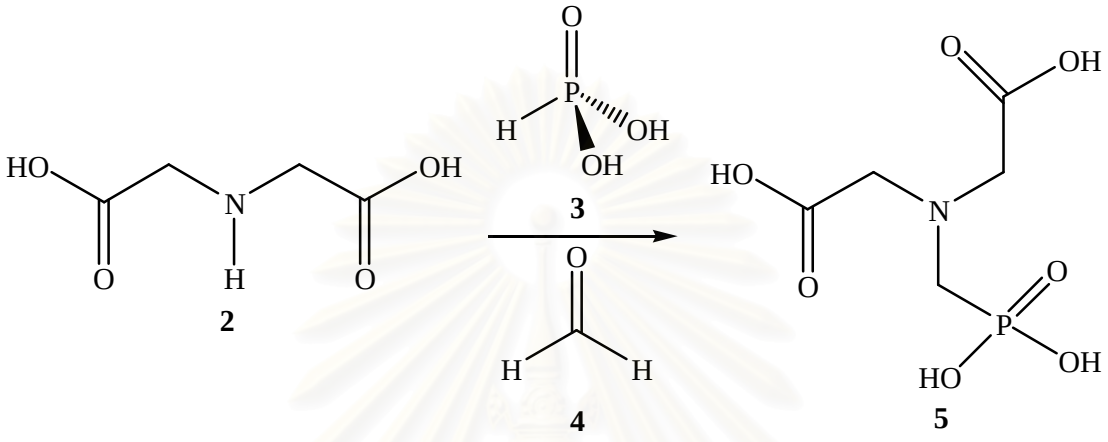
Figure 1.1 Structure of glyphosate (*N*-phosphonomethylglycine) ($C_3H_8O_5NP$).

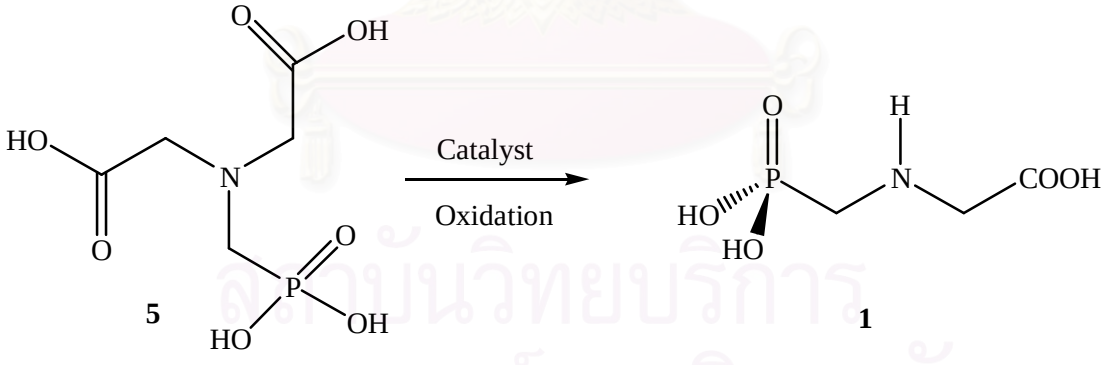
At present, preparation of glyphosate in industry has 2 steps

1. Preparation of *N*-phosphonomethyliminodiacetic acid from iminodiacetic acid, formaldehyde (CH_2O) and phosphorous acid (H_3PO_3) in concentrated sulfuric acid (H_2SO_4).



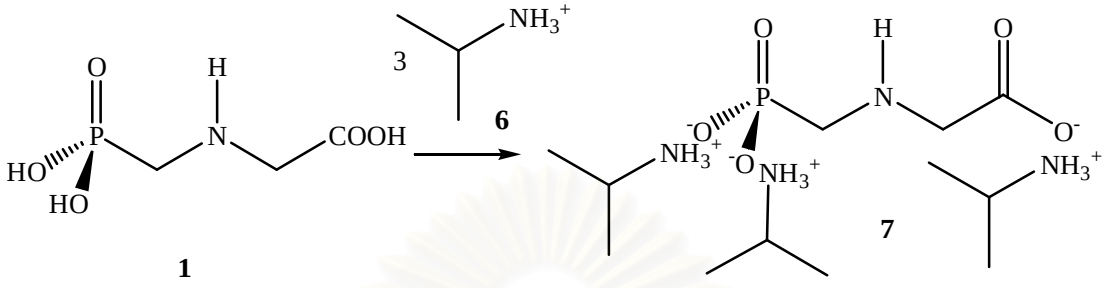
(1.1)

2. Preparation of glyphosate from *N*-phosphonomethyliminodiacetic acid using metal transition as catalyst in air oxidation.



(1.2)

Preparation of glyphosate salt from glyphosate with isopropylamine in present was presented as equation 1.3.



(1.3)

The glyphosate and certain salts are the only effective and approved post-emergence herbicides in the field. The present commercial compound is the isopropylamine salt of *N*-phosphonomethylglycine.

In present, zeolites were used in many the industry, such as paper, oil, synthesis, etc. A reaction usually catalyzed by strong mineral acids, which have to be neutralized at the end of the reaction. Zeolites are used to displace mineral acids because of their nonpolluting and regenerating properties. Another advantage of zeolites is in high stability and selectivity contributing to the distinct pore size. However, the major concern is the formation of *N*,*N*-di(phosphonomethyl)glycine as a main product. The use of zeolites is therefore expected to enhance the selectivity of the product to the desired glyphosate.

1.2 Objective

Investigation on the direct synthesis of glyphosate from glycine, formaldehyde and phosphorous acid using acid treated molecular sieve 3A, 4A and 5A as catalysts.

1.3 The scope of this study

1. Characterization of the acid treated molecular sieve 3A, 4A and 5A using the following methods;
   - Analysis of acid activated catalysts by acid-base titration
   - Analysis of structure of catalysts by X-ray fluorescence (XRF)

2. Investigation of the synthesis of glyphosate from glycine, formaldehyde and phosphorous acid without catalysts and with catalysts (acid treated molecular sieves 3A, 4A, 5A) under the following conditions;
   - Reaction temperature 30-120 °C
   - Reaction time 1-4 hours
   - Mole ratio of reactants
   - Type of molecular sieves
   - Amount of acid molecular sieves
   - Type of acid

3. Investigation of the conventional synthesis of glyphosate. The products were analysed by proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR), paper chromatography and FTIR spectroscopy.

CHAPTER II

THEORY

2.1 Mannich reaction [1, 2]

The Mannich reaction is condensation of a primary or secondary amine or ammonia (usually as the hydrochloride) with formaldehyde and a compound containing at least one reactive hydrogen atom. The reaction is also known as Mannich condensation reaction. The Mannich reaction is an organic reaction and consists of a amino alkylation of an acidic proton placed next to a carbonyl functional group with formaldehyde and ammonia or any primary or secondary amine. The final product is a β-amino-carbonyl compound. The electrophilic species is often generated from the amine and formaldehyde. The reaction is usually limited to secondary amines, because dialkylation can occur with primary amines (Figure 2.1).

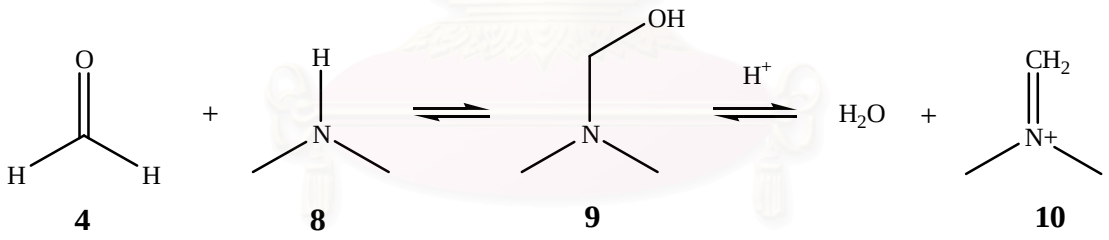


Figure 2.1 Typical reaction of secondary amine with carbonyl compound in the mannich reaction [1].

Formation of the Schiff base electrophile in a nucleophile addition and amino alkylation of compound contains an acidic hydrogen shown in Figure 2.3.

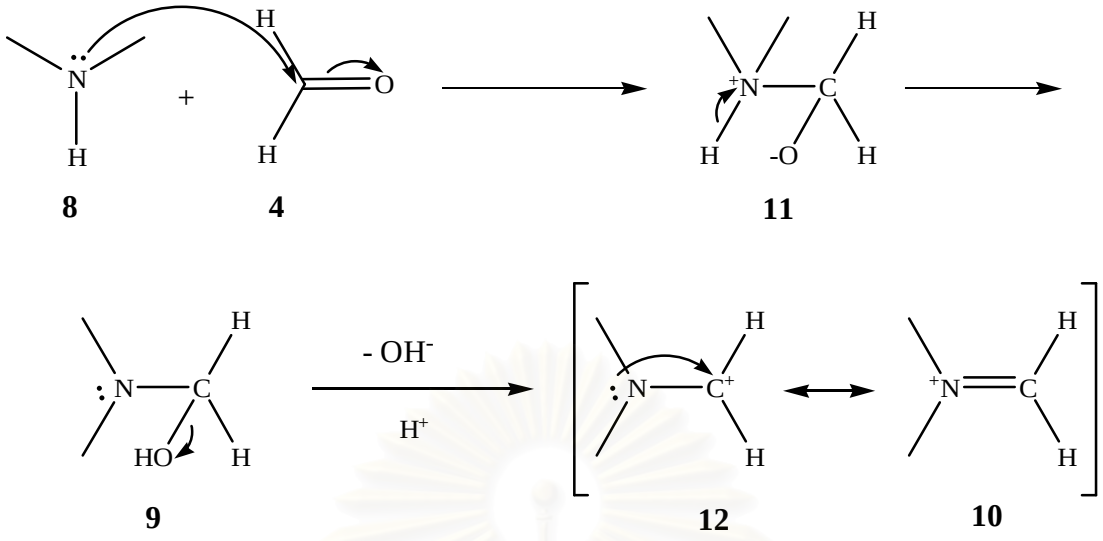


Figure 2.2 Mechanism of secondary amine in mannich reaction.

2.2 Oxidative decarboxylation [2]

The reactions are oxidation reactions in which a carboxylate group is removed, forming carbon dioxide and other. For examples in the preparation of carbocation from alkyl carboxylic acid, carboxylic acids are oxidized by lead tetraacetate. Decarboxylation and the product may be an alkene, alkane, acetate ester under modified conditions a halide. A free-radical mechanism operates and the product composition depends on the fate of the radical intermediate. The reaction is catalyzted by cupric salts, which function by oxidizing the intermediate radical to a carbocation (step 3 in the mechanism). Cu(II) is more reactive than $Pb(OAc)_4$ in this step.

$$Pb(OAc)_4 + RCO_2H \rightleftharpoons RCO_2Pb(OAc)_3 + CH_3CO_2H$$

$$RCO_2Pb(OAc)_3 \longrightarrow R\cdot + CO_2 + Pb(OAc)_3$$

$$R\cdot + Pb(OAc)_4 \longrightarrow R^+ + Pb(OAc)_3 + CH_3CHO_2^-$$

and

$$R\cdot + Pb(OAc)_3 \longrightarrow R^+ + Pb(OAc)_2 + CH_3CHO_2^-$$

2.3 Phosphorous nucleophiles [2]

Both neutral and anionic phosphorous compounds are good nucleophiles toward alkyl halides [see Figure 2.3], but they are weak nucleophiles.

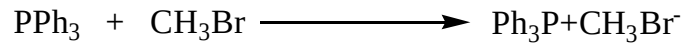


Figure 2.3 Reaction of phosphorous compound with alkyl halide.

Sometime phosphorous compounds can be good nucleophiles if alkyl groups ($-R_3$) are donating group.

Table 2.1 Hardness and softness of some common ions and molecules [1]

	Bases (nucleophiles)	Acids (electrophiles)
Soft	RSH, RS^-, I^-, R_3P	I_2, Br_2, RS-X, RSe-X, RCH_2-X
	$^-C{\equiv}N$, $^-C{\equiv}O^+$, RCH=CHR	Cu(I), Ag(I), Pd(II), Pt(II), Hg(II)
	Benzene	zerovalent metal complexes
Borderline	Br^-, N_3^-, $ArNH_2$,	Cu(II), Zn(II), Sn(II)
	Pyridine	R_3C^+, R_3B
Hard	H_2O, OH^-, ROH, RO^-, RCO_2^-	H-X, H^+, Li^+, Na^+, K^+
	F^-, Cl^-, NO_3^-, NH_3, RNH_2	Mg^{2+}, Ca^{2+}, Al(III), Sn(IV), Ti(IV), R_3Si-X

2.4 Molecular sieves for using in catalytic reaction [3]

Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates. These crystals are characterized by a three-dimensional pore system, with pores of precisely defined diameter. The corresponding crystallographic structure is formed by tetrahedrals of (AlO_4) and (SiO_4). These

tetrahedrals are the basic building blocks for various zeolite structures, such as zeolites A and X, the most common commercial adsorbents.

Molecular sieve type A Molecular sieve type X

Figure 2.4 Structure of molecular sieve type A and X.

Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. For instance, the sodium form of zeolite A has a pore opening of approximately 4 angstrom (4×10^{-10} m), called 4A molecular sieve. If the sodium ion is exchanged with the larger potassium ion, the pore opening is reduced to approximately 3 angstrom (3A molecular sieve). On ion exchange with calcium, one calcium ion replaces two sodium ions. Thus, the pore opening increases to approximately 5 angstrom (5A molecular sieve). Ion exchange with other cations is sometimes used for particular separation purposes.

Molecular sieve 4Å Molecular sieve 3Å

Figure 2.5 Ion exchange from Na^+ to K^+.

2.5 Zeolite [4]

In zeolites, the metal atoms (classically, silicon or aluminum) are surrounded by four oxygen anions to form an approximate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes. The tetrahedral metals are called T-atoms for short, and these tetrahedral then stack in beautiful, regular arrays such that channels form. The possible ways for the stacking to occur is virtually limitless and hundreds of unique structures are known. Graphical depictions of several representative types are given under “Representative Structures”.

The zeolitic channels (or pore) are microscopically small, and in fact, have molecular size dimensions such that they are often termed “molecular sieves”. The size and shape of the channels have extraordinary effects on the properties of these materials for adsorption processes, and this property leads to their use in separation processes. Molecules can be separated via shape and size effects related to their possible orientation in the pore, or by differences in strength of adsorption.

Since silicon typically exits in a 4+ oxidation state, the silicon-oxygen tetrahedral are electrically neutral. However, in zeolites, aluminum typically exits in the 3+ oxidation state so that aluminum-oxygen tetrahedral form centers that are electrically deficient one electron. Thus, zeolite frameworks are typically anionic, and charge-compensating cations populate the pores to maintain electrical neutrality. These cations can participate in ion-exchange processes, and this yields some important properties for zeolites. When charge-compensating cations are “soft” cations such as sodium, zeolites are excellent water softeners because they can pick up the “hard” magnesium and calcium cations in water leaving behind the soft cations. When the zeolitic cations are protons, the zeolite becomes a strong solid acid. Such solid acids form the foundations of zeolite catalysis applications including the important fluidized bed cat-cracking refinery process. Other types of reactive metal cations can also populate the pores to form catalytic materials with unique properties. Thus, zeolites are also commonly used in catalytic operations and catalysis which zeolites is often called “shape-selective catalysis”.

2.6 Structure of zeolite [5]

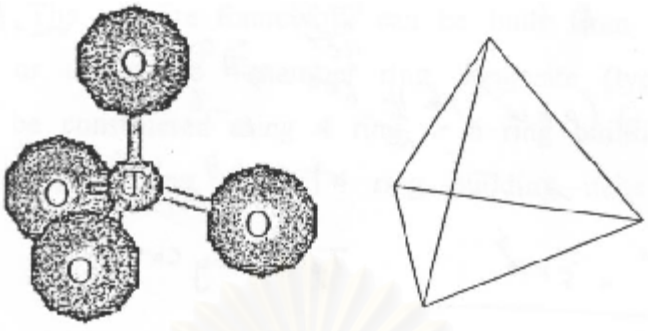


Figure 2.6 TO_4 tetrahedral (T = Si or Al) [5].

Zeolites are porous, crystalline aluminosilicate that develop uniform pore structure having minimum channel diameter of 0.1-0.3 nm. This size depends primarily upon the type of zeolite. Zeolites provide high activity and unusual selectivity in a variety of acid-catalyzed reactions. Most of the reactions are caused by the acidic nature of zeolites.

The structure of zeolite consists of a three-dimensional framework of SiO_4 or AlO_4 tetrahedra, each of which contains a silicon or aluminum atom in the center (Figure 2.6) [5]. The oxygen are shared between adjoining tetrahedra, which can be presented in various ratios and arranged in a variety of way. The framework thus obtained contains pores, channels, and cage, or interconnected voids.

A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. There are sixteen such building units, which can be used to describe all of known zeolite structures; for example, 4 (S4R), 6 (S6R), and 8 (S8R)-member single ring, 4-4 (D4R), 8-8 (D8R)-member double rings. The topologies of these units are shown in Figure 2.7 [6]. Also listed are the symbols used to describe them. Most zeolite framework can be generated from several different SBU's. Descriptions of known zeolite strutures based on their SBU's are list in Table 2.2 [3]. Both zeolite ZSM-5 and Ferrierite and described by their 5-1 building units. Offertile, zeolite L, Cancreinite, and Erionite are generated using only single 6-member rings. Some zeolite structures can be described by several building units. The sodalite framework can be built from either the single 6-member ring or the single 4-member ring. Faujasite (type X or type Y) and zeolite A can be constructed using 4 ring or 6 ring

building units. Zeolite A can also be formed using double 4 ring building units, whereas Faujasite can not be formed.

Zeolite may be represented by the general formula

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]wH_2O$$

M is an alkali or alkaline earth cation of n valence but if M is a proton, the zeolites becomes a strong Bronsted acid. As catalysts, zeolite are unique in their ability to discriminate between reactant molecular size and shape [7], y is a number between 2 and 10, and w is a number between 2 and 7. The principle cations are sodium, potassium, magnesium, calcium, strontium, and barium. The cations are loosely bound in the structure and may be exchanged, to varying degrees, by each other. The framework contain channels and interconnected voids occupied by cations and water molecules. Most zeolites can be reversibly dehydrated.

Molecular sieves are materials that, because of their internal structure, can selectively adsorb molecules according to their size and/or shape. All zeolites are molecular sieves, but not all molecular sieves are zeolites. Activated carbon, activated clay, alumina powder, and silica gels are examples of molecular sieves that are not zeolites.

Table 2.2 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 2.7 [3]

ZEOLITE	SECONDARY BUILDING UNITS								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4=1
Bikitaite								X	
Li-A (BW)	X	X	X						
Analcime	X	X							
Yagawaralite	X		X						
Episitbite								X	
ZSM-5								X	
ZSM-11								X	
Ferrierite								X	
Dachiardite								X	
Brewsterite	X								
Laumonite		X							
Mordenite								X	
Sodalite	X	X							
Henulandite									X
Stibite									X
Natrolite							X		
Thomsonite							X		
Edingtonite							X		
Cancrinite		X							
Zeolite L		X							
Mazzite	X								
Merlinoite	X		X			X			
Philipsite	X		X						
Zeolite Losod		X							
Erionite	X	X							
Paulingite	X								
Offretite		X							
TMA-E(AB)	X	X							
Gismondine	X		X						
Levyne		X							
ZK-5	X	X	X		X				
Chabazite	X	X			X				
Gmelinite	X	X	X		X				
Rho	X	X	X			X			
Type A	X	X	X	X					
Faujasite	X	X			X				

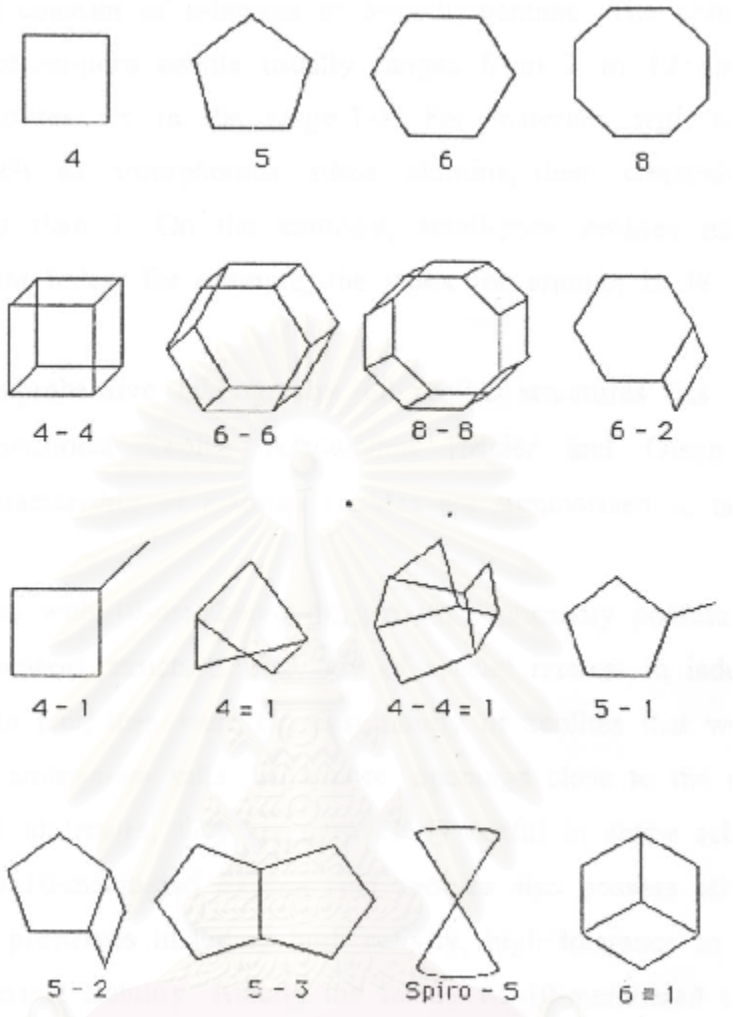


Figure 2.7 Secondary building units (SBU's) found in zeolite structures [6].

2.7 Zeolite active sites

2.7.1 Acid sites

Classical Bronsted and Lewis acid models of activity have been used to classify the active sites on zeolites. Bronsted acidity is proton donor acidity; a tridiagonally coordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [7, 8].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolites [9]. Since the numbers of acidic OH groups depend on the number of aluminum in zeolites framework, decrease in Al content is expected to reduce

catalytic activity of zeolite. If the effect of increasing in the acidic centers, increase in Al content, shall result in enhancement of catalytic acitivity.

Based on electrostatic consideration, the charge density at a cation site increases with increasing Si/Al ratio. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to difference in the order of aluminum in zeolite crystal – the location of Al in crystal structure [8].

An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxyl groups, which is parallel to that of Al content [7]. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites.

2.7.2 Generation of acid centers

Protonic acid centers of zeolite are generated in various ways. Figure 2.8 depics the thermal decomposition of ammonium-exchanged zeolites yielding the hydrogen form [3].

The Bronsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 2.9 [10].

$$M^{n+} + xH_2O \longrightarrow M(OH)_x^{(n-x)} + xH^+ \qquad (2.1)$$

The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very centers by hydrolysis phenomena.

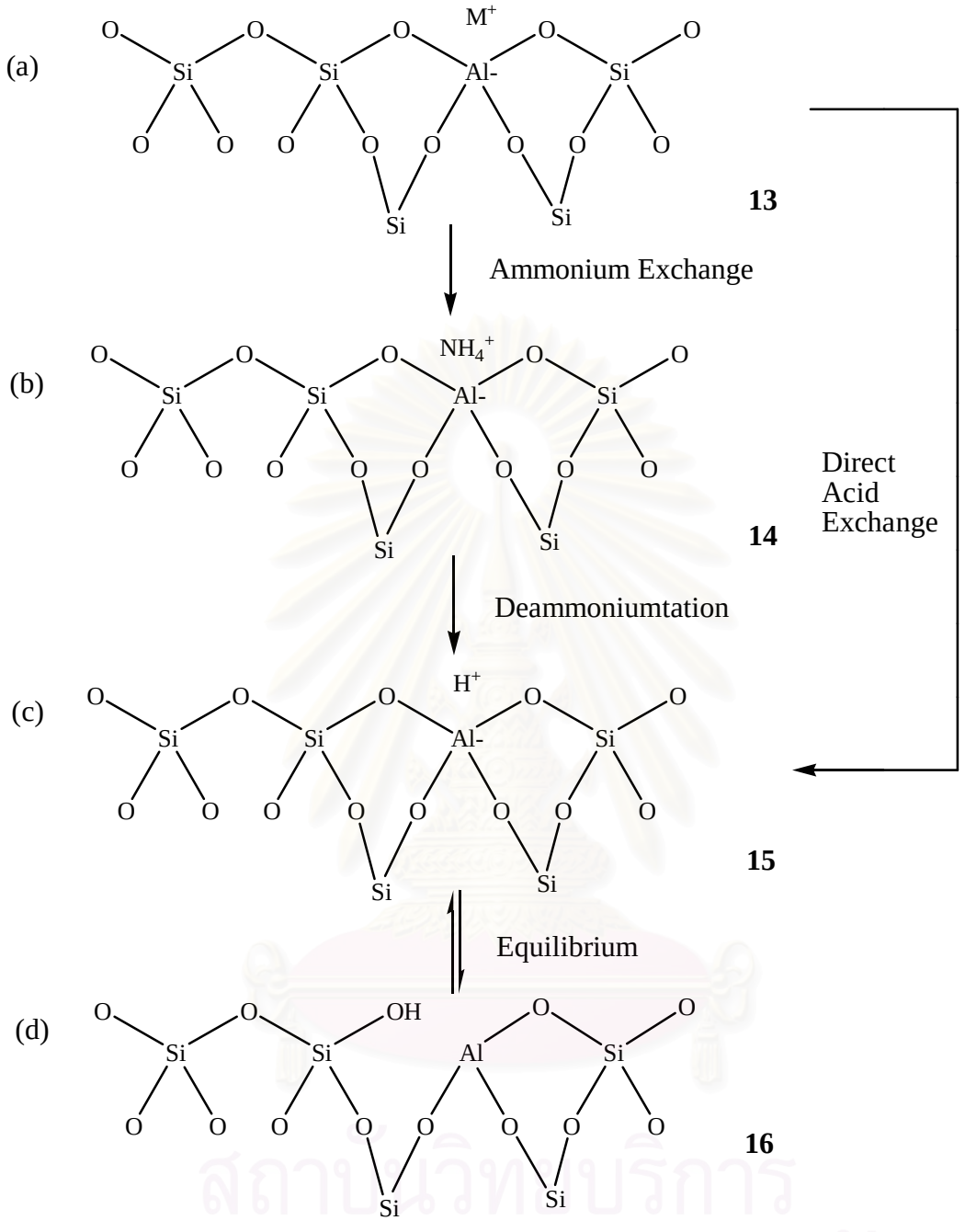


Figure 2.8 Diagram of the surface of a zeolite framework [3].

a) In the as-synthesis from M^+ is either an organic cation or an alkali metal cation

b) Ammonium in exchange produces the NH_4^+ exchanged form.

c) Thermal treatment is used to remove ammonia, producing the H^+, acid form.

d) The acid form in c) is in equilibrium with the form shown in d), where there is a silanol group adjacent to tricoordinate aluminum.

The formation of Lewis acidity from Bronsted acid sites is depicted in Figure 2.10 [3]. The dehydration reaction decreases the number of protons and increases that of Lewis sites. Bronsted (-OH) and Lewis (-Al-) sites can be present simultaneously in the structure of zeolite at high temperature. Dehydroxylation is thought to occure in ZSM-5 zeolite above 500 °C and calcinations at 800 to 900 °C produces irreversible dehydroxylation, which causes defection in crystal structure of zeolite.

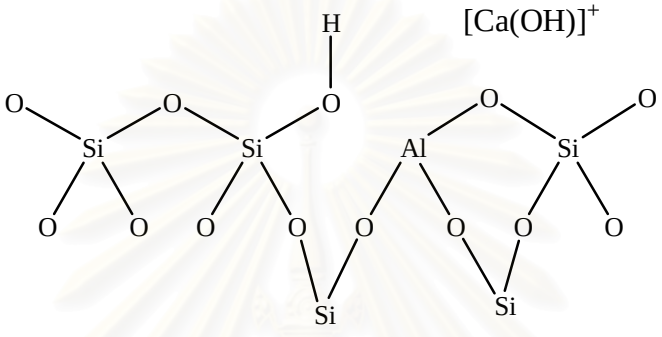


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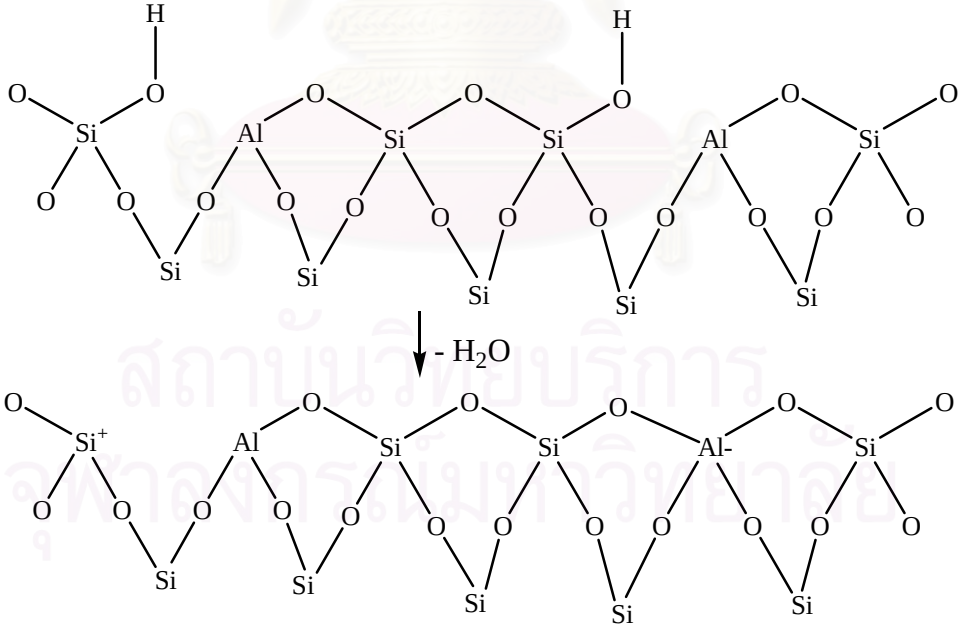
Figure 2.9 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity [10].



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18

Figure 2.10 Lewis acid site developed by dehydroxylation of Bronsted acid site [10].

Dealumination is believed to occur during dehydroxylation which may result from the steam generation within the sample. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in Figure 2.11 The extent of dealumination monotonously increases with the partial pressure of steam.

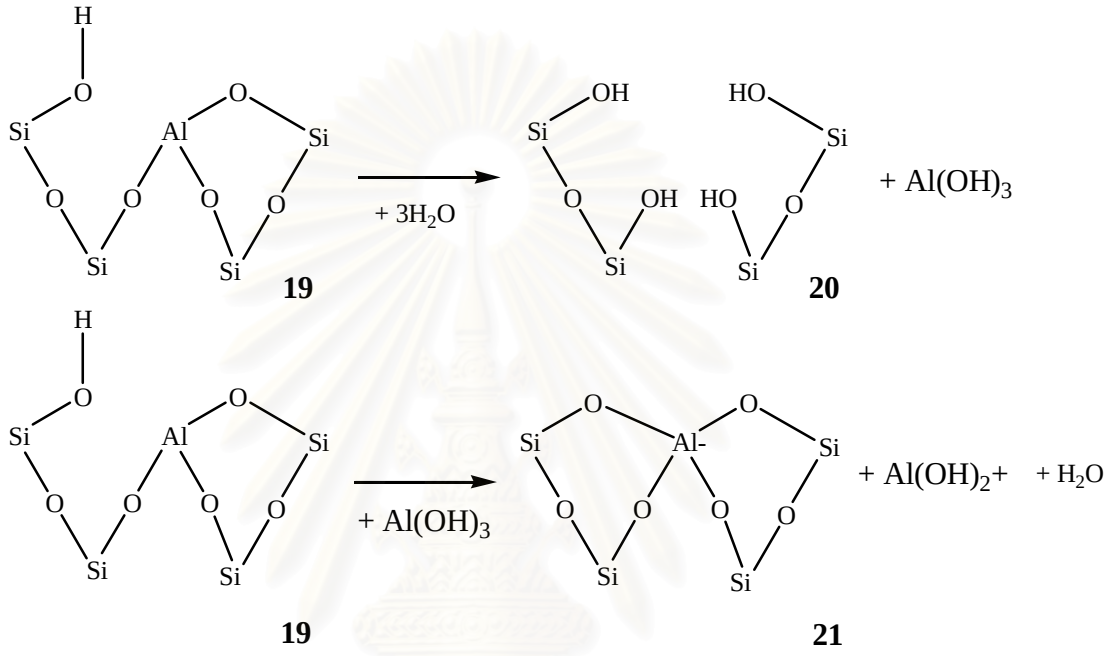


Figure 2.11 Steam dealumination process in zeolite [10].

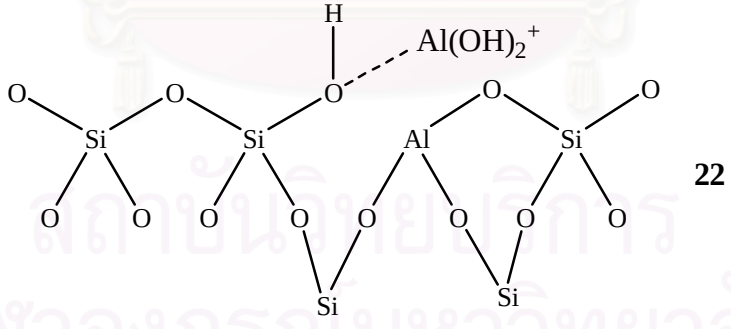


Figure 2.12 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [10].

The enhancement of the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites tentatively expressed in Figure 2.12 [11]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

2.7.3 Basic sites

In certain instances reaction have been shown to be catalyzed at basic (cation) site in zeolite without any influences from acid sites. The best-characterized example of this is the K-Y which splits n-hexane isomers at 500 °C. The potassium cation has been shown to control the unimolecular cracking (*b* - scission). Free radical mechanisms also contribute to surface catalytic reactions in these studies [3].

2.8 Shape selective [12]

Many reactions involving carbonium intermediates are catalyzed by acidic zeolites. With respect to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any other acidic oxides. That zeolite add is shape selectivity effect. The shape selectivity characteristics of zeolites influence their catalytic phenomena by three modes; reactants shape selectivity, products shape selectivity and transition states shape selectivity. These types of selectivity are illustrated in Figure 2.13 [3].

Reactants of charge selectivity results from the limited diffusibility of some the reactants, which can not effectively enter and diffuse inside crystal pore structures of the zeolites. Product shape selectivity occurs as slowly diffusing product molecules can not escape from the crystal and undergo secondary reactions. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect arising from local environment around the active site, the rate constant for a certain reaction mechanism is reduced of the shape required for formation of necessary transition state is restricted.

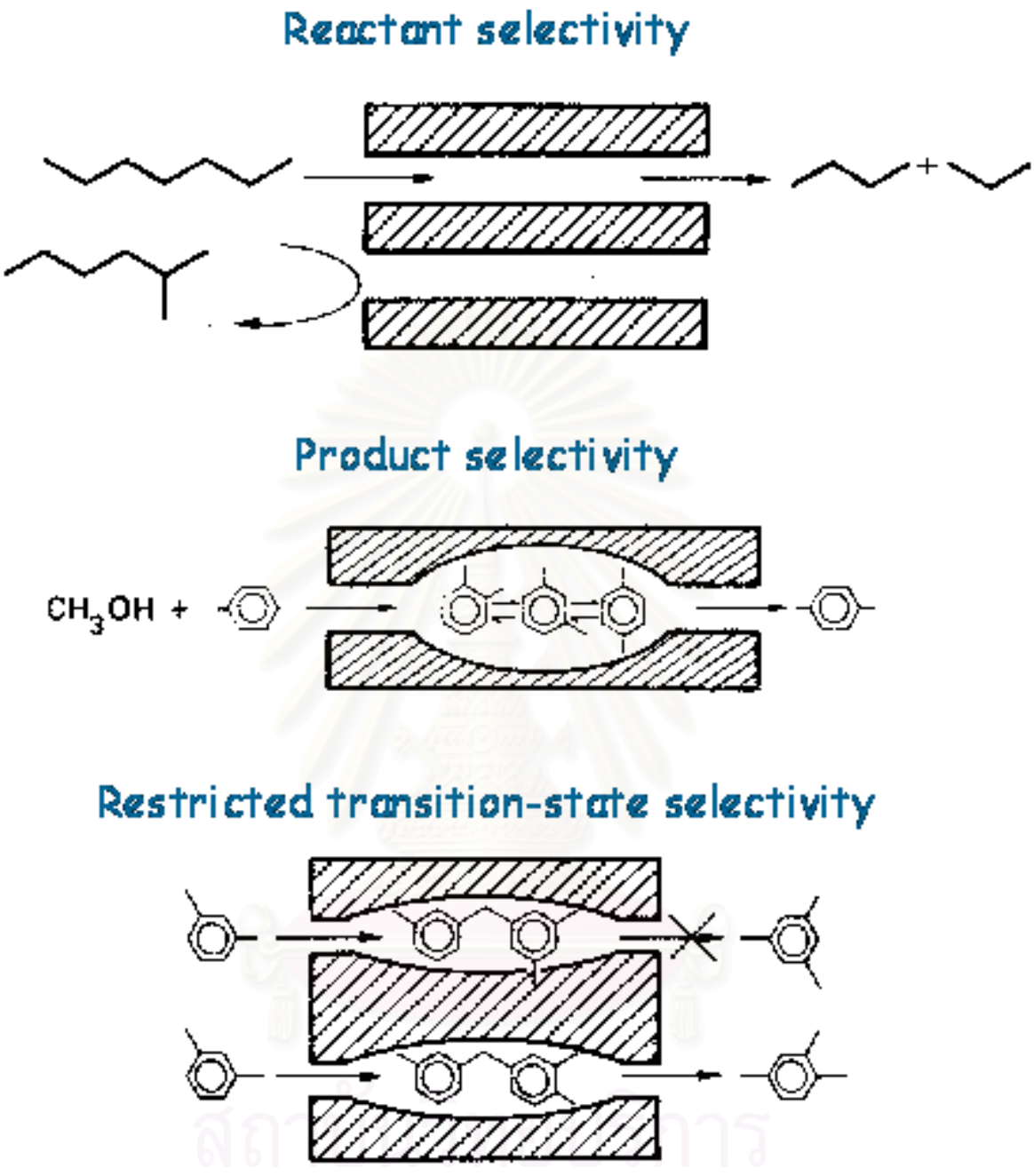


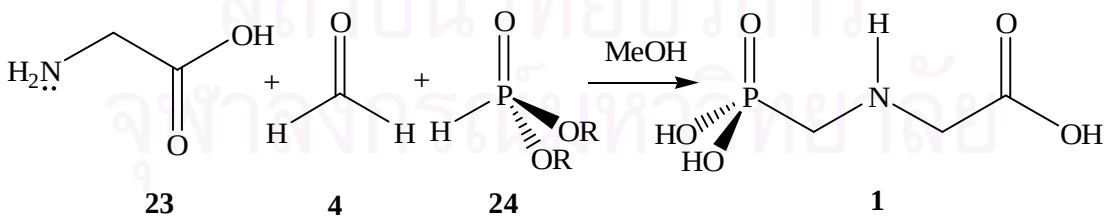
Figure 2.13 Diagram depicting the three type of selectivity [3].

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selectivity effects. However, molecules are deformable and can pass through openings, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

2.9 Related literature

In this section, special attention of related papers devoted directly to the synthesis of glyphosate. However, the other points which related to this reaction are also mentioned so that all information can contribute and lead to some interesting subjects concerned in this research.

Ehrat R. (1980), studied the preparation of *N*-phosphonomethylglycine from glycine, formaldehyde and a tertiary base in alcoholic solution. After completion of the reaction, a dialkylphosphite is added. The reaction product is acidified to a pH of 1.5 by means of concentrated hydrochloric acid. The *N*-phosphonomethylglycine begins to precipitate slowly, the mixture is filtered, washed with water and dried to give 98% pure white to yellowish crystals having a weight of 65 to 71 g. The yield calculated on the basis of glycine is about 38 to 42%. The yield calculated on the basis of diethylphosphite is about 57 to 64%.

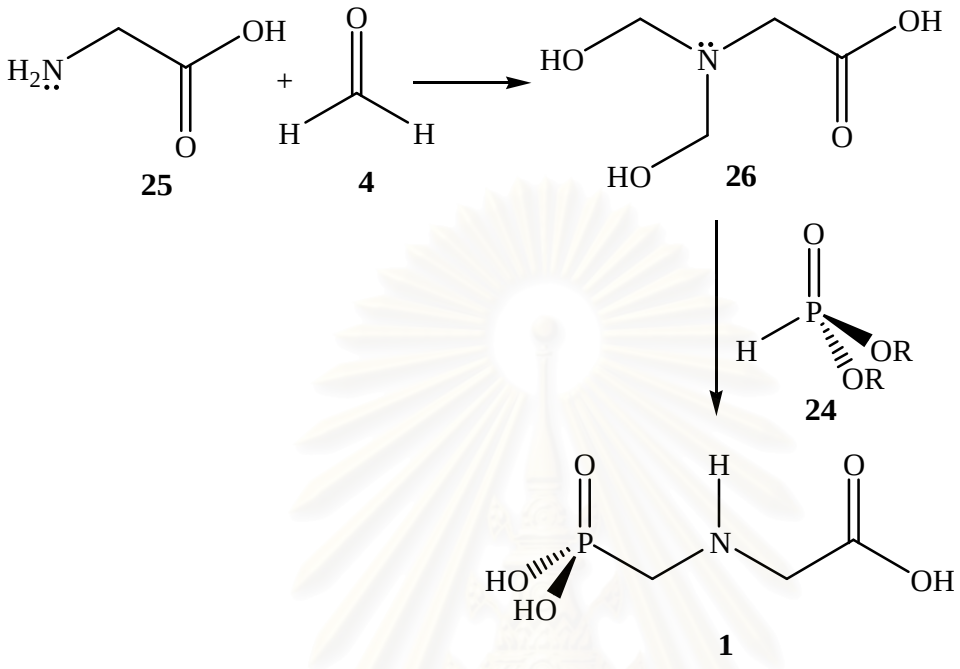


23 **4** **24** **1**

(2.2)

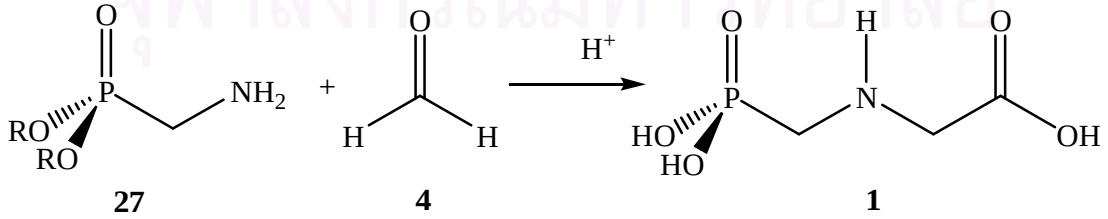
Brendel nee Hajnoczki, M., *et al.* (1984), studied the reaction of *N*-phosphonomethylglycine from glycine and *p*-formaldehyde to obtain *N,N*-bis-hydroxy-methylglycine as an intermediate product which was reacted with dialkyl

phosphate. Products was analyzed by NMR and HPLC, purity and yield related to glycine of *N*-phosphonomethylglycine are above 96% and 68.1% respectively.



(2.3)

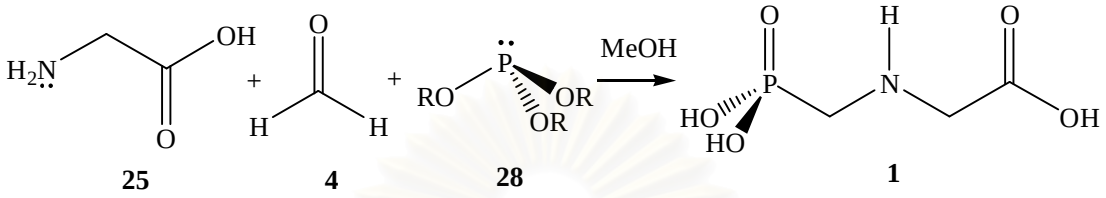
Felix, R. A. (1984), reported the preparation of *N*-phosphonomethylglycine by comprising : (a) reaction of *O,O*-dialkylaminomethylphosphonate and formaldehyde to produce triazine compound as intermediate; (b) reaction of the triazine formed in step (a) with an acyl cyanide to form the *O,O*-dialkyl-*N*-phosphonomethyl-*N*-cyanomethyl amide; and (c) hydrolyzation of the amide formed in step (b) to yield *N*-phosphonomethylglycine and structure was confirmed by ^{1}H NMR, IR and Mass spectroscopy in step by step.



(2.4)

Donadello, G. (1991), reported the preparation of *N*-phosphonomethylglycine from glycine and formaldehyde in aqueous-alcoholic solution, a base selected from

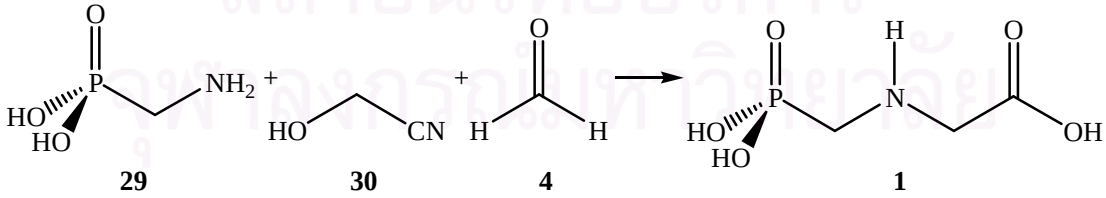
the group consisting of alkaline-earth metal hydroxides, the reaction of the solution thus obtained with trialkylphosphite and hydrolysis in an aqueous medium, with recovery the *N*-phosphonomethylglycine by crystallization and analyzed by HPLC. Molar ratio between glycine and formaldehyde, temperature and reaction time were investigated.



25 **4** **28** **1**

(2.5)

Miyata, H., *et al.* (1998), studied the method for producing *N*-phosphonomethylglycine which comprises reacting an aminomethylphosphonic acid with glycolonitrile, formaldehyde and hydrogen cyanide under an alkaline condition to convert the aminomethylphosphonic acid into a mixture of an *N*-phosphonomethylglycinonitrile salt and *N*-phosphonomethylglycinonitrile. The reaction solution was analyzed by HPLC and was found to contain 89 mmol of *N*-phosphonomethylglycine, the reaction yield bared on *N*-phosphonomethylglycinonitrile as a raw material was 89%. The product was hydrolyzed under an acidic condition. The *N*-phosphonomethylglycine was separated by filtration, washed with water and dried to obtain 11.2 g of a purified product. The purity of this product as determined by HPLC was 96%.

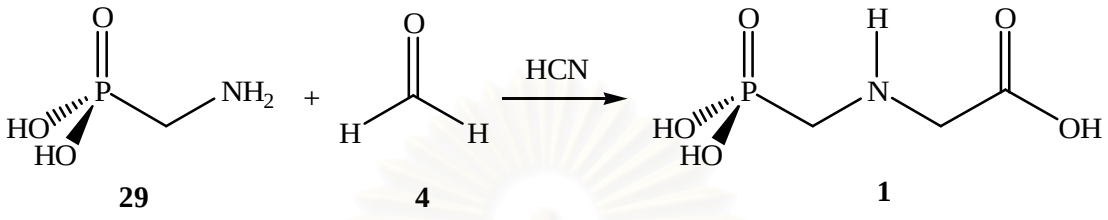


29 **30** **4** **1**

(2.6)

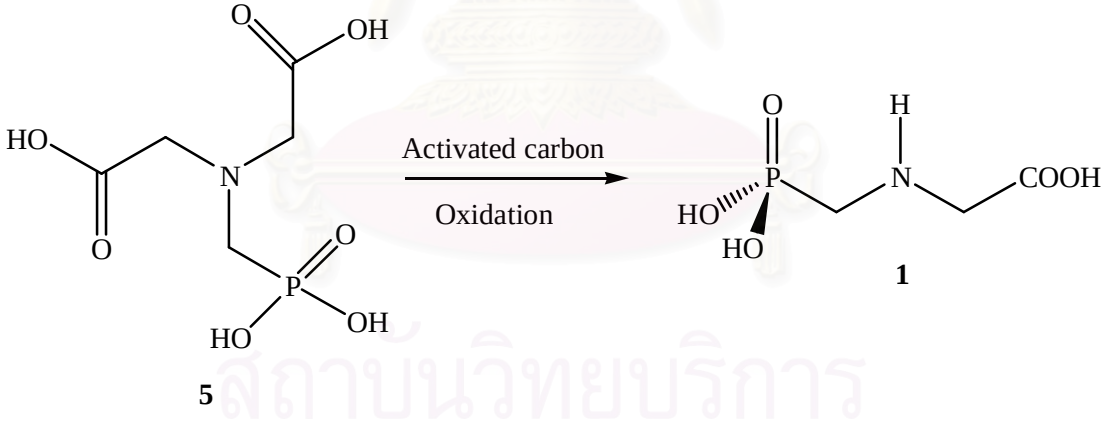
Worley, J. W., *et al.* (1999), studied the invention relates to a process for the preparation of *N*-phosphonomethylglycine and its salts. More particularly, this invention is directed to a method for preparing *N*-phosphonomethylglycine involving the reaction of aminomethylphosphonic acid, an alkali metal cyanide or hydrogen

cyanide, and formaldehyde and hydrolyzing the product of that reaction to form *N*-phosphonomethylglycine and its salts. The product mixture was assayed for glyphosate using HPLC. The isolated yield of *N*-phosphonomethylglycine was 85% with a purity of 99%.



(2.7)

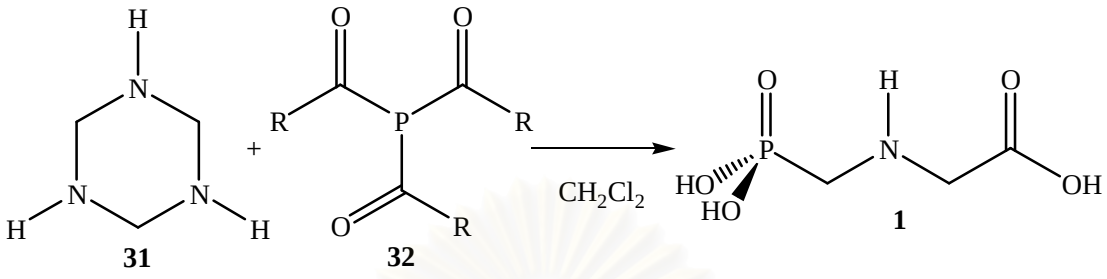
Pinel, C., *et al.* (1999), studied the oxidative decarboxylation reaction for the preparation of *N*-phosphonomethylglycine from *N*-phosphonomethyliminodiacetic acid (PMIDA) with various catalysts including activated carbon, carbon blacks and graphite as catalyst. The reaction depended on catalytic activity, the surface area of the catalyst.



(2.8)

Wulff, C., *et al.* (2006), studied the invention relates to a process for preparing N-phosphono-methylglycine by reacting a hexahydrotriazine compound with a triacyl phosphite in an organic solvent, hydrolyzing the resulting phosphono compound after prior extraction into an aqueous phase and separation from the organic phase. The reaction discharge was adjusted to pH=1.0 and the *N*-phosphonomethylglycine was filtered off and washed, the product were individually analyzed by P elemental

analysis, quantitative HPLC and ^{1}H NMR to obtain maximum yield at 85% of *N*-phosphonomethylglycine.



(2.9)

De Angelis, A., *et al.* (2004), studied the condensation reaction of ketones and aldehyde with aromatics (hydroxyalkylation) by using solid acid catalysts. In this paper, preparation of methylenedianiline (MDA) by using different types of zeolites : zeolite-beta, mordenite, ERB-1, ZSM-12, zeolite-Y and ZSM-5. The maximum productivity (260 g of MDA/g of zeolite) was obtained with mordenite because effective of pore size of zeolites.

Srinivas, N., *et al.* (2002), studied the shape-selective synthesis of collidines over modified zeolites. The number of water molecules per unit cell as estimated from the TG weight loss of the catalyst between 150 and 250 °C, showed that the Pb-, Mn- and La-ZSM-5 samples adsorbed a larger number of water molecules than the H-ZSM-5 sample, while the Fe-, Co- and Cu-ZSM-5 samples adsorbed a smaller number.

Ilao, M. C., *et al.* (1996), studied the methylamine synthesis from methanol and ammonia over small-pore zeolite catalysts. The types of zeolites were studied: faujasite (H-FAU), mordinite (H-MOR), ZSM-5 (H-MFI), ferrierite (H-FER) and chabazite (H-CHA). The temperature were varied from 573 to 673 K and then the products were investigated by IR spectroscopy, In many respects, comparison between big pore (Eley-Rideal in mordinite) and reaction in small pore (Langmuir-Hinshelwood in chabazite) was studied. The results showed that chabazite (H-CHA) catalyzed the reaction with higher selectivity to methylamine than others zeolite.

CHAPTER III

EXPERIMENTAL

3.1 Materials

The following materials were obtained from commercial suppliers.

Chemicals

- Cobalt(II) chloride, AR grade (Merck, Germany)
- Ethyl acetate, AR grade (Scharlau, United Kingdom)
- Formaldehyde 40% w/v, AR grade (Carlo erba, Italy)
- Glycine, AR grade (Fisher Chemical, Germany)
- Hydrochloric acid fuming 37% w/v, AR grade (Merck, Germany)
- Iminodiacetic acid, AR grade (Fluka, St. New York)
- Methanol 95% w/v, com. grade (J.T. Baker, St. New Jersey)
- Molecular sieves 3A, 4A, 5A, AR grade (Acros Organics, Belgium)
- *p*-Formaldehyde, com. grade (Riedel-dehaënag seelze, Gemany)
- Phosphorous acid 99% wt, AR grade (Aldrich, France)
- Sodium hydroxide, AR grade (Carlo erba, Italy)
- Sulfuric acid 96% w/v, AR grade (Merck, Germany)
- Triethylamine, AR grade (Fluka, St. New York)

3.2 Instruments and equipments

3.2.1 Fourier transform infrared spectrophotometer (FT-IR)

The FT-IR spectra were recorded on a Nicolet Impact 410 spectrophotometer. Spectra of solid samples were recorded as KBr pellets.

3.2.2 Nuclear magnetic resonance spectrometer (NMR)

The ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded at 400 and 200 MHz on Varian Mercury NMR spectrometer. Chemical shifts were expressed in part per million (ppm) using residual protonated solvents as reference. Sample (glyphosate) was prepared in salt form and weight into NMR tube using D_2O as a solvent.

3.2.3 X-ray fluorescence (XRF)

The X-ray fluorescence spectra were recorded on a wavelength dispersive X-ray fluorescence spectrometer, Philips PW2400 model.

3.2.4 Rotary evaporator

The products were dried by digital water bath (SB-100 model), diaphragm type dry vacuum pump (DTC-21 model), temperature controller (CCA-1110 model) and rotary evaporator (N-100 model) of Eyela.

3.2.5 Vacuum drying oven

The molecular sieves were dried by vacuum drying oven (D 41) from Yamato Scientific, Japan.

3.2.6 Digital camera

The pictures were recorded by digital camera of Sanyo, VPC-C6 model and digital camera of casio, EX-M1 model.

3.3 Procedure

3.3.1 Preparation of the acid treated molecular sieves [13]

Ten grams of molecular sieves were stirred with 100 ml 1 M HCl in 500 ml beaker at room temperature for 2-4 hours. The resulting white solid was washed by deionized water and dried at 100 °C. The solid catalysts were calcined prior to reaction at 200-400 °C for 2 hours prior to use.

3.3.2 Determination of molecular sieves properties

Acidity [14]

Acidity of molecular sieves was determined by volumetric titration. 0.2 g of the molecular sieve 3A, 4A or 5A, previously dried at 120 °C for 6 hours, was taken into a conical flask and then 15 ml of 0.1 N NaOH was added. After stirring the flask for 10 minutes, excess NaOH was titrated with 0.1 N HCl. Acidity was determined as milliequivalents of NaOH used per 100 g of molecular sieve.

$$\text{Acidity of molecular sieve (meq/100 g molecular sieve)} = \frac{(V1\text{-}V2) \times [HCl] \times 100}{\text{amount of molecular sieve}} \quad (3.1)$$

Where: V1 is the volume of NaOH, V2 is the volume of HCl and [HCl] is the HCl concentration.

Characterization of acid treated molecular sieves form 3A, 4A and 5A

The percentage of metals in the molecular sieves were characterized by X-ray fluorescence (XRF) spectroscopy (their composition and percentage were calculated by this instrument with the library search program).

3.3.3 Quantification of *N*-phosphonomethylglycine by proton NMR spectroscopy using sodium acetate as an internal standard [15]

A stock solution of sodium acetate (1 g) in deuterium oxide (20 ml) was prepared, *N*-phosphonomethylglycine salt was accurately weighed directly into each NMR tube (in Table 3.1); the quantity of standard stock solution was added in an amount calculated to give peak intensity of both peaks of interest (CH_3 of sodium acetate and CH_2-P of *N*-phosphonomethylglycine salt).

Table 3.1 Internal standard in each concentration

Weight of *N*-phosphonomethylglycine salt (mg)	Volume of sodium acetate solution from stock solution (ml)
5	0.5
10	0.5
25	0.5
50	0.5
100	0.5

Calculation of purity of N-phosphonomethylglycine

The purity of the analysis is calculated from equation (3.2), (3.3) and (3.4)

$$\% \text{ purity} = \frac{n_{anal} MW_{anal}}{w_{anal}} \times 100 \quad (3.2)$$

$$\frac{n_{anal}}{V_{sample}} = \frac{n_{std}}{V_{sample}} \frac{I_{anal}}{I_{std}} \frac{\rho_{std}}{\rho_{anal}} \quad (3.3)$$

$$n_{std} = \frac{w_{std} P_{std}}{MW_{std}} \quad (3.4)$$

Where anal is the analysis, std the internal standard reference material, n is the amount of substance, V is the volume used. Hence n/V is the concentration, the number of atom in the molecule that gives rise to the measured NMR peak, I is the integrated peak, P_{std} is the purity of the internal standard, w is the weight and MW is the molecular weight.

3.3.4 Preparation of *N*-phosphonomethylglycine

3.3.4.1 Preparation of *N*-phosphonomethylglycine by conventional method (modified from [16], [17])

***N*-(phosphonomethyl)iminodiacetic acid (6).** To an iminodiacetic acid **3** (11.7 g, 88 mmol) and phosphorous acid **4** (11.4 g, 139 mmol) were refluxed with 98% sulfuric acid (8.2 ml) in two-necked round bottom flask. After that, the mixture was heated to 110 °C and 40% w/v formaldehyde **5** (5.9 ml, 79 mmol) was added drop-wise over an one hour period. After another 2 hours at 110 °C, the mixture was cooled to room temperature. The mixture was filtered and the solid was washed with water to give a colorless solution, then the solution was concentrated by evaporation. A two-necked round bottom flask was charged with the concentrated solution, iminodiacetic acid **3** (13.1 g, 98 mmol) and phosphorous acid **4** (8.2 g, 100 mmol). The mixture was heated to 110 °C and 40% w/v formaldehyde **5** (5.2 ml, 69 mmol) was added drop-wise over one hour period. After another 2 hours at 110 °C, the mixture was cooled to room temperature. The mixture was filtered and the solid was washed with water to give a colorless solution, then the solution was concentrated by evaporation. A two-necked round bottom flask was charged with the concentrated solution, iminodiacetic acid **3** (13.1 g, 98 mmol), phosphorous acid **4** (8.2 g, 100 mmol) and 98% sulfuric acid (1.7 ml). The mixture was heated to 110 °C and 40% w/v formaldehyde **5** (5.2 ml, 69 mmol) was added drop-wise over one hour period. After another 2 hour at 110 °C, the mixture was cooled to room temperature. The mixture was filtered and the solid was washed with water to give 37.3 g of *N*-(phosphonomethyl)iminodiacetic acid **6** as a colorless solid, then the filtrate and washed solution were concentrated by evaporation. A two-necked round bottom flask was charged with the concentrated solution, iminodiacetic acid **3** (13.1 g, 98 mmol),

phosphorous acid **4** (8.2 g, 100 mmol), water (3 ml) and 98% sulfuric acid (1.7 ml). The mixture was heated to 110 °C and 40% w/v formaldehyde **5** (5.2 ml, 69 mmol) was added drop wise over one hour period. After another 2 hour at 110 °C the mixture was cooled to room temperature. The mixture was filtered and the solid was washed with water to give 47.9 g of *N*-(phosphonomethyl)iminodiacetic acid **6** as a colorless solid. The *N*-(phosphonomethyl)iminodiacetic acid **6** was obtained total 86.2 g (98% yield). ^{1}H NMR (D_2O) δ 3.57 (d, 2H, *J* = 16 Hz) and 3.91 (s, 2H); ^{13}C NMR (D_2O) δ 53, 55, 61 and 180.

***N*-phosphonomethylglycine (1).** *N*-(phosphonomethyl)iminodiacetic acid **6** (1.36 g, 100 mmol), $CoCl_2.6H_2O$ (71.3 mg, 50 mmol) and sodium hydroxide (0.8 g, 20 mmol) were added into a 100 ml two-necked round bottom flask. A vigorous stream of air was passed through the solution at 85 °C and stirred for 4 hours. After the reaction was completed, the mixture was allowed to separate by filtration to give a black solid (Cobalt). Then, the solution was concentrated on a vacuum rotary evaporator to give 0.78 g (75% yield) product as a colorless solid. ^{1}H NMR (D_2O) δ 2.38 (d, 2H, *J* = 16 Hz) and 3.02 (s, 2H); ^{13}C NMR (D_2O) δ 43, 47, 51 and 171.

3.3.4.2 Preparation of *N*-phosphonomethylglycine by direct condensation (modified from [18])

A) Effect of temperature : various reaction temperatures (30, 60, 70, 80, 100 and 120 °C) were studied for the temperature effect on preparation of *N*-phosphonomethylglycine from glycine using hydrochloric acid as catalyst and preparation of *N*-phosphonomethylglycine from glycine using the hydrochloric acid and acid treated molecular sieves 3A, 4A and 5A as catalyst to find the optimum reaction temperature in direct condensation.

Preparation of N-phosphonomethylglycine from glycine without acid treated molecular sieves and variation of reaction temperature

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux

condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture were refluxed at 30, 60, 70, 80, 100 and 120 °C for 2 hour. After the reaction was completed, the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** at 30, 60, 70, 80, 100 and 120 °C were 0, 15, 35, 21, 15 and 10%, respectively (phosphorous acid as a limiting reagent). ^{1}H NMR (D_2O) δ 2.26 (s, 3H), 2.60 (s), 2.82 (d, 2H, *J* = 14 Hz), 2.99 (d, 2H, *J* = 14 Hz), 3.20 (d, 2H, *J* = 14 Hz), 3.37 (s, 2H), 3.44 (d, 2H, *J* = 14 Hz) 3.56 (s, 2H) 3.72 (s, 2H), 3.91 (s, 2H) and 4.28 (s)

Preparation of N-phosphonomethylglycine from glycine with acid treated molecular sieves and variation of reaction temperature

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) and acid treated molecular sieve 3A (50 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture were refluxed at 30, 60, 70, 80, 100 and 120 °C for 2 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** at 30, 60, 70, 80, 100 and 120 °C were 0, 18, 28, 17, 10 and 10%, respectively (phosphorous acid as a limiting reagent).

B) Effect of time : the effect of times on direct condensation were studied at 1, 2, 3 and 4 hours for all of catalyst concentrations and without catalyst to obtain the optimum reaction time.

Preparation of N-phosphonomethylglycine from glycine without acid treated molecular sieves and variation of reaction time

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture was refluxed at 70 °C for 1, 2, 3 and 4 hour. After the reaction was completed, the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** for 1, 2, 3 and 4 hour were 16, 35, 16 and 14%, respectively (phosphorous acid as a limiting reagent).

Preparation of N-phosphonomethylglycine from glycine with acid treated molecular sieves and variation of reaction time

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) and acid treated molecular sieve 3A (50 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture was refluxed at 70 °C for 1, 2, 3 and 4 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** for 1, 2, 3 and 4 hour were 13, 28, 10 and 11%, respectively (phosphorous acid as a limiting reagent).

C) Effect of molar ratio of glycine and phosphorous acid : the effect of molar ratio of glycine and phosphorous acid on direct condensation were performed using 1:0.5, 1:1, 1:1.5 and 1:2 under the optimum temperature (70 °C) and time (2 hour) to find the optimum molar ratio between glycine and phosphorous acid of direct condensation.

Preparation of N-phosphonomethylglycine from glycine without acid treated molecular sieves

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (1.02, 2.05, 3.08 and 4.10 g (12, 25, 38 and 50 mmol)) was added and the mixture was refluxed at 70 °C for 2 hour. After the reaction was completed, the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** (1.02, 2.05, 3.08 and 4.10 g (12, 25, 38 and 50 mmol) of phosphorous acid **4**) were 19, 35, 11 and 7%, respectively (phosphorous acid as a limiting reagent).

Preparation of N-phosphonomethylglycine from glycine with acid treated molecular sieves

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) and acid treated molecular sieve 3A (50 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (1.02, 2.05, 3.08 and 4.10 g (12, 25, 38 and 50 mmol)) was added and the mixture was refluxed at 70 °C for 2 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary

evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** (1.02, 2.05, 3.08 and 4.10 g (12, 25, 38 and 50 mmol) of phosphorous acid **4**) were 39, 28, 18 and 6%, respectively (phosphorous acid as a limiting reagent).

D) Effect of molar ratio of glycine and formaldehyde : the effect of molar ratio of glycine and formaldehyde on direct condensation were performed using 1:1, 1:2 and 1:3 under the optimum temperature (70 °C), time (2 hour) and molar ratio between glycine and phosphorous acid (1:1) to find the optimum molar ratio between glycine and phosphorous acid of direct condensation.

Preparation of N-phosphonomethylglycine from glycine without acid treated molecular sieves

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (2, 4 and 6 ml (25, 50 and 75 mmol)) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture was refluxed at 70 °C for 2 hour. After the reaction was completed, the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analyzed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** (2, 4 and 6 ml (25, 50 and 75 mmol) of 40% w/w formaldehyde **5**) gave 20, 35 and 10%, respectively (phosphorous acid as a limiting reagent).

Preparation of N-phosphonomethylglycine from glycine with acid treated molecular sieves

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) and acid treated molecular sieve 3A (50 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved 40% w/w formaldehyde **5** (2, 4 and 6 ml (25, 50 and 75 mmol)) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture was refluxed at 70 °C for 2 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analysed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** (2, 4 and 6 ml (25, 50 and 75 mmol) of 40% w/w formaldehyde **5**) gave 14, 28 and 13.%, respectively (phosphorous acid as a limiting reagent).

E) Effect of type of catalyst : the effect of type of catalyst was studied using different catalyst (acid treated molecular sieve 3A, 4A and 5A). The experiment was done under the optimum reaction temperature (70 °C), time (2 hour), molar ratio between glycine and phosphorous acid (1:1) to find the most suitable type of catalyst.

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) and acid treated molecular sieve 3A, 4A and 5A (50 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved 40% w/w formaldehyde **5** (4 ml) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture was refluxed at 70 °C for 2 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analysed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** for acid treated molecular sieve 3A, 4A and 5A (50 mg) were 28, 16 and 14%, respectively (phosphorous acid as a limiting reagent).

F) Effect of content of catalyst : the effect of content of catalyst (acid treated of molecular sieve 3A) was studied using 2, 4, 8 and 12 g (per glycine 1 mole) under the optimum reaction temperature (70 °C), time (2 hours) and molar ratio between glycine and phosphorous acid (1:1) to find the optimum content of catalyst for direct condensation.

Glycine **29** (1.87 g, 25 mmol), 37% w/v hydrochloric acid (4 ml) and acid treated molecular sieve 3A (25, 50, 100 and 150 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture was refluxed at 70 °C for 2 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analysed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** for acid treated molecular sieve 3A (25, 50, 100 and 150 mg) were 17, 28, 14 and 11.6%, respectively (phosphorous acid as a limiting reagent).

G) Effect of type of acid : the effect of type of acid was studied using hydrochloric acid and sulfuric acid under the optimum reaction temperature (70 °C), time (2 hour), molar ratio between glycine and formaldehyde (1:2) and molar ratio between glycine and phosphorous acid (1:1) to find the optimum type of acid for direct condensation.

Preparation of N-phosphonomethylglycine from glycine without acid treated molecular sieves

Glycine **29** (1.87 g, 25 mmol), 98% w/v sulfuric acid (4 ml) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4**

(2.05 g, 25 mmol) was added and the mixture were refluxed at 70 °C for 2 hour. After the reaction was completed, the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analysed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** in 98% w/v sulfuric acid was 19% (phosphorous acid as a limiting reagent).

Preparation of N-phosphonomethylglycine from glycine with acid treated molecular sieves

Glycine **29** (1.87 g, 25 mmol), 98% w/v sulfuric acid (4 ml) and acid treated molecular sieve 3A (50 mg) were added to a 100 ml two-neck round bottom flask, equipped with thermometer and reflux condenser. When the mixture was completely dissolved, 40% w/w formaldehyde **5** (4 ml, 50 mmol) was added into a two-neck round bottom flask, then phosphorous acid **4** (2.05 g, 25 mmol) was added and the mixture were refluxed at 70 °C for 2 hour. After the reaction was completed, the solid (acid treated molecular sieve) was separated by filter and the mixture solution was concentrated using a vacuum rotary evaporator to give the crude product. The crude product was investigated and analysed for quantitative determination using sodium acetate as an internal standard by proton nuclear magnetic resonance technique. The yield of *N*-phosphonomethylglycine **1** in 98% w/v sulfuric acid and acid treated molecular sieve 3A was 8% (phosphorous acid as a limiting reagent).

3.4 Characterization and quantitative analysis of sample

The synthetic samples were characterized and determined quantitative analysis by NMR spectroscopic technique. Quantitative analysis was studied using peak intensity of the reactant, the product and internal standard.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Determination of molecular sieve properties [11]

The difference in properties of acid treated molecular sieves 3A, 4A, 5A in terms of acidity and structure of the molecular sieve samples were determined.

4.1.1 Acidity characterization

Figure 4.1 shows the total acidity of molecular sieve, determined by sodium hydroxide titrations and expressed in milliequivalent of NaOH used per 100 g of molecular sieve. Molecular sieve 3A after acid activation exhibited the maximum acidity (137 meq/100 g) followed by molecular sieve 4A (115 meq/100 g) and molecular sieve 5A (108 meq/100 g), respectively.

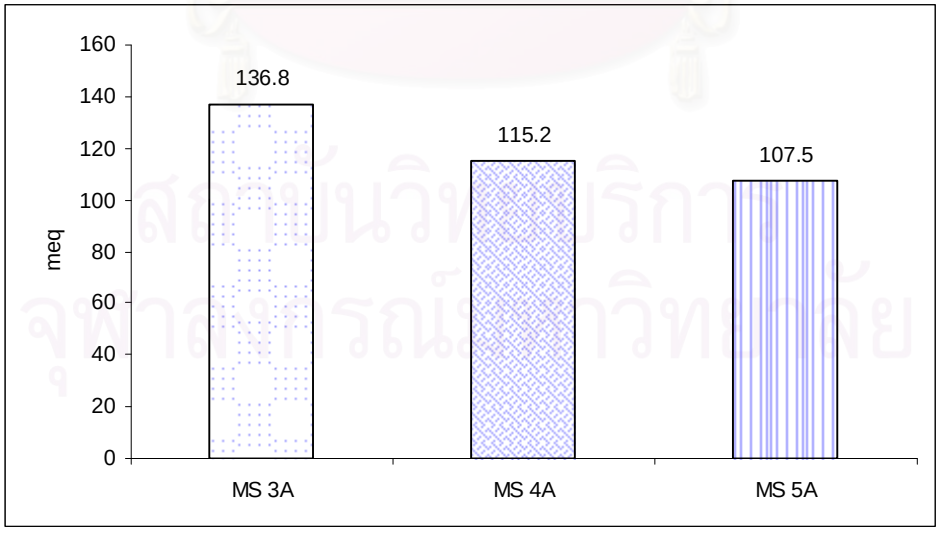


Figure 4.1 Acidity of molecular sieve 3A, 4A and 5A (meq/100 g).

4.1.2 Characterization of acid treated molecular sieves 3A, 4A and 5A

Molecular sieve 3A, 4A and 5A were subjected to cation exchanged with HCl to produce acid treated molecular sieve 3A, 4A and 5A. The reaction is shown as equation 4.1.

$$\text{Na, K, Ca/Molecular sieve (s)} + \text{HCl (aq)} \longrightarrow \text{H/Molecular sieve (s)} + \text{Metal chloride (aq)} \quad \text{....(4.1)}$$

The acid treated molecular sieves were then measured for the elemental concentration by XRF technique. The results of elemental analysis of molecular sieve 3A, 4A and 5A are shown in Table 4.1, Table 4.2 and Table 4.3, respectively.

Table 4.1 Comparison between concentration (%) of molecular sieve 3A and acid treated molecular sieve 3A

Element	Compound	Molecular sieve 3A (%)	Acid treated molecular sieve 3A (%)	% Remain
Na	Na_2O	10.95	2.48	22.64
Al	Al_2O_3	31.46	26.35	-
Si	SiO_2	46.26	51.47	-
Cl	Cl	-	15.45	-
K	K_2O	10.23	0.69	6.74
Ca	CaO	0.88	0.53	60.23
	Other	0.22	3.03	-

Table 4.2 Comparison between concentration (%) of molecular sieve 4A and acid treated molecular sieve 4A

Element	Compound	Molecular sieve 4A (%)	Acid treated molecular sieve 4A (%)	% Remain
Na	Na_2O	22.02	4.54	20.62
Al	Al_2O_3	31.61	27.61	-
Si	SiO_2	46.07	57.40	-
Cl	Cl	-	10.30	-
K	K_2O	0.11	0.04	36.36
Ca	CaO	0.16	0.05	31.25
	Other	0.03	0.06	-

Table 4.3 Comparison between concentration (%) of molecular sieve 5A and acid treated molecular sieve 5A

Element	Compound	Molecular sieve 5A (%)	Acid treated molecular sieve 5A (%)	% Remain
Na	Na_2O	11.48	3.93	34.23
Al	Al_2O_3	31.59	27.30	-
Si	SiO_2	46.17	48.23	-
Cl	Cl	-	18	-
K	K_2O	0.23	0.19	82.61
Ca	CaO	10.45	4.32	41.34
	Other	0.08	0.03	-

The results in Table 4.1, 4.2 and 4.3 showed that the concentration of exchanged sodium of molecular sieve 4A was higher than that of molecular sieve 3A and 5A because % remaining sodium in molecular sieve 4A was lower than that in molecular sieve 3A and 5A. However, the concentration of exchanged potassium of molecular sieve 3A was higher than that of molecular sieve 4A because % remaining in potassium of molecular sieve 4A was lower than that in molecular sieve 3A.

Table 4.4 Comparison between % replacements of elements (Na, K, Ca) of acid treated molecular sieve 3A, 4A and 5A

Element	Concentration of molecular sieve (g/100 g of total element)			% Replacements		
	3A	4A	5A	3A	4A	5A
Na	11.48	22.02	11.48	77.36	79.38	65.77
K	10.23	0.11	0.23	93.26	63.64	17.39
Ca	0.88	0.16	10.45	39.77	68.75	58.66

The results in Table 4.4 showed % replacement of hydrogen ion was increased in a series of acid treated molecular sieve 5A > 4A > 3A, the cation exchange efficiency was increased in a series of acid treated molecular sieve 5A < 4A < 3A as well. Finally, % replacements of molecular sieve 3A, 4A and 5A complied with acidity of molecular sieve 3A, 4A and 5A, so the optimum acid treated molecular sieve was molecular sieve 3A which was used for various direct condensations in synthesis part.

4.2 Preparation of *N*-phosphonomethylglycine

4.2.1 Preparation of *N*-phosphonomethylglycine by conventional method

4.2.1.1 Preparation of *N*-(phosphonomethyl)iminodiacetic acid from iminodiacetic acid with recycle of the filtrate using sulfuric acid as a catalyst [modified from (16)]

N-(phosphonomethyl)iminodiacetic acid **6** could be prepared from condensation of compound **3** with formaldehyde **5** (Figure 4.2) to give intermediate **22**, then the hydrogen ion was protonated at oxygen atom of alcohol **23** and lose of water formed intermediate **24**. The reaction between intermediate **25** and phosphorous acid **26** using concentrated sulfuric acid as a catalyst gave **6** as the final product. The crystallization was done in the acid condition, the product obtained was colorless solid in 98% yield (iminodiacetic acid as a limiting reagent).

N-(phosphonomethyl)iminodiacetic acid **6** was characterized by ^{1}H NMR, chemical shift of *N*-(phosphonomethyl)iminodiacetic acid at 3.57 (d, J = 16 Hz) and 3.91 (s) ppm (Figure B3) were assigned for CH_2-P and C$\underline{H}_2$-COOH. The spectrum of ^{13}C NMR, chemical shift of *N*-(phosphonomethyl)iminodiacetic acid at 53 (d), 61 (s) and 180 (s) ppm (Figure B4) were assigned for CH_2-P, $\underline{C}H_2$-COOH and COOH, respectively.

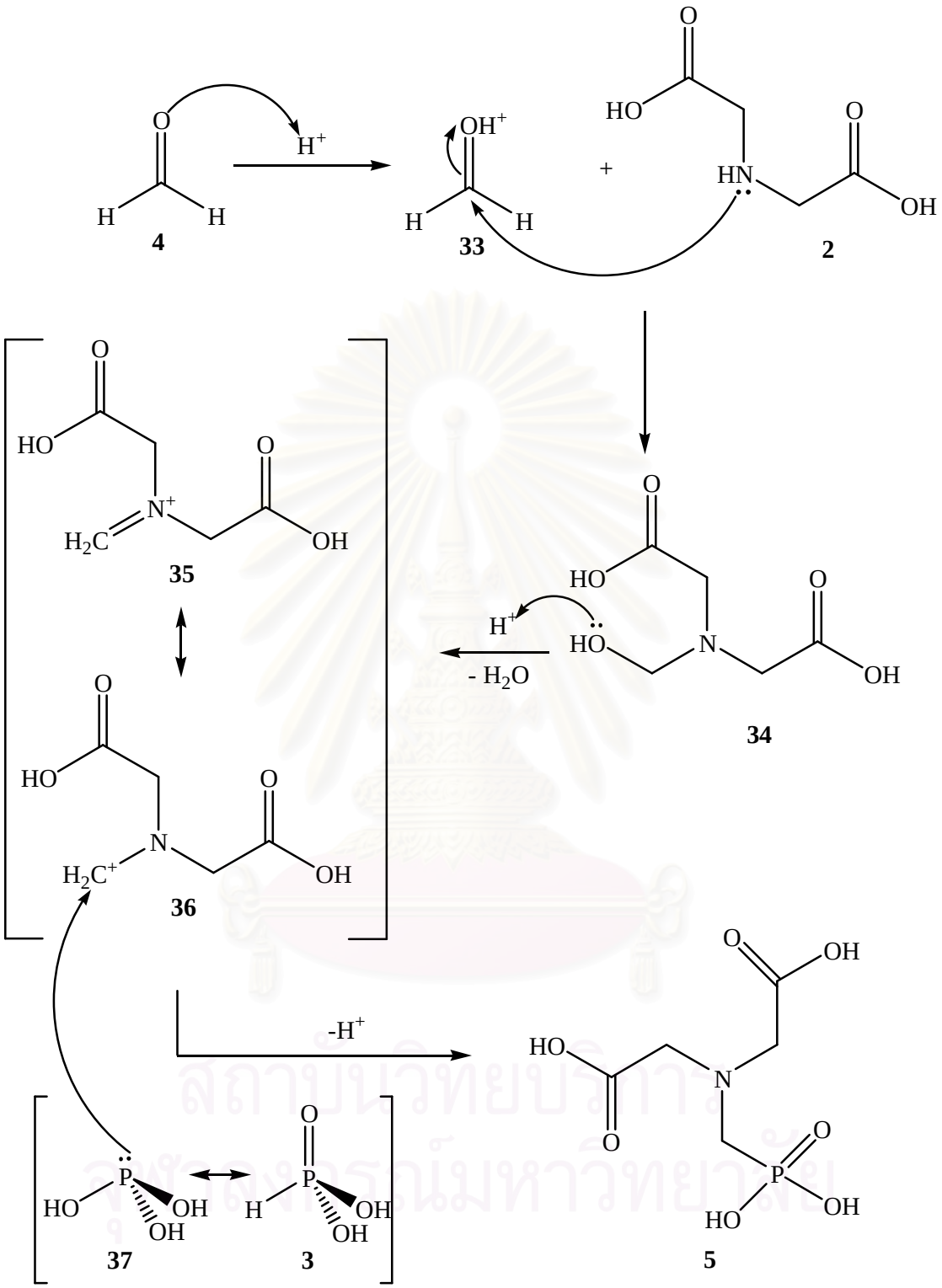


Figure 4.2 Synthesis of *N*-(phosphonomethyl)iminodiacetic acid from iminodiacetic acid and formaldehyde using sulfuric acid as a catalyst.

4.2.1.2 Preparation of *N*-phosphonomethylglycine from *N*-(phosphonomethyl) iminodiacetic acid by oxidative decarboxylation using cobalt(II) as a catalyst [17]

N-phosphonomethylglycine **1** was prepared from oxidative decarboxylation of *N*-(phosphonomethyl)iminodiacetic acid **6** using cobalt(II) ion as a catalyst. The product was obtained as colorless solid in 75% yield.

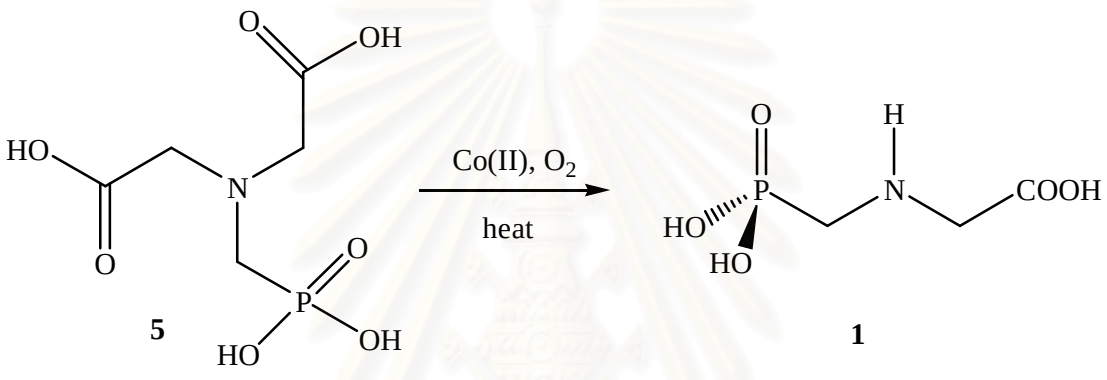


Figure 4.3 Synthesis of *N*-phosphonomethylglycine from *N*-(phosphonomethyl) iminodiacetic acid.

N-phosphonomethylglycine **1** was characterized by ^{1}H NMR, chemical shifts at 2.38 (d, J = 16 Hz) and 3.02 (s) ppm (Figure B1) were assigned for CH_2-P and $C\underline{H}_2$-COOH. The spectrum of ^{13}C NMR showed chemical shift of glyphosate at 43 (d), 51 (s) and 171 (s) ppm (Figure B2) which were assigned for CH_2-P, $\underline{C}H_2$-COOH and COOH respectively. In addition, the conversion of iminodiacetic acid to glyphosate was found to be 68% overall yield (phosphorous acid as a limiting reagent).

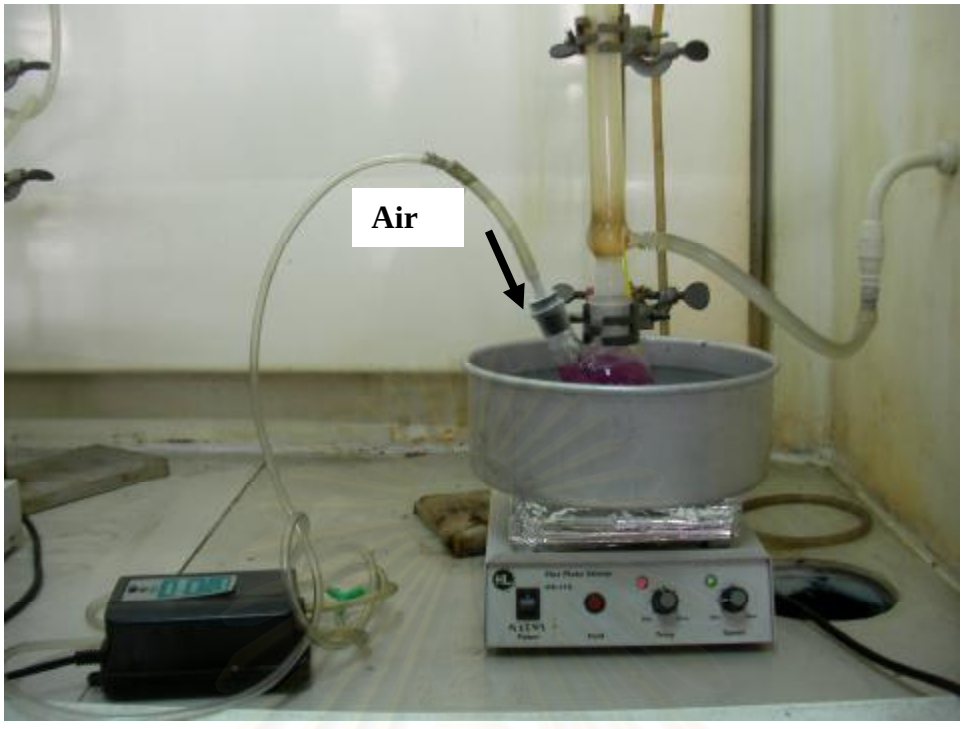


Figure 4.4 The oxidative decarboxylation system.

4.2.2 Preparation of *N*-phosphonomethylglycine by direct condensation

4.2.2.1 Preparation of *N*-phosphonomethylglycine from glycine with recycle of the filtrate using hydrochloric acid as a catalyst [modified from (18)]

N-phosphonomethylglycine could be prepared from glycine, formaldehyde and phosphorous acid using 37% w/v hydrochloric acid as a catalyst. The product was obtained as yellow liquid. The product mixture was characterized by ^{1}H NMR technique and the result is shown in Figure 4.5.

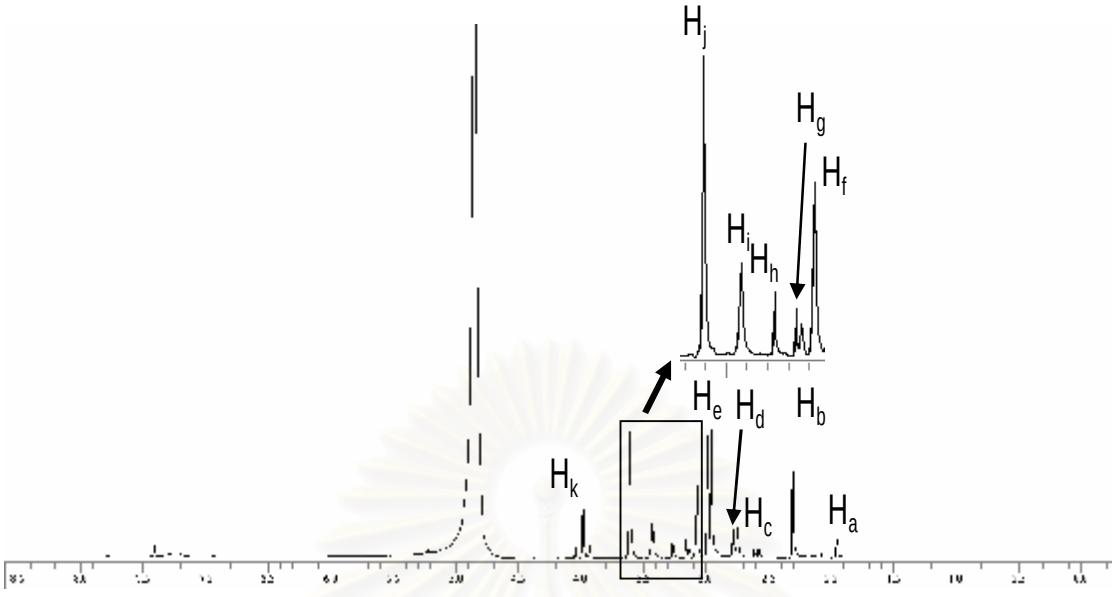
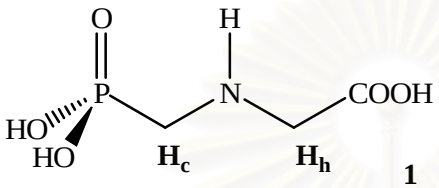
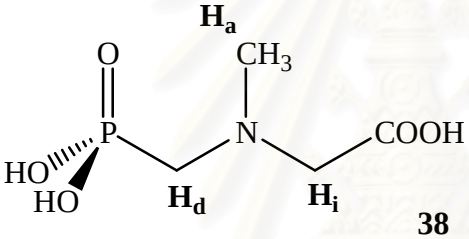
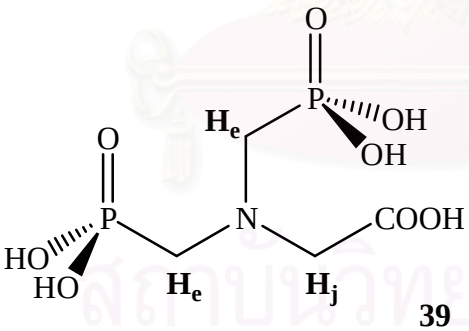
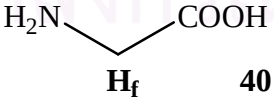
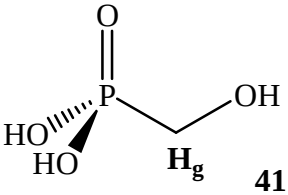


Figure 4.5 ^{1}H NMR spectrum of the product mixture from direct condensation (without molecular sieve).

The peak of H_a, H_d and H_i have integrated peak ratio as 3, 2 and 2, respectively. The chemical shift of H_a, H_d and H_i at 1.96 (s), 2.75 (d, J = 14 Hz) and 3.43 (s) ppm were assigned for CH_3-N, CH_2-P and C$\underline{H}_2$-COOH, respectively, which belonged to *N*-(methyl)phosphonomethylglycine (see the structure **27** in Table 4.5). The peak of H_c and H_h have integrated peak ratio as 1 and 1. The chemical shift of H_c and H_h at 2.58 (d, J = 14 Hz) and 3.27 (s) ppm were assigned for CH_2-P and C$\underline{H}_2$-COOH, which could be *N*-phosphonomethylglycine **1**. The peak of H_e and H_j have integrated peak ratio as 2 and 1 (or 4 and 2). The chemical shift of H_c and H_h at 2.96 (d, J = 14 Hz) and 3.61 (s) ppm were assigned for CH_2-P and C$\underline{H}_2$-COOH, which could be *N*,*N*-di(phosphonomethyl)glycine **28** (Table 4.5). The chemical shift of H_f at 3.08 (s) ppm was assigned for C$\underline{H}_2$-COOH, which could be glycine **29** (Table 4.5). Finally, the chemical shift of H_g at 3.14 (d, J = 14 Hz) ppm was assigned for CH_2-P, which could be phosphonomethyl alcohol **30** (Table 4.5). The direct condensation of glycine, formaldehyde and phosphorous acid produced five products. Their mechanisms were proposed as shown in Figure 4.6.

Table 4.5 The assignments of ^{1}H NMR spectrum of the product mixture from direct condensation

Structure of mixture compounds in product	Chemical shift (δ, ppm)
 **1**	2.58, 2.61 (H_c, J = 14 Hz) 3.27 (H_h)
 **38**	1.96 (H_a) 2.75, 2.78 (H_d, J = 14 Hz) 3.43 (H_i)
 **39**	2.96, 2.99 (H_e, J = 14 Hz) 3.61 (H_j)
 **40**	3.08 (H_f)
 **41**	3.14, 3.17 (H_g, J = 14 Hz)

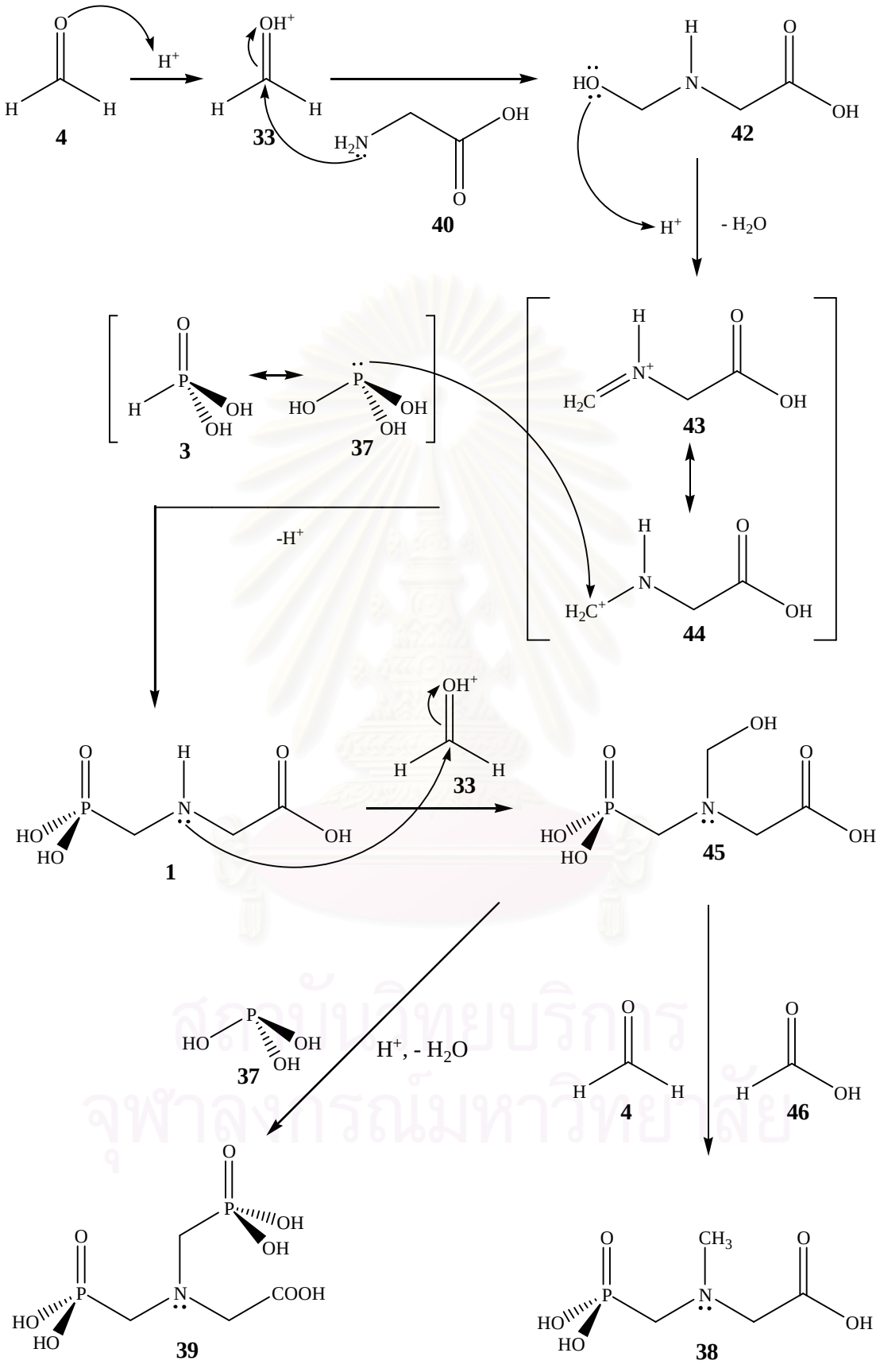


Figure 4.6 Mechanism of direct condensation of glycine, formaldehyde and phosphorous acid.

Effect of reaction temperature

The effect of reaction temperature on direct condensation of glycine, formaldehyde and phosphorous acid was varied from 30, 60, 70, 80, 100 and 120 °C for 2 hour, mole ratio between glycine with phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 using 37% w/v hydrochloric acid. The results indicated that increasing the reaction temperature from 60 to 70 °C also increased the *N*-phosphonomethylglycine product because the energy of reactants was increased to react. However, the use of high reaction temperature from 70 to 120 °C led to the decrease of *N*-phosphonomethylglycine product because the energy of reactants was increased to be overmuch react, gave *N*,*N*-di(phosphonomethyl)glycine is a main product. Another reason, the high reaction temperature could cause formaldehyde to lose and the low temperature was not enough to form *N*-phosphonomethylglycine (Figure 4.7). Thus, reaction temperature at 70 °C gave the maximum yield as 35% yield.

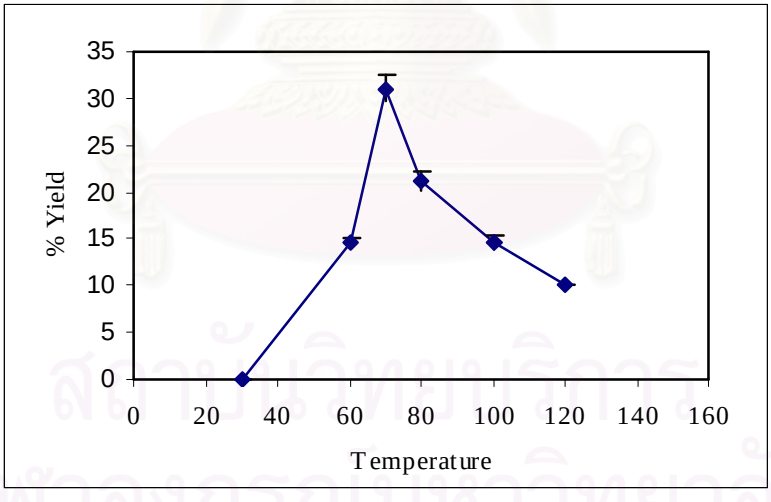


Figure 4.7 Effect of temperature on % yield of *N*-phosphonomethylglycine for 2 hour, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 and 37% w/v hydrochloric acid.

Effect of the reaction time

The effect of reaction time on direct condensation of glycine, formaldehyde and phosphorous acid was varied for 1, 2, 3 and 4 hour at 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 using 37% w/v hydrochloric acid. The results indicated that the maximum yield of *N*-phosphonomethylglycine was reached within 2 hour, (Figure 4.8). The reason of effect of the reaction time was explained by same as effect of the reaction temperature.

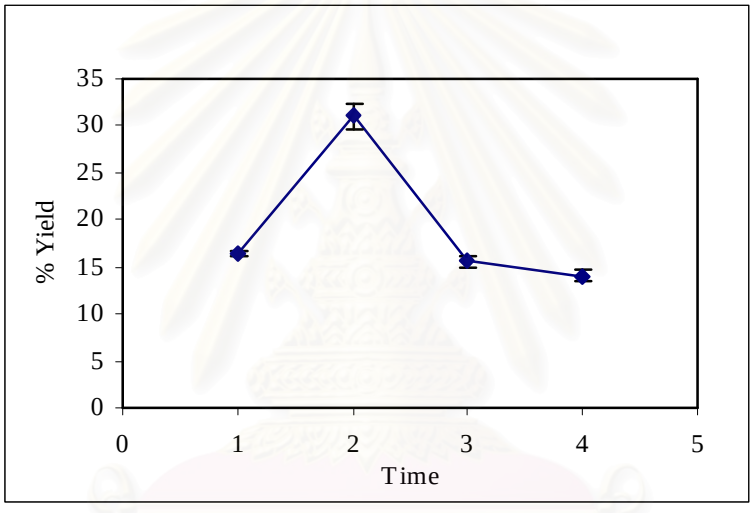


Figure 4.8 Effect of reaction time on % yield of *N*-phosphonomethylglycine at 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 and 37% w/v hydrochloric acid.

Effect of mole ratio between glycine and phosphorous acid

The effect of mole ratio between glycine and phosphorous acid on direct condensation of glycine, formaldehyde and phosphorous acid was varied from 1:0.5, 1:1, 1:1.5 and 1:2 for 2 hour, 70 °C, mole ratio between glycine and formaldehyde as 1:2 using 37% w/v hydrochloric acid. The results indicated that at mole ratio between glycine and phosphorous acid as 1:1 gave the maximum yield of *N*-

phosphonomethylglycine as 35% (Figure 4.9). Also, the use of quantitative phosphorous acid was slighted to produce glyphosate but the use of quantitative increase of phosphorous acid was gave to produce *N*,*N*-di(phosphonomethyl)glycine is a main product.

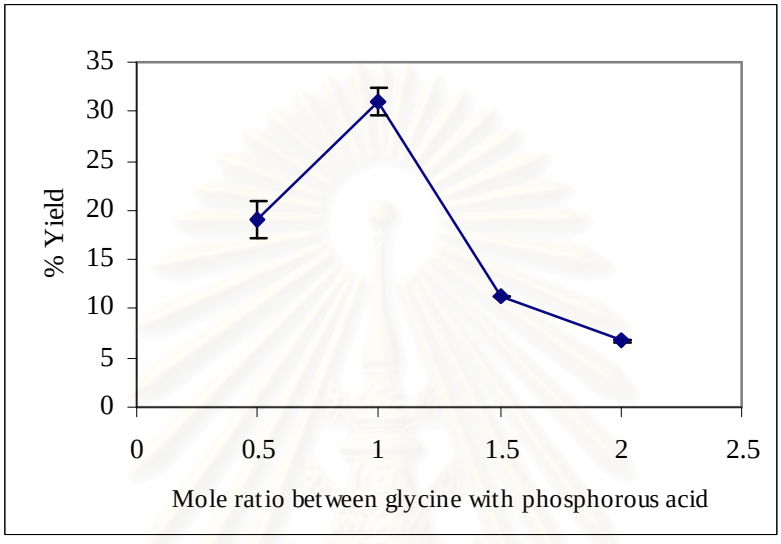


Figure 4.9 Effect of mole ratio between glycine and phosphorous acid on % yield of *N*-phosphonomethylglycine for 2 hour, 70 °C, mole ratio between glycine and formaldehyde as 1:2 and 37% w/v hydrochloric acid.

Effect of mole ratio between glycine and formaldehyde

The effect of mole ratio between glycine and formaldehyde on direct condensation of glycine, formaldehyde and phosphorous acid was varied from 1:1, 1:2 and 1:3 for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid as 1:1 using 37% w/v hydrochloric acid. The result indicated that at mole ratio between glycine and formaldehyde as 1:2 gave the maximum yield of *N*-phosphonomethylglycine as 35% (Figure 4.10). Also, the use of quantitative formaldehyde was slighted to produce glyphosate but the use of quantitative increase of formaldehyde was gave to produce *N*,*N*-di(phosphonomethyl)glycine is a main product.

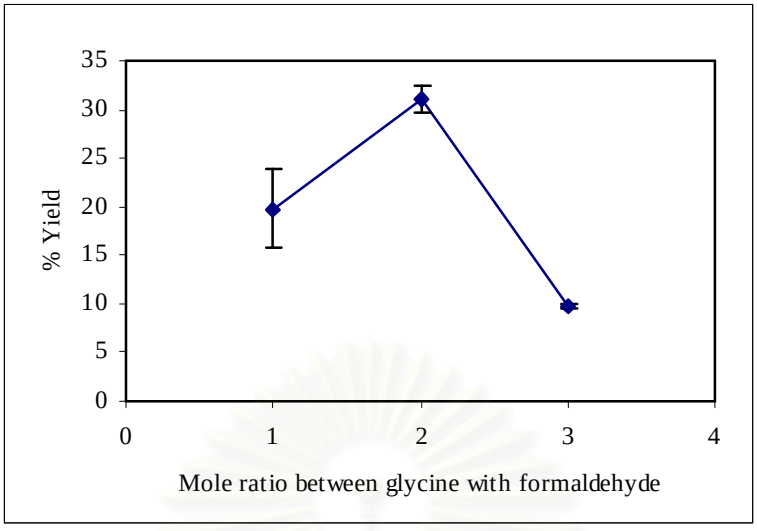


Figure 4.10 Effect of mole ratio between glycine and formaldehyde on % yield of *N*-phosphonomethylglycine for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid as 1:1 and 37% w/v hydrochloric acid.

4.2.2.2 Preparation of *N*-phosphonomethylglycine from glycine using hydrochloric acid and acid treated molecular sieves 3A, 4A and 5A as catalysts

N-phosphonomethylglycine could be prepared from glycine, formaldehyde and phosphorous acid using 37% w/v hydrochloric acid and acid treated molecular sieves as catalysts. The product was obtained as yellow liquid. The product mixture was characterized by ^{1}H NMR technique and used sodium acetate as an internal standard for quantitative determination. The results are shown in Figure 4.11.

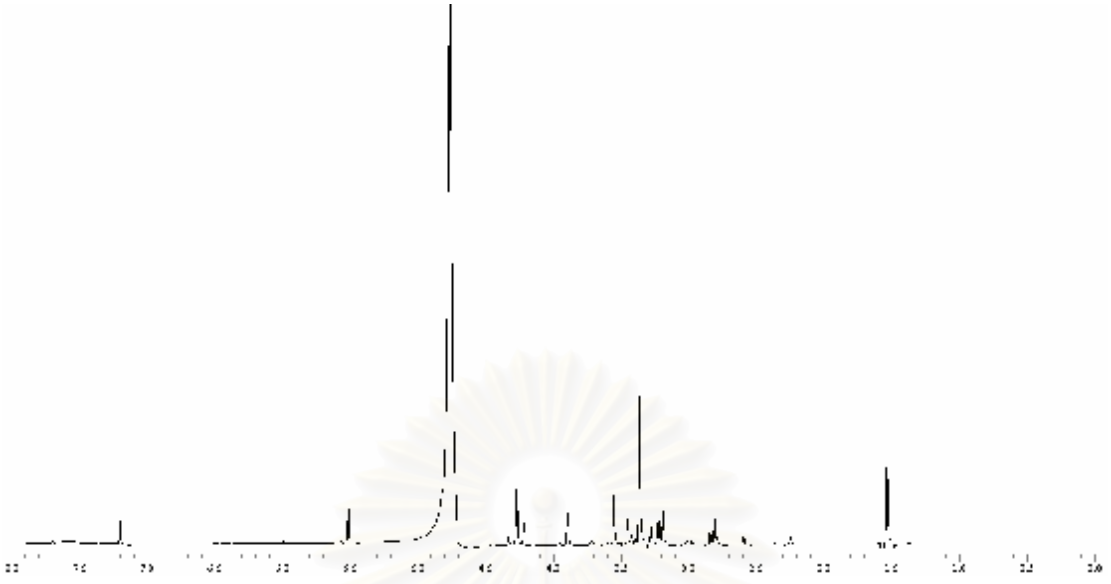


Figure 4.11 ^{1}H NMR spectrum of the product mixture from direct condensation using acid treated molecular sieve as a catalyst and sodium acetate as an internal standard.

The ^{1}H NMR spectrum of the product mixture from direct condensation using acid treated molecular sieve in Figure 4.11, was similar to Figure 4.5 but signed at 1.53 ppm was sodium acetate which used as internal standard. The chemical shift of proton of sodium acetate at 1.53 ppm was assigned for CH_3-COO^-. The internal standard was used in quantitative determination of *N*-phosphonomethylglycine.

Effect of reaction temperature

The effect of reaction temperature on direct condensation of glycine, formaldehyde and phosphorous acid was varied from 30, 60, 70, 100 and 120 °C for 2 hour, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2, acid treated molecular sieve 3A (4 g per glycine 1 mole) using 37% w/v hydrochloric acid. The results indicated that increasing the reaction temperature from 60 to 70 °C also increased the *N*-phosphonomethylglycine product. However, the use of high reaction temperature from 70 to 120 °C led to the decrease of *N*-phosphonomethylglycine product and reaction temperature at 30 °C

gave none of *N*-phosphonomethylglycine (Figure 4.12). Thus, the maximum yield from reaction temperature 70 °C was 29%. The reason of effect of the reaction temperature was explained by same as effect of the reaction temperature without acid treated molecular sieve 3A.

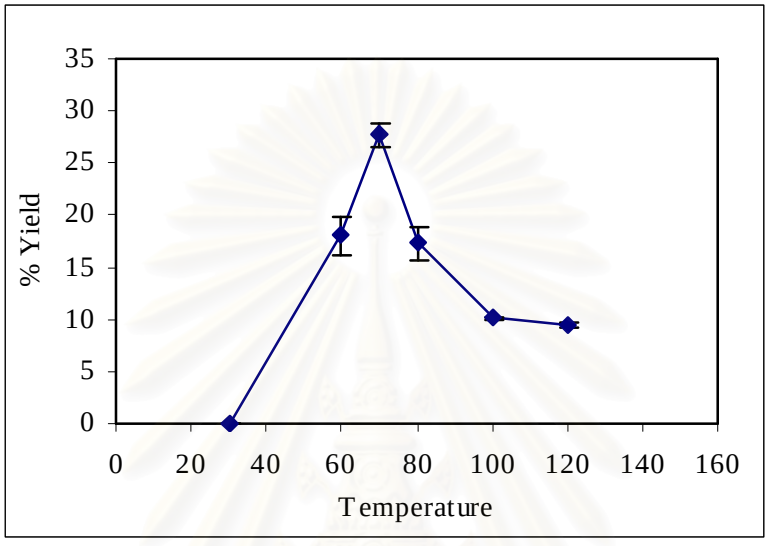


Figure 4.12 Effect of temperature on % yield of *N*-phosphonomethylglycine for 2 hour, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2, acid treated molecular sieve 3A (4 g per glycine 1 mole) and 37% w/v hydrochloric acid.

Effect of the reaction time

The effect of reaction time on direct condensation of glycine, formaldehyde and phosphorous acid was varied at 1, 2, 3 and 4 hour for 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2, acid treated molecular sieve 3A (4 g per glycine 1 mole) using 37% w/v hydrochloric acid. The results indicated that maximum yield of *N*-phosphonomethylglycine was reached within 2 hour (Figure 4.13). After that, increasing the reaction time from 2 to 4 hour, decreased the yield of *N*-phosphonomethylglycine. The reason of effect of the reaction time was explained by same as effect of the reaction temperature without acid treated molecular sieve 3A.

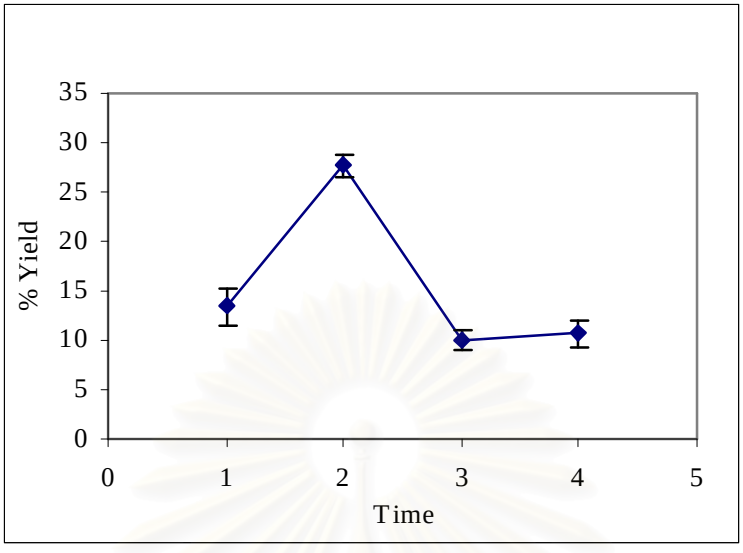


Figure 4.13 Effect of reaction time on % yield of *N*-phosphonomethylglycine at 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2, acid treated molecular sieve 3A (4 g per glycine 1 mole) and 37% w/v hydrochloric acid.

Effect of mole ratio between glycine and phosphorous acid

The effect of mole ratio between glycine and phosphorous acid on direct condensation of glycine, formaldehyde and phosphorous acid was varied from 1:0.5, 1:1, 1:1.5 and 1:2 for 2 hour, 70 °C, mole ratio between glycine and formaldehyde as 1:2, acid treated molecualar sieve 3A (4 g per glycine 1 mole) using 37% w/v hydrochloric acid. The results indicated that at mole ratio between glycine and phosphorous acid of 1:0.5 obtained the maximum yield (39% yield) of *N*-phosphonomethylglycine (Figure 4.14). The reason of effect of the mole ratio between glycine and phosphorous acid was explained by same as effect of mole ratio between glycine and phosphorous acid without acid treated molecular sieve 3A.

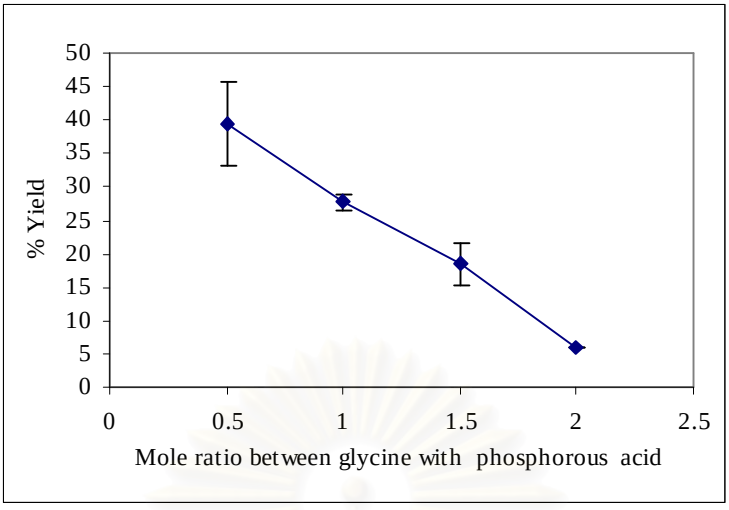


Figure 4.14 Effect of mole ratio between glycine and phosphorous acid on % yield of *N*-phosphonomethylglycine at 2 hour, 70 °C, mole ratio between glycine and formaldehyde as 1:2, acid treated molecular sieve 3A (4 g per glycine 1 mole) and 37% w/v hydrochloric acid.

Effect of mole ratio between glycine and formaldehyde

The effect of mole ratio between glycine and formaldehyde on direct condensation of glycine, formaldehyde and phosphorous acid was varied from 1:1, 1:2 and 1:3 for 2 hour, 70 °C, mole ratio between glycine and formaldehyde as 1:2, acid treated molecualar sieve 3A (4 g per glycine 1 mole) using 37% w/v hydrochloric acid. The results indicated that at mole ratio between glycine and formaldehyde of 1:2 afforded the maximum yield of *N*-phosphonomethylglycine as 39% (Figure 4.15). The reason of effect of the mole ratio between glycine and formaldehyde was explained by same as effect of mole ratio between glycine and formaldehyde without acid treated molecular sieve 3A.

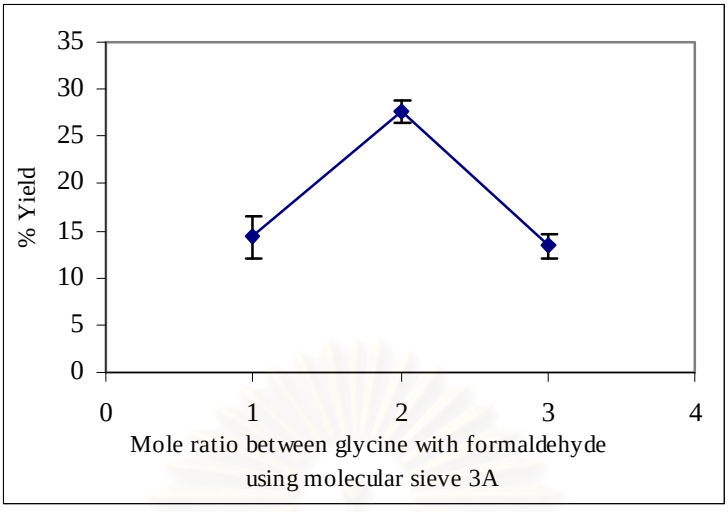


Figure 4.15 Effect of mole ratio between glycine and formaldehyde on % yield of *N*-phosphonomethylglycine for 2 hour, 70 °C, mole ratio between glycine and formaldehyde as 1:2, acid treated molecular sieve 3A (4 g per glycine 1 mole) and 37% w/v hydrochloric acid.

Effect of type of acid treated molecular sieve

The effect of type of molecular sieve on direct condensation was studied on acid treated molecular sieve 3A, 4A and 5A (4 g per glycine 1 mole) for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 using 37% w/v hydrochloric acid. The results indicated that acid treated molecular sieve 3A gave the maximum yield as 28%, while acid treated molecular sieve 4A gave lower percent yield as 16% and acid treated molecular sieve 5A gave the lowest percent yield as 14% (Figure 4.16). The argument of maximum yield of acid treated molecular sieve 3A was acidity site on the surface of molecular sieve and pore size of acid treated molecular sieve 3A that selective with glyphosate more than *N*,*N*-di(phosphonomethyl)glycine, which indicated that higher acidity and optimal pore size would give higher percent yield.

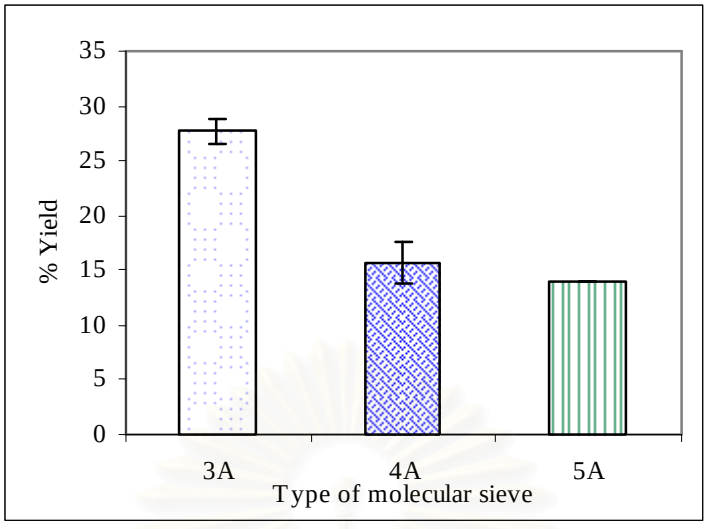


Figure 4.16 Effect of type of acid treated molecular sieve on % yield of *N*-phosphonomethylglycine for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid, mole ratio between glycine and formaldehyde as 1:2 as 1:1 and 37% w/v hydrochloric acid.

Effect of content of acid treated molecular sieve 3A

The effect of content of acid treated molecular sieve 3A on direct condensation of glycine, formaldehyde and phosphorous acid was varied at 2, 4, 8 and 12 g (per glycine 1 mole) for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 using 37% w/v hydrochloric acid. The results indicated that increasing the content of acid treated molecular sieve 3A from 2 to 4 g per glycine 1 mole also increased the yield of *N*-phosphonomethylglycine as a product. However, the use of high content of acid treated molecular sieve 3A from 4 to 12 g led to the decrease the yield of *N*-phosphonomethylglycine (Figure 4.17). Also, the use of more content of acid treated molecular sieve 3A was gave to produce *N*,*N*-di(phosphonomethyl)glycine is a main product.

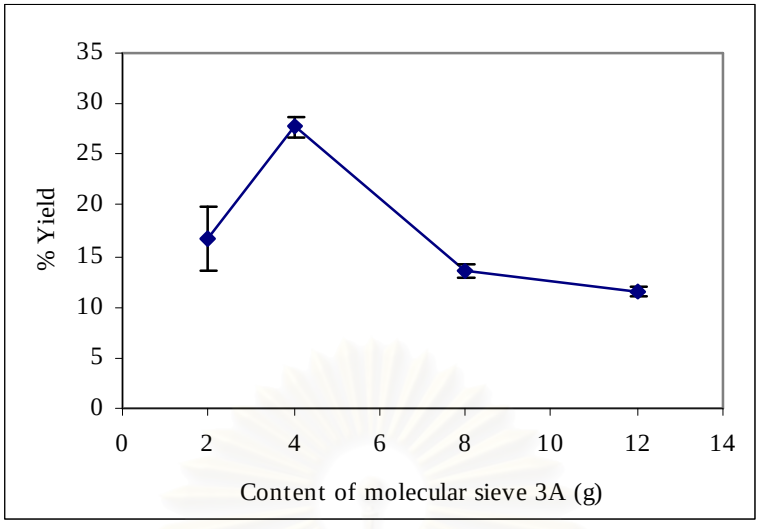


Figure 4.17 Effect of content of acid treated molecular sieve 3A on % yield of *N*-phosphonomethylglycine for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid, mole ratio between glycine and formaldehyde as 1:2 as 1:1 using 37% w/v hydrochloric acid.

Effect of hydrochloric acid and sulfuric acid

The effect of 37% w/v hydrochloric acid and 98% sulfuric acid on direct condensation are varied in the reaction with molecular sieve and without molecular sieve for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 and acid treated molecular sieve 3A (4 g per glycine 1 mole). The results indicated that the efficiency of using hydrochloric acid was better than sulfuric acid because formaldehyde was dissolved very well in hydrochloric acid. In addition, the use of hydrochloric acid and acid treated molecular sieve 3A gave higher percent yield than that using sulfuric acid and acid treated molecular sieve 3A because the solubility of reactant in hydrochloric acid was better than sulfuric acid. Thus, the maximum yield of *N*-phosphonomethylglycine was obtained using hydrochloric acid without molecular sieve (Figure 4.18).

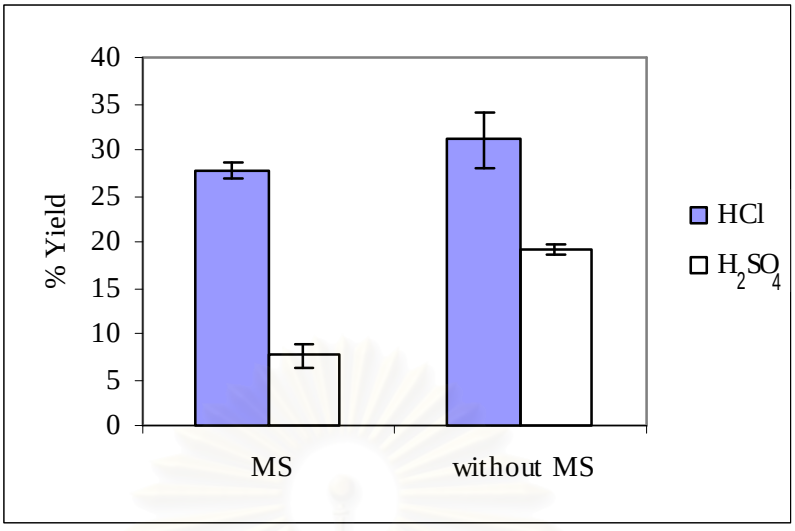


Figure 4.18 Effect of hydrochloric acid and sulfuric acid on % yield of *N*-phosphonomethylglycine for 2 hour, 70 °C, mole ratio between glycine and phosphorous acid, mole ratio between glycine and formaldehyde as 1:2 as 1:1 using 37% w/v hydrochloric acid.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The properties of acid treated molecular sieves 3A, 4A, 5A in terms of acidity revealed that the molecular sieve 3A after acid treatment exhibited the maximum acidity (137 meq/100 g) followed by molecular sieve 4A (115 meq/100 g) and molecular sieve 5A (108 meq/100 g), respectively. In addition, the results of the exchanged of metals were confirmed by XRF technique.

Preparation of *N*-phosphonomethylglycine by conventional method using iminodiacetic acid, formaldehyde and phosphorous acid as reactants and sulfuric acid as a catalyst, gave 98% of *N*-(phosphonomethyl)iminodiacetic acid. *N*-phosphonomethylglycine was prepared from oxidative decarboxylation of *N*-(phosphonomethyl)iminodiacetic acid using cobalt(II) ion as a catalyst in 75% yield. The overall conversion of iminodiacetic acid to glyphosate was found to be 68% yield (phosphorous acid as a limiting reagent).

Preparation of *N*-phosphonomethylglycine by direct condensation using glycine, formaldehyde and phosphorous acid as reactants, mole ratio between glycine and phosphorous acid as 1:0.5, mole ratio between glycine and formaldehyde as 1:2 and 37% hydrochloric acid at 70 °C for 2 hour gave a mixture of products. At this condition, using molecular sieve in reaction showed higher yield of *N*-phosphonomethylglycine (39%) than that without using molecular sieve. Finally, using hydrochloric acid as a catalyst gave more *N*-phosphonomethylglycine than using sulfuric acid.

The identity of *N*-phosphonomethylglycine was characterized by ^{1}H NMR and spectroscopic data. The summary of optimal reaction conditions are shown in Table 5.1.

Table 5.1 The optimum condition and % yield of *N*-phosphonomethylglycine for direct condensation of glycine using molecular sieve and without molecular sieve

Optimum condition	without molecular sieve	with molecular sieve
Temperature (°C)	70	70
Time (hour)	2	2
Mole ratio between glycine and phosphorous acid	1:1	1:0.5
Mole ratio between glycine and formaldehyde	1:2	1:2
Type of treated molecular sieve	-	3A
Content of acid treated molecular sieve 3A (g per glycine 1 mole)	-	4
Type of acid (hydrochloric acid, sulfuric acid)	Hydrochloric acid	Hydrochloric acid
% maximum yield of *N*-phosphonomethylglycine	35	39
% maximum yield of *N*-phosphonomethylglycine from conventional method	68	

The results indicated that acid treated molecular sieve 3A gave the maximum yield because acid treated molecular sieve 3A has acidity site on the surface of molecular sieve, which indicated that higher acidity would give higher percent yield. However, % yield from the reaction with acid treated molecular sieve 3A is slightly improved, compared with that obtained from the condition employed hydrochloric acid alone.

5.2 Suggestion for the future work

The use of close system is recommended to be developed in this synthesis in order to prevent unwanted loss of formaldehyde in the open system currently used.

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APPENDIXES

APPENDIX A

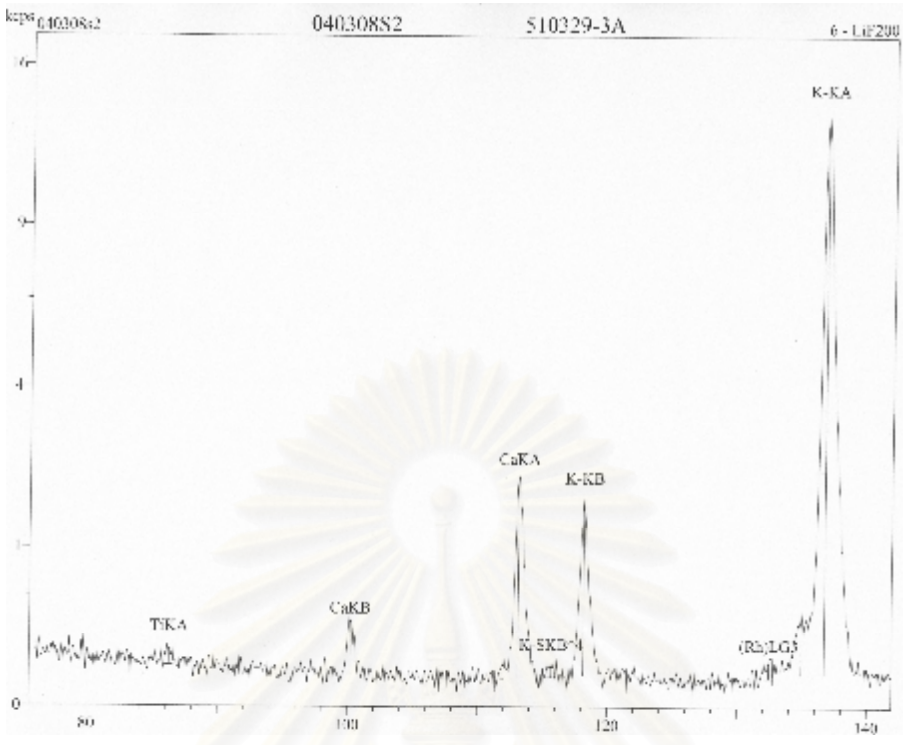

Figure A1 XRF spectrum of the acid molecular sieve 3A of Ca and K.

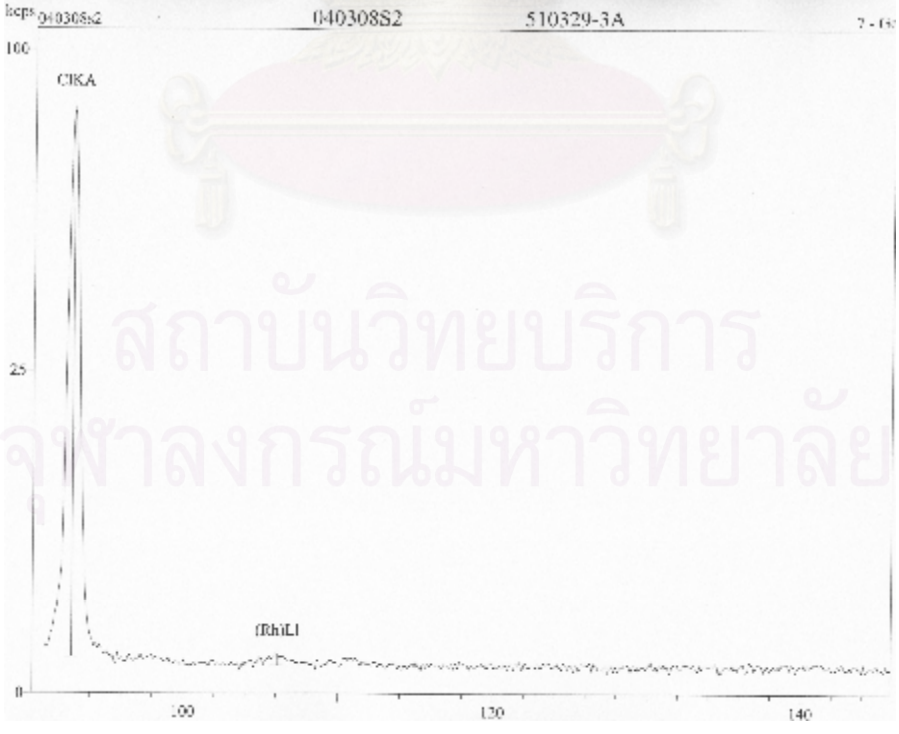

Figure A2 XRF spectrum of the acid molecular sieve 3A of Cl.

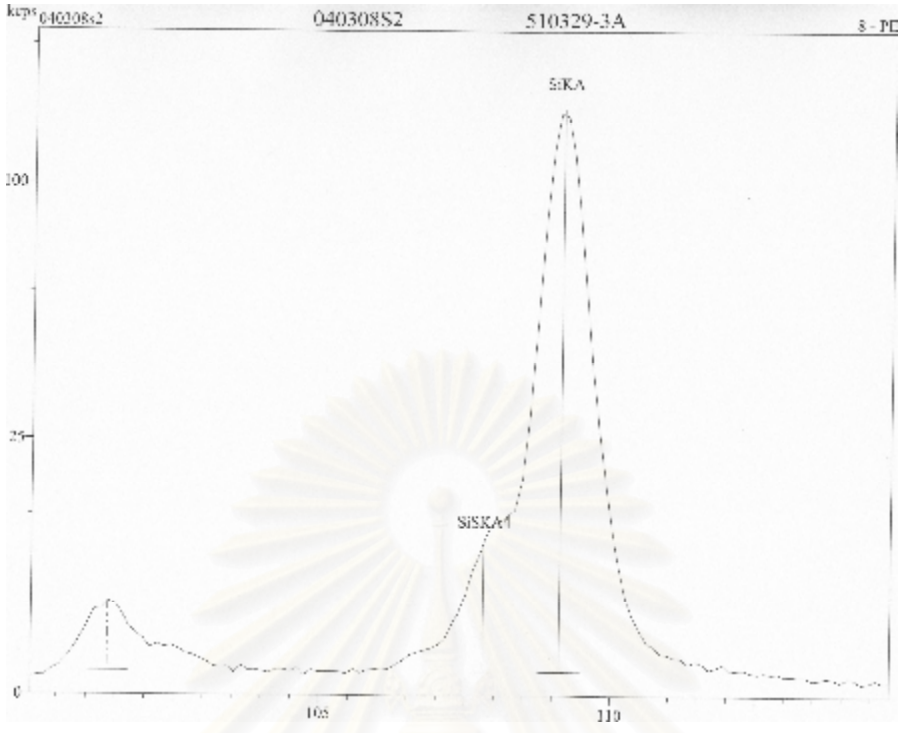

Figure A3 XRF spectrum of the acid molecular sieve 3A of Si.

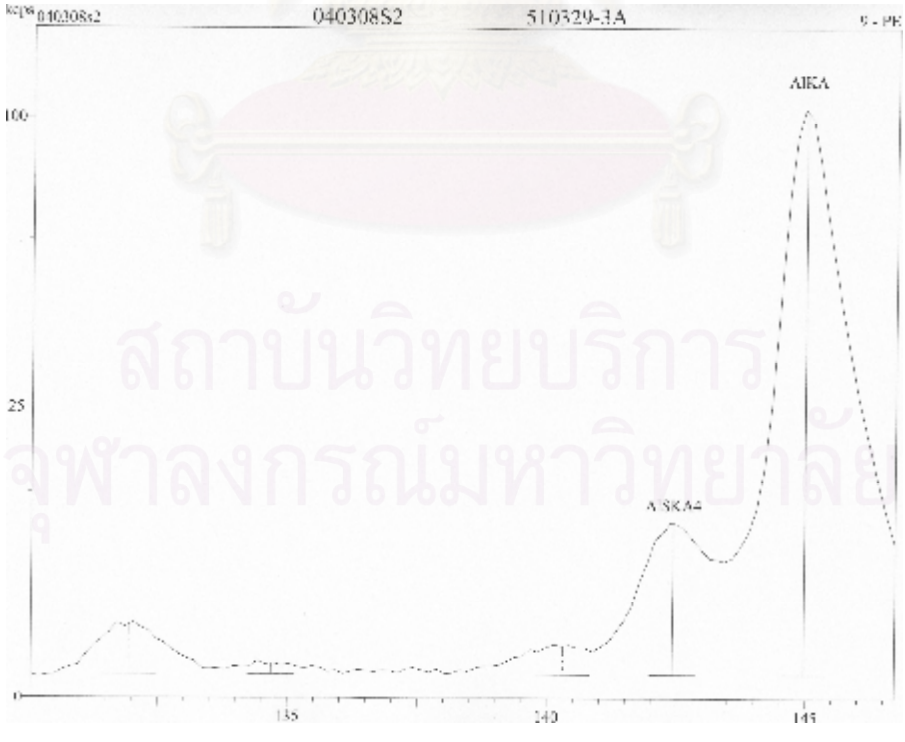

Figure A4 XRF spectrum of the acid molecular sieve 3A of Al.

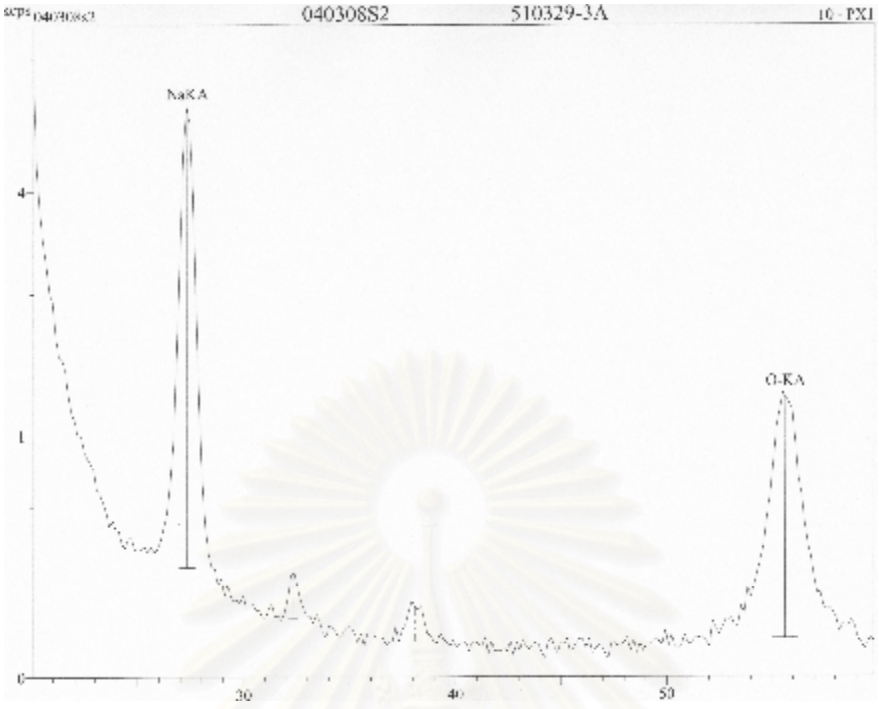

Figure A5 XRF spectrum of the acid molecular sieve 3A of Na.

Figure A6 XRF spectrum of the acid molecular sieve 4A of Cl.

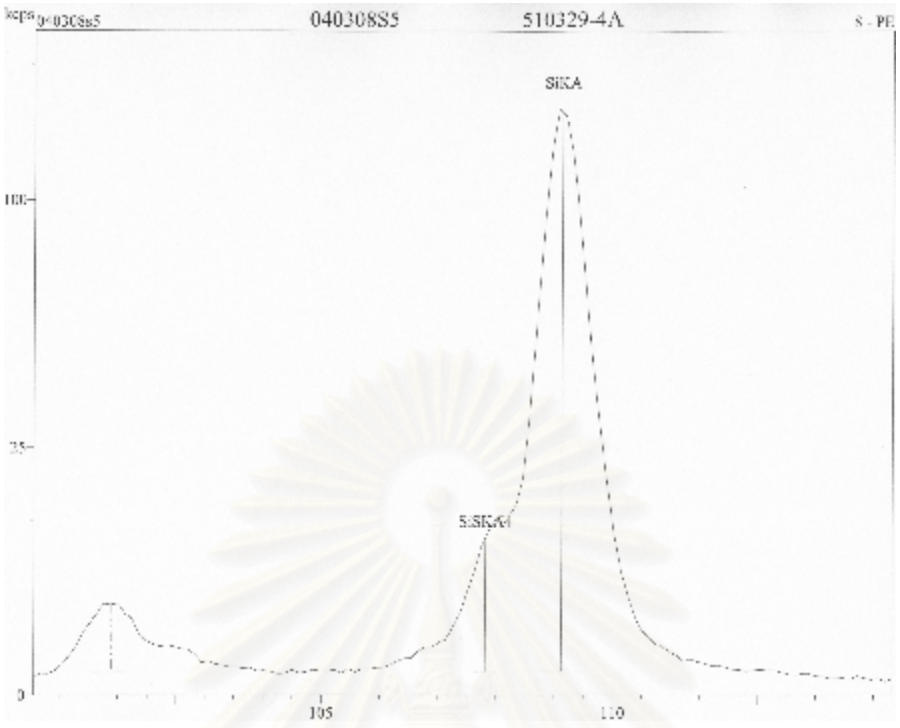

Figure A7 XRF spectrum of the acid molecular sieve 4A of Si.

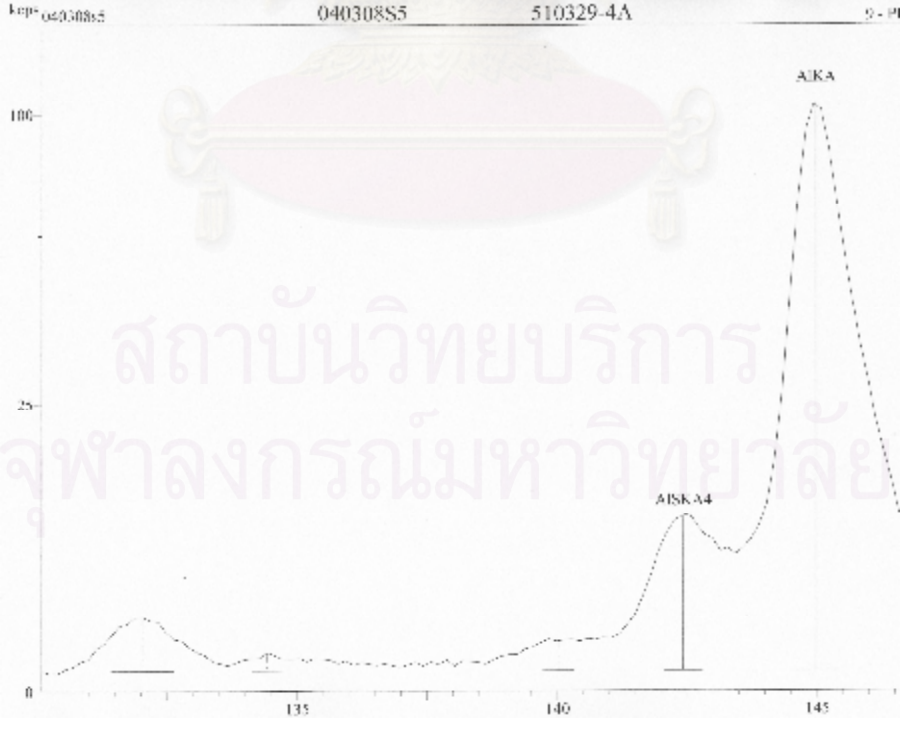

Figure A8 XRF spectrum of the acid molecular sieve 4A of Al.

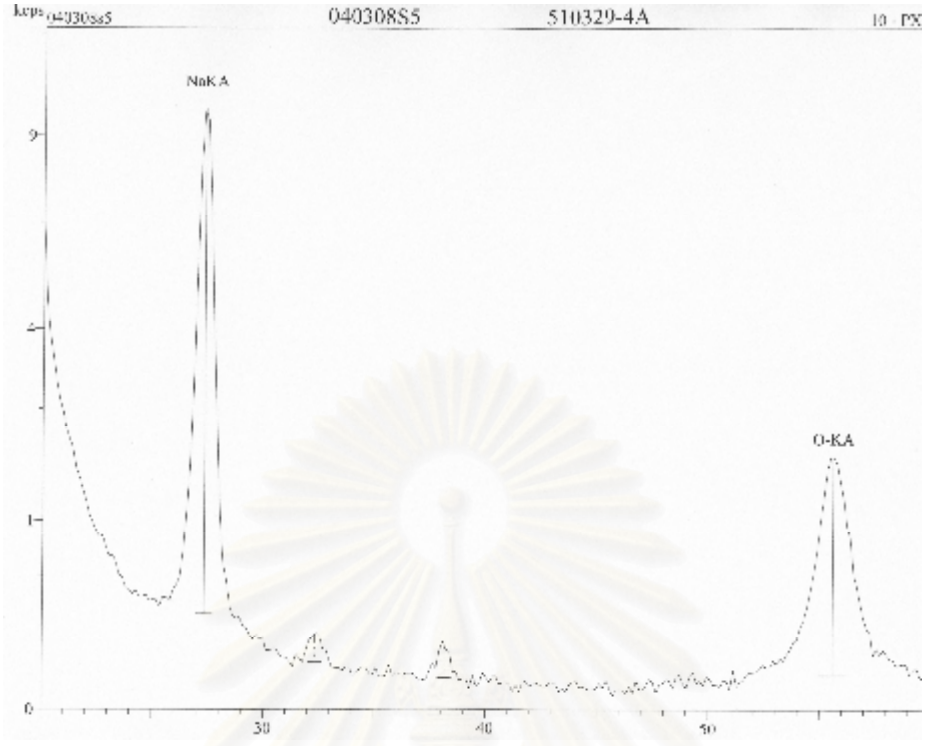

Figure A9 XRF spectrum of the acid molecular sieve 4A of Na.

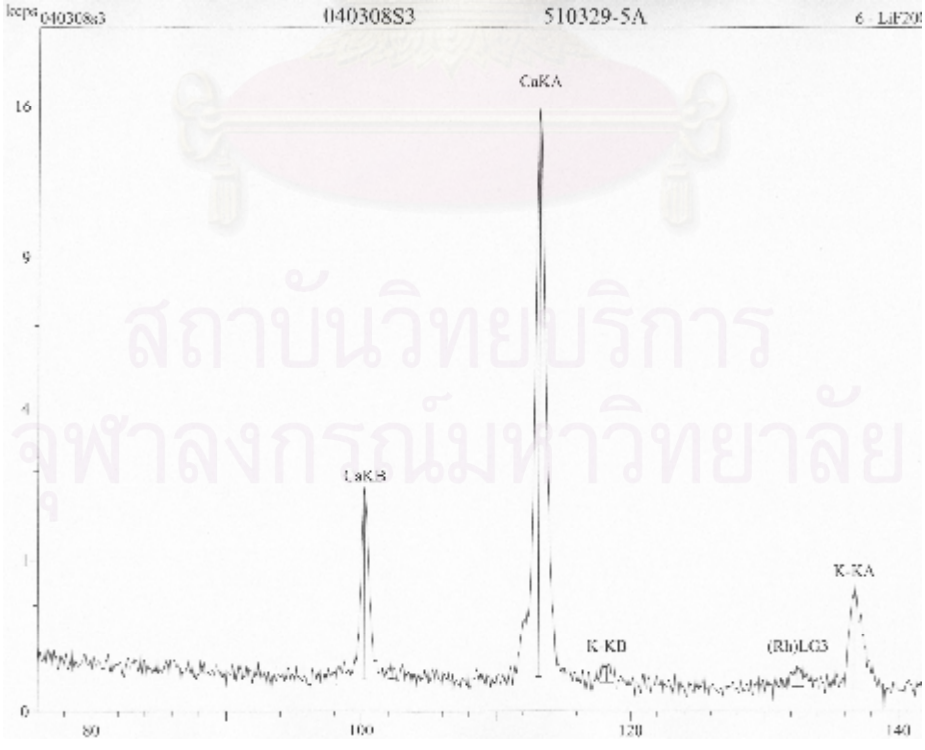

Figure A10 XRF spectrum of the acid molecular sieve 5A of Ca and K.

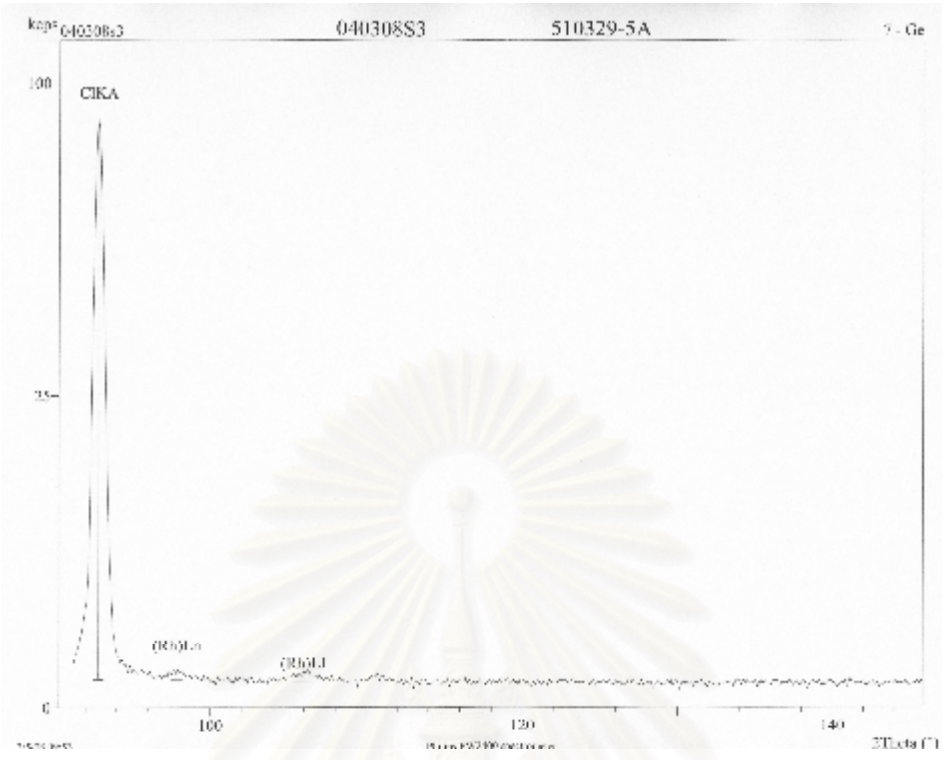

Figure A11 XRF spectrum of the acid molecular sieve 5A of Cl.

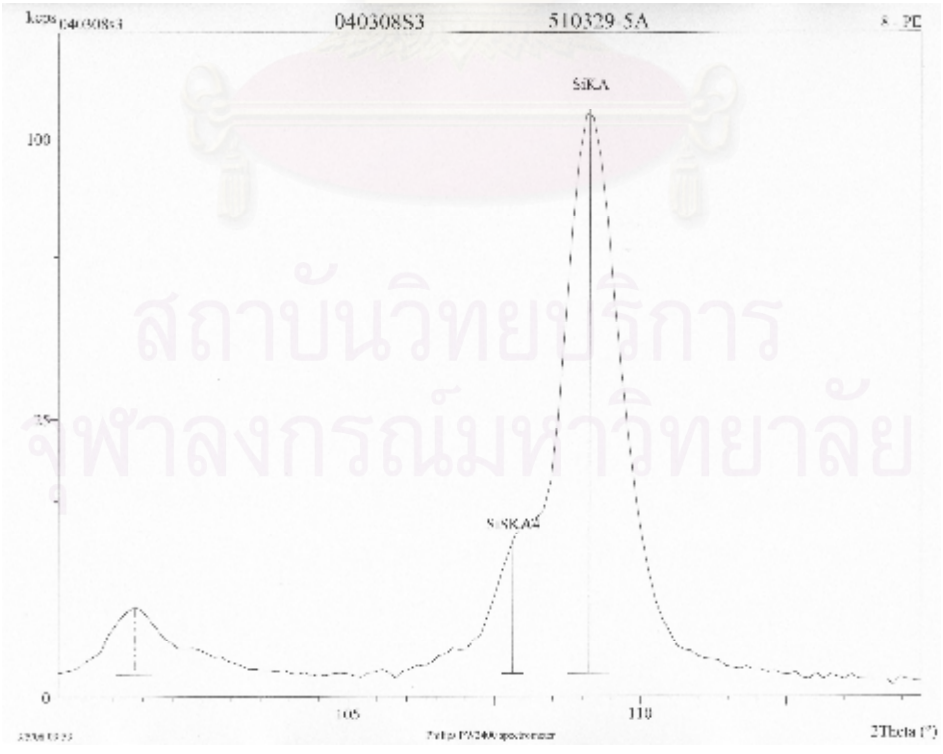

Figure A12 XRF spectrum of the acid molecular sieve 5A of Si.

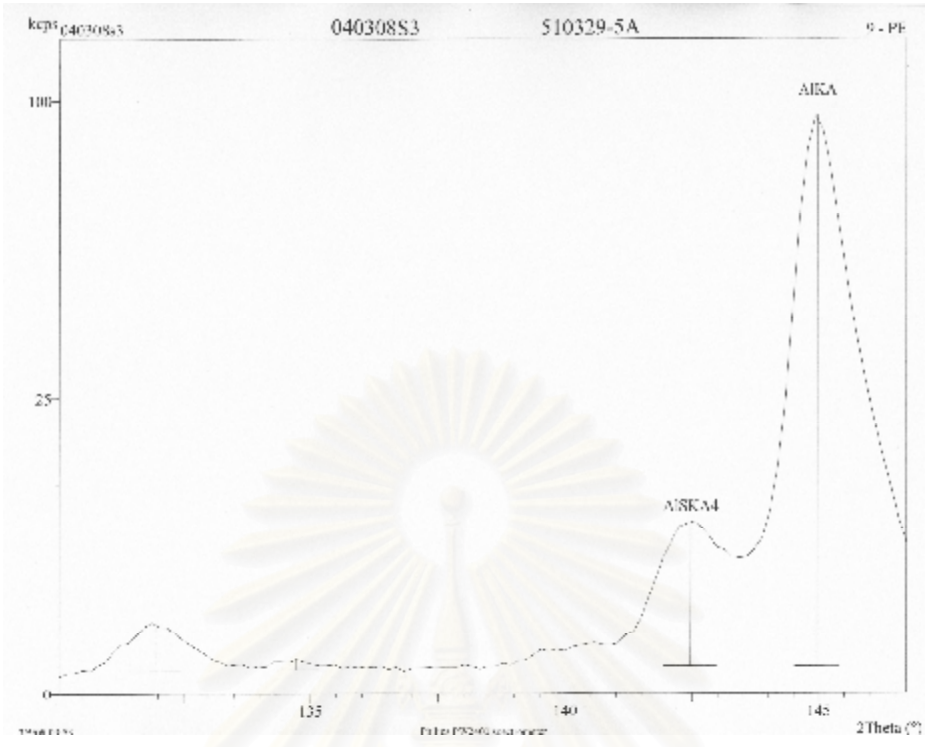

Figure A13 XRF spectrum of the acid molecular sieve 5A of Al.

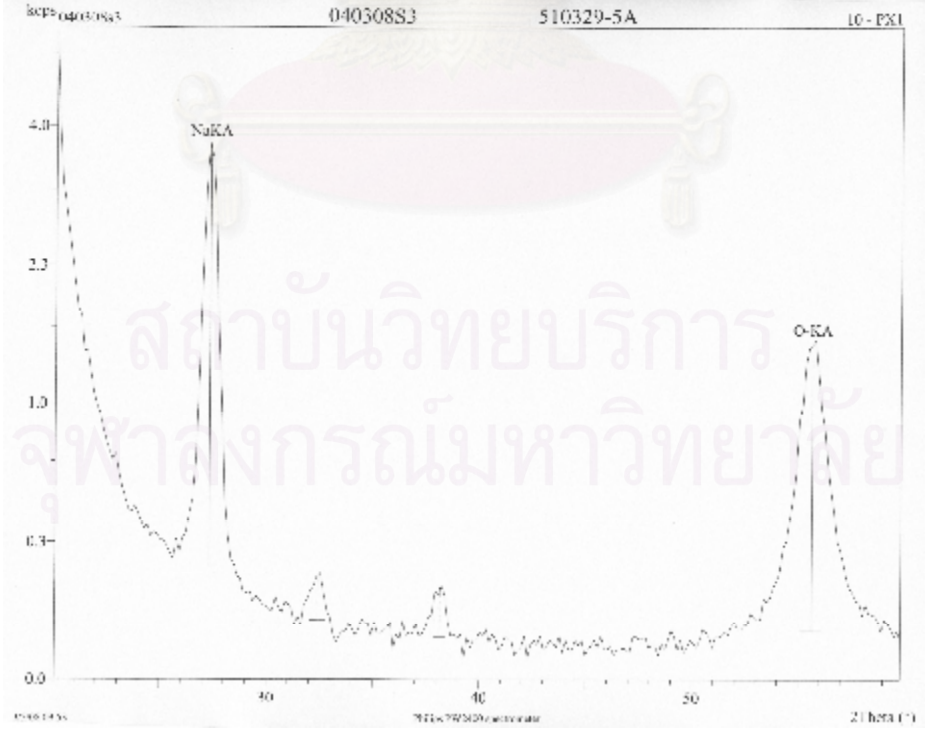

Figure A14 XRF spectrum of the acid molecular sieve 5A of Na.

APPENDIX B

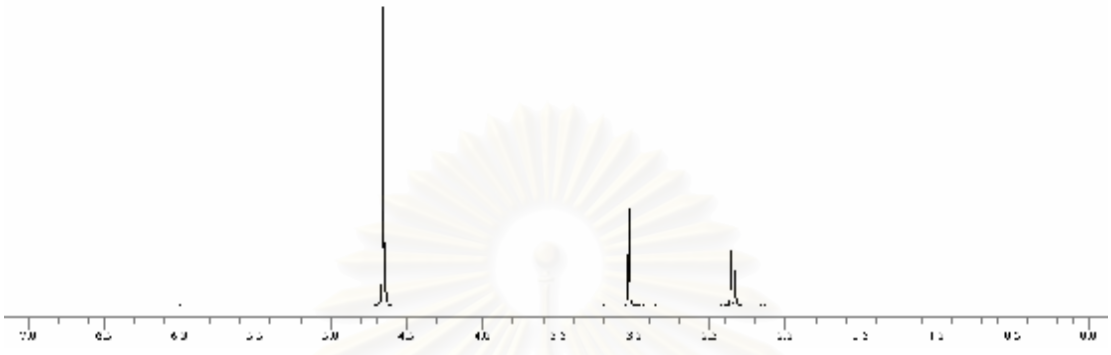

Figure B1 ^{1}H NMR spectrum of *N*-phosphonomethylglycine salt at 2.38 (d) and 3.02 (s) ppm were assigned for CH_2-P and $C\underline{H}_2$-COOH in D_2O.

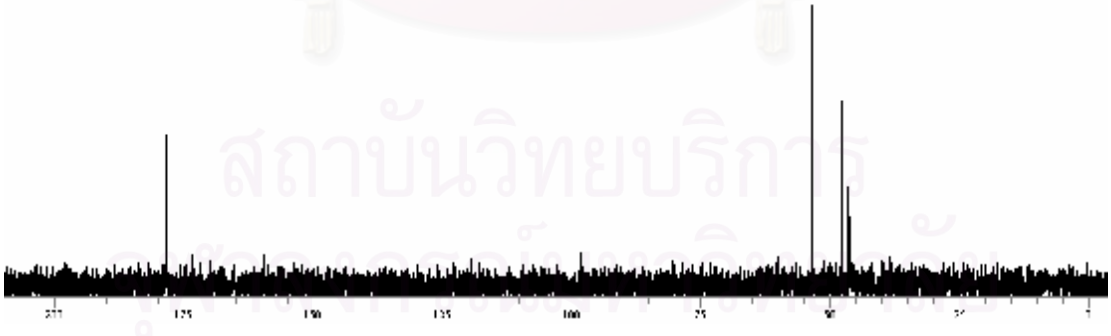

Figure B2 ^{13}C NMR spectrum of *N*-phosphonomethylglycine salt acid at 43 (d), 51 (s) and 171 (s) ppm were assigned for CH_2-P, $\underline{C}H_2$-COOH and COOH in D_2O.

Figure B3 ^{1}H NMR spectrum of *N*-(phosphonomethyl)iminodiacetate at 3.57 (d) and 3.91 (s) ppm were assigned for CH_2-P and $C\underline{H}_2$-COOH in D_2O.

Figure B4 ^{13}C NMR spectrum of *N*-(phosphonomethyl)iminodiacetate at 53 (d), 61 (s) and 180 (s) ppm were assigned for CH_2-P, $\underline{C}H_2$-COOH and COOH in D_2O.

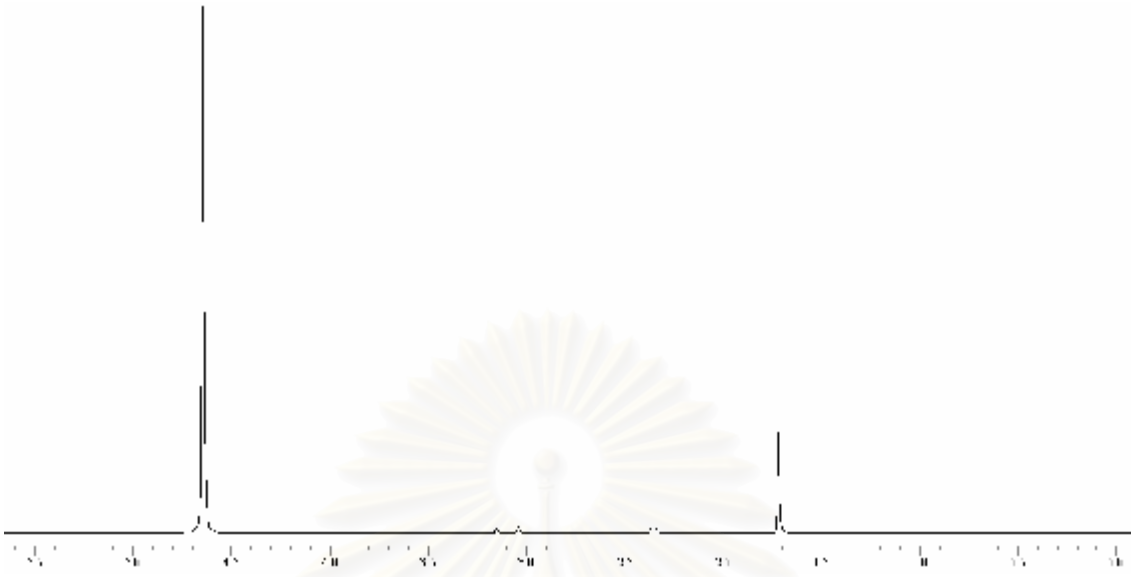

Figure B5 ^{1}H NMR spectrum of 5 mg *N*-phosphonomethylglycine and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

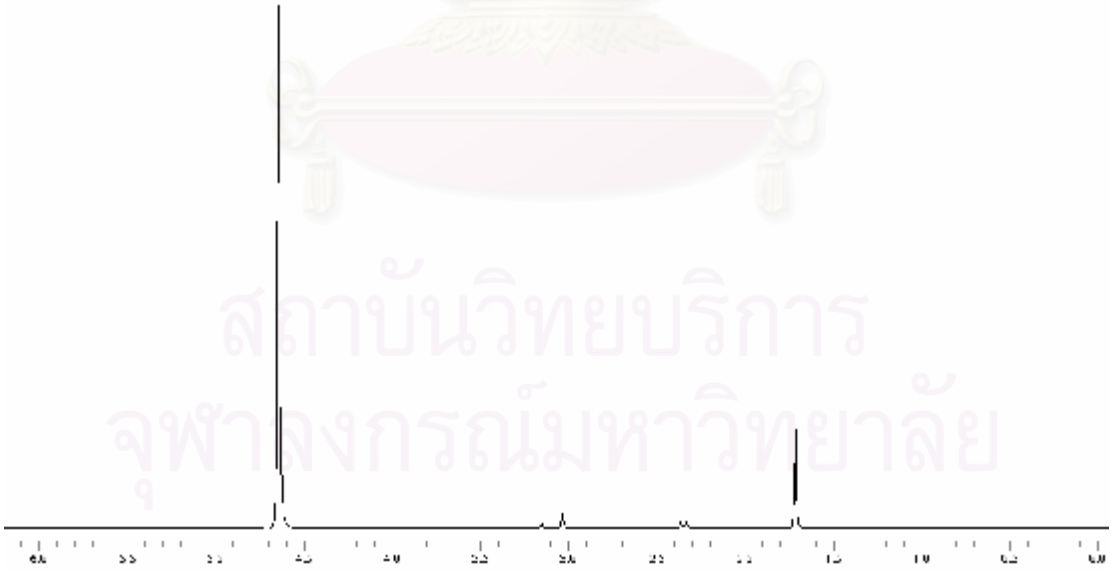

Figure B6 ^{1}H NMR spectrum of 10 mg *N*-phosphonomethylglycine and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

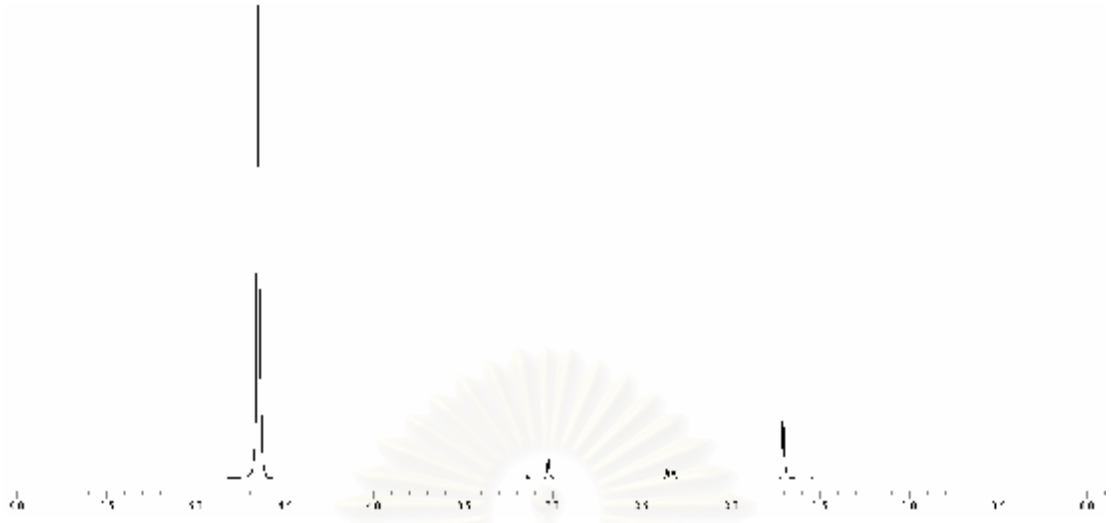

Figure B7 ^{1}H NMR spectrum of 25 mg *N*-phosphonomethylglycine and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

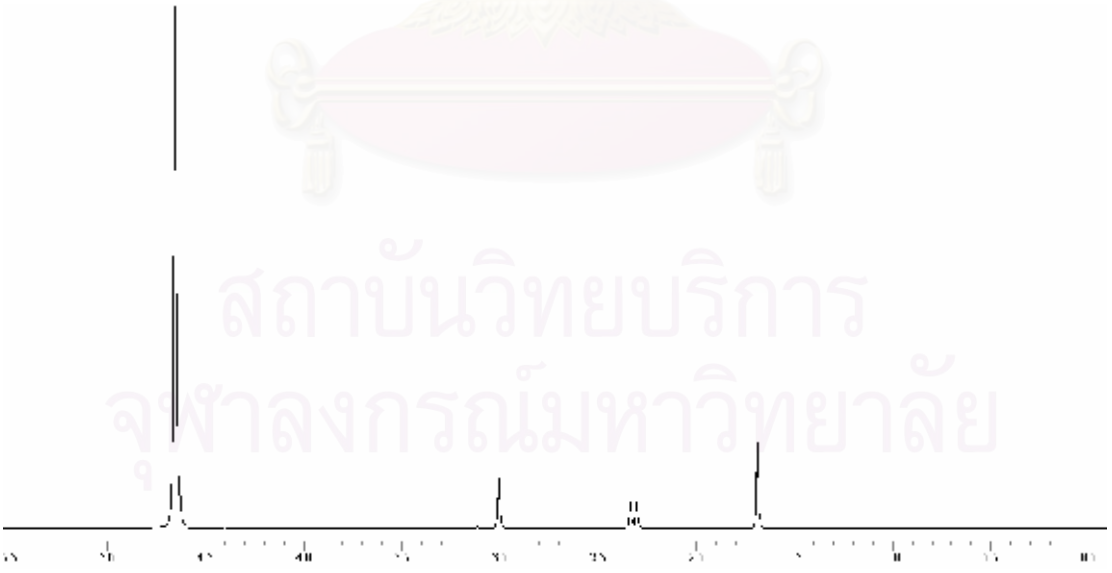

Figure B8 ^{1}H NMR spectrum of 50 mg *N*-phosphonomethylglycine and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

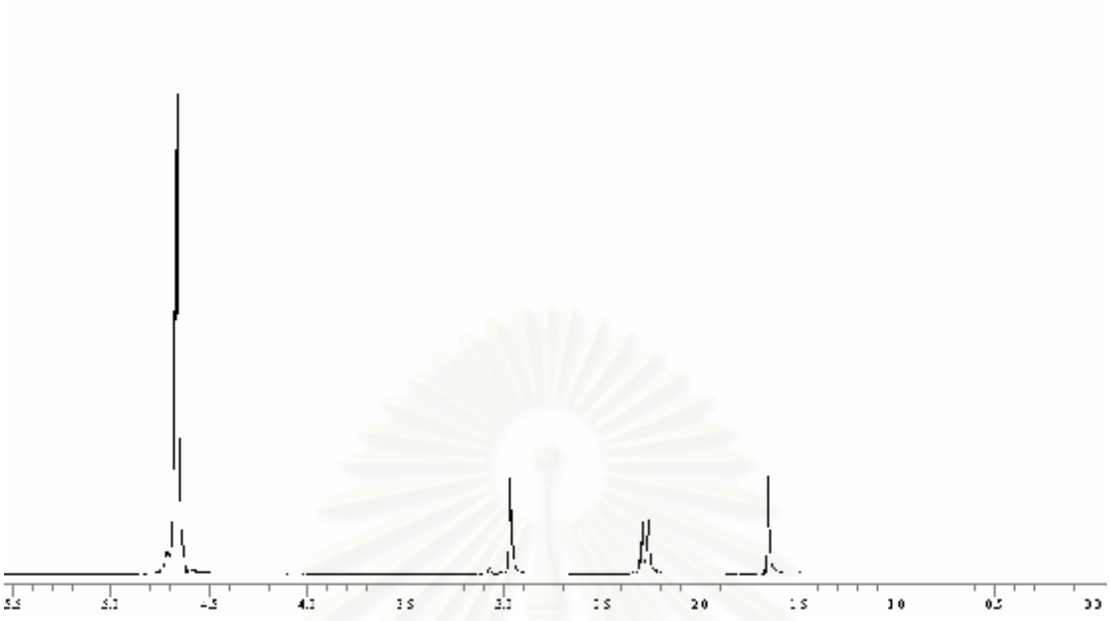

Figure B9 ^{1}H NMR spectrum of 100 mg *N*-phosphonomethylglycine and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

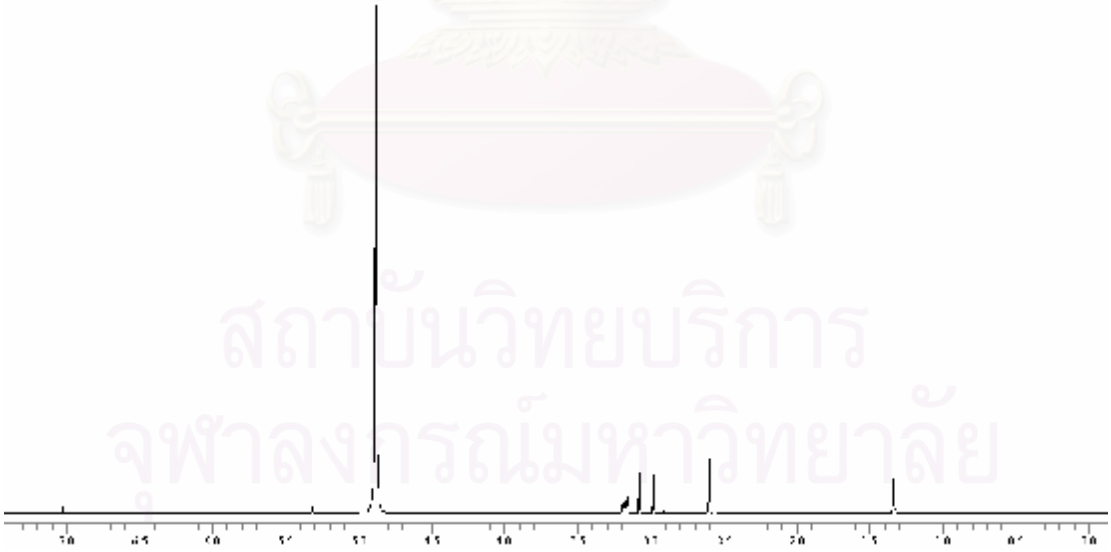

Figure B10 ^{1}H NMR spectrum of 200 mg the product mixture at room temperature and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

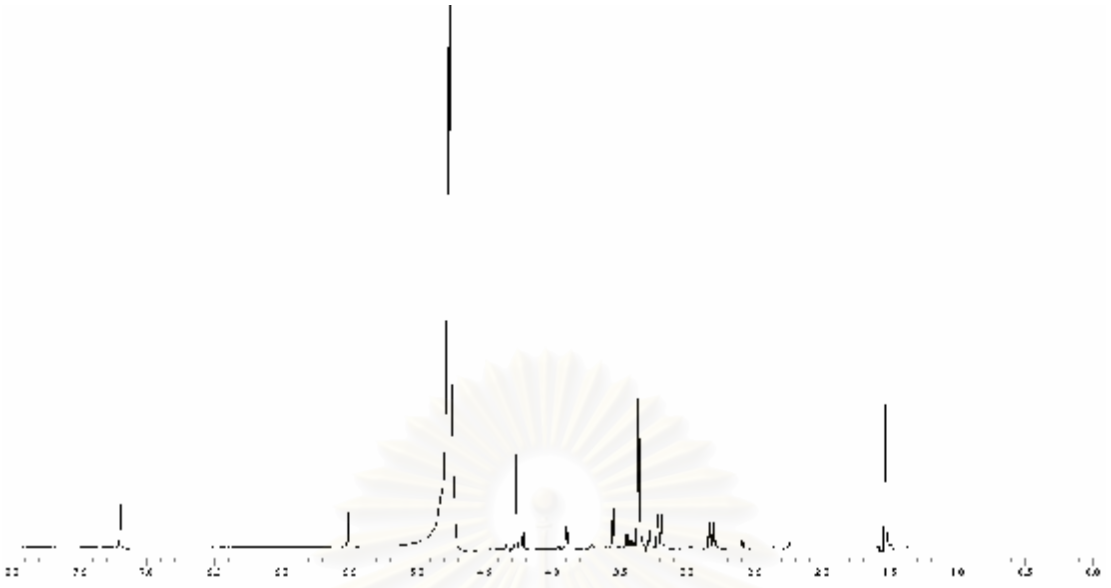

Figure B11 ^{1}H NMR spectrum of 200 mg the product mixture at 60 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

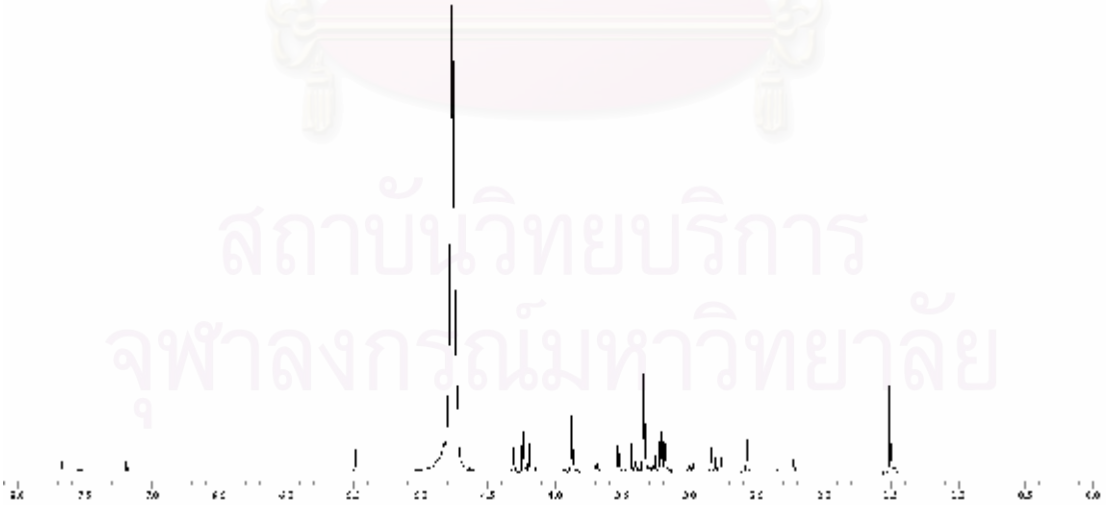

Figure B12 ^{1}H NMR spectrum of 200 mg the product mixture at 70 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

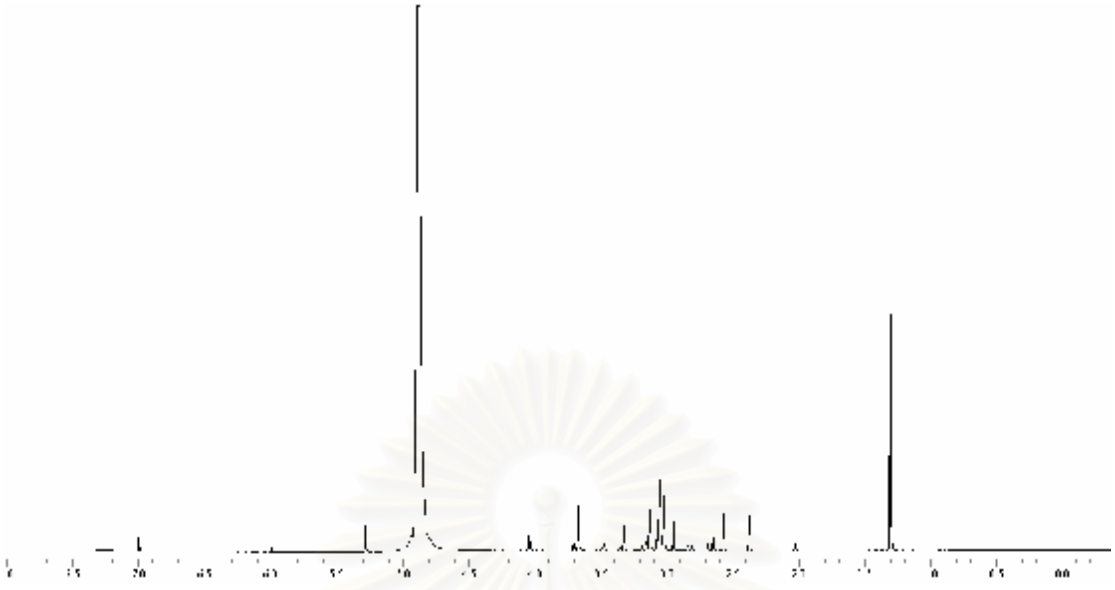

Figure B13 ^{1}H NMR spectrum of 200 mg the product mixture at 80 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

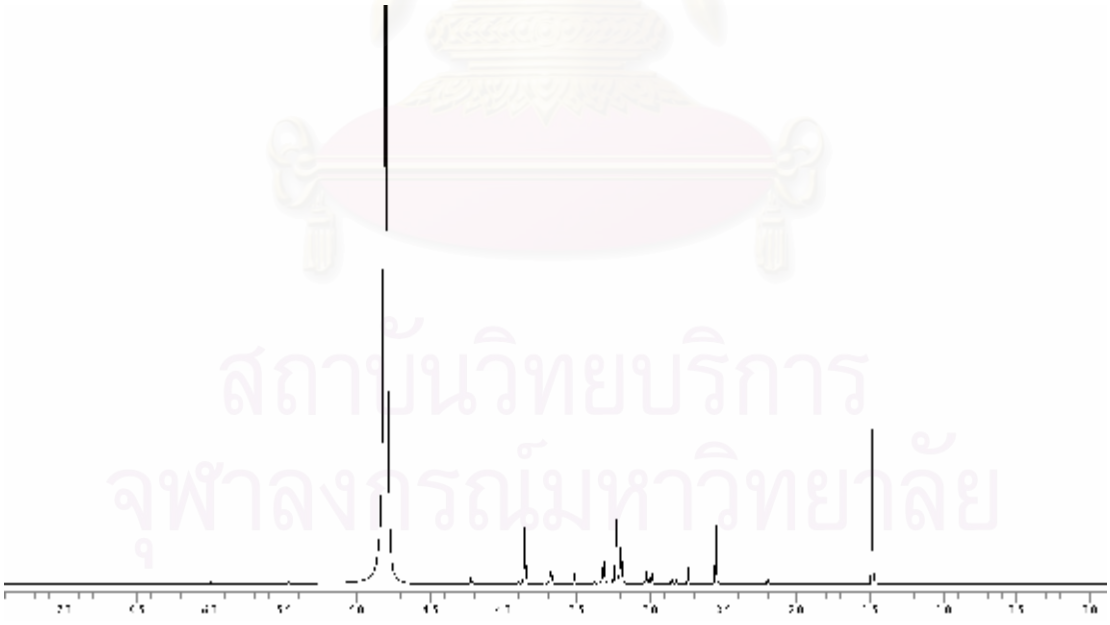

Figure B14 ^{1}H NMR spectrum of 200 mg the product mixture at 100 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

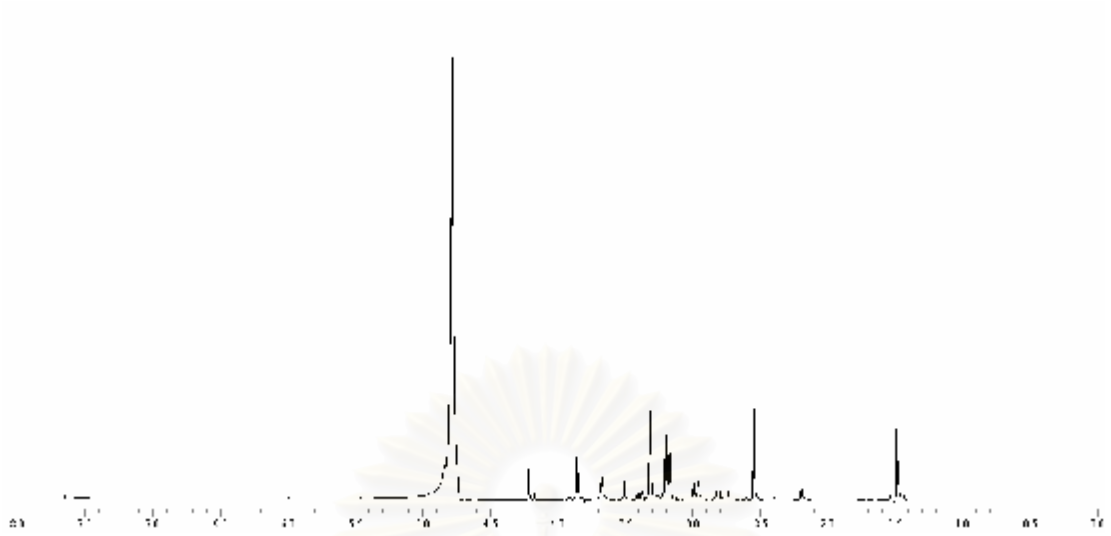

Figure B15 ^{1}H NMR spectrum of 200 mg the product mixture at 120 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

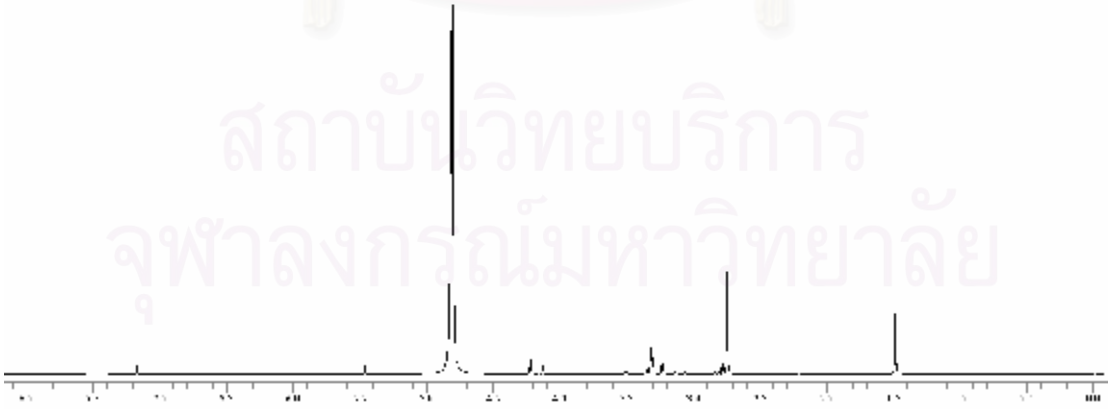

Figure B16 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at room temperature and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

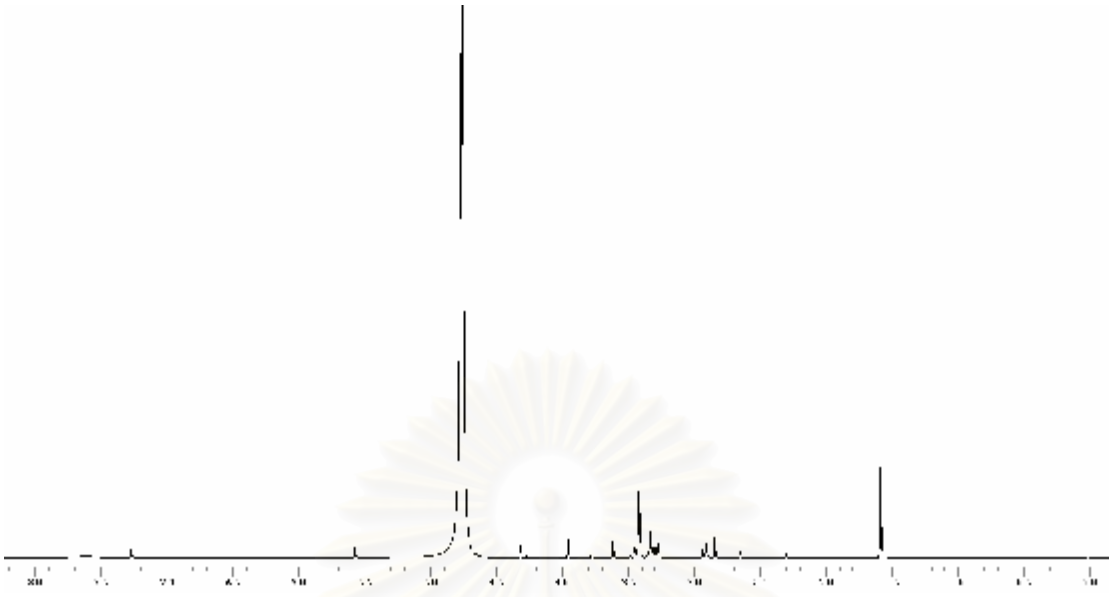

Figure B17 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 60 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

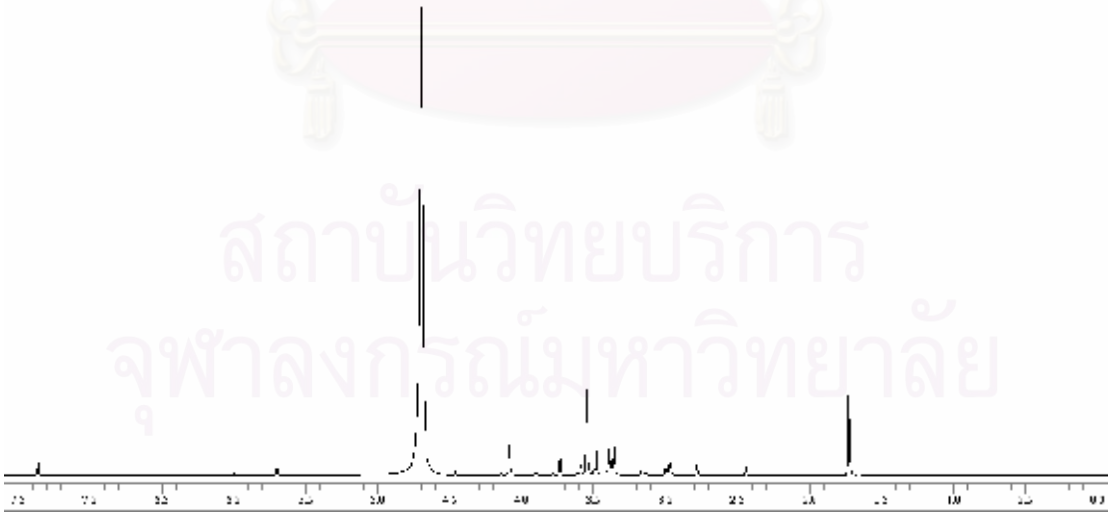

Figure B18 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 70 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

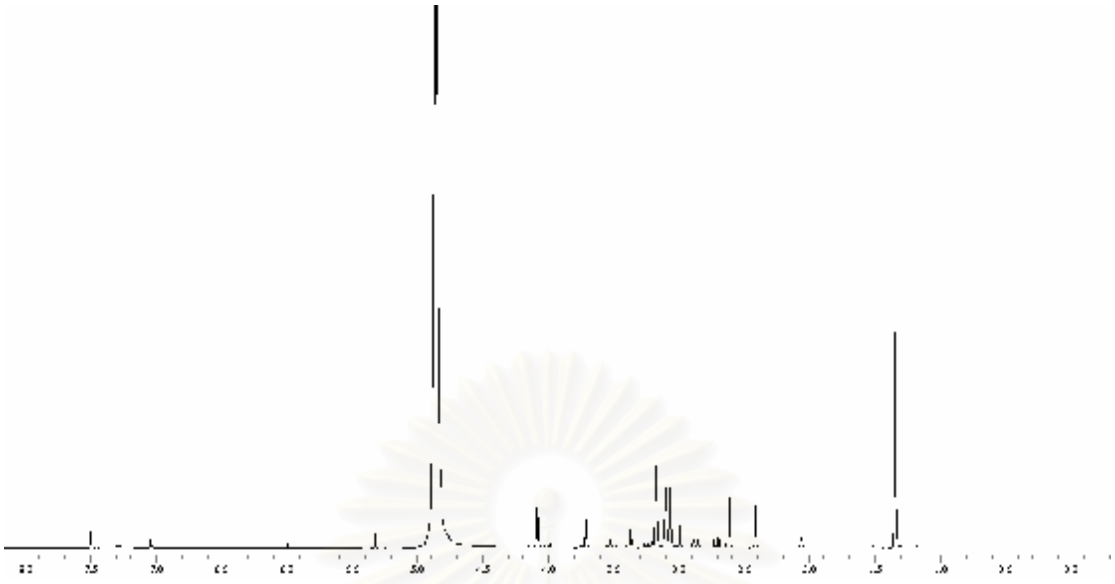

Figure B19 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 80 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

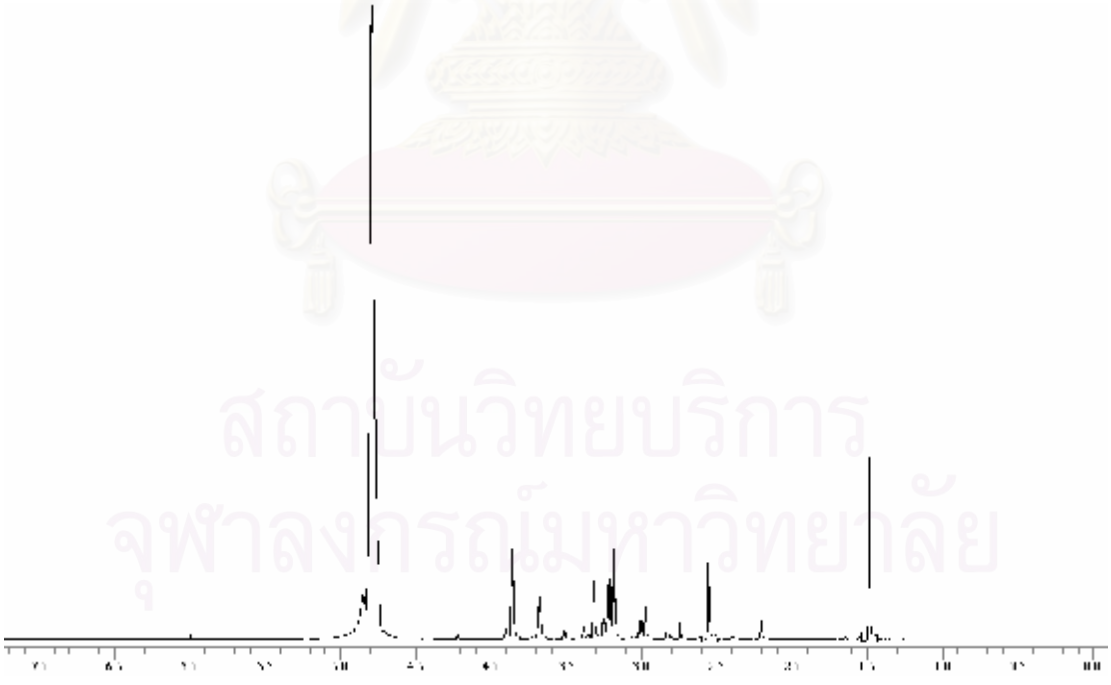

Figure B20 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 100 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

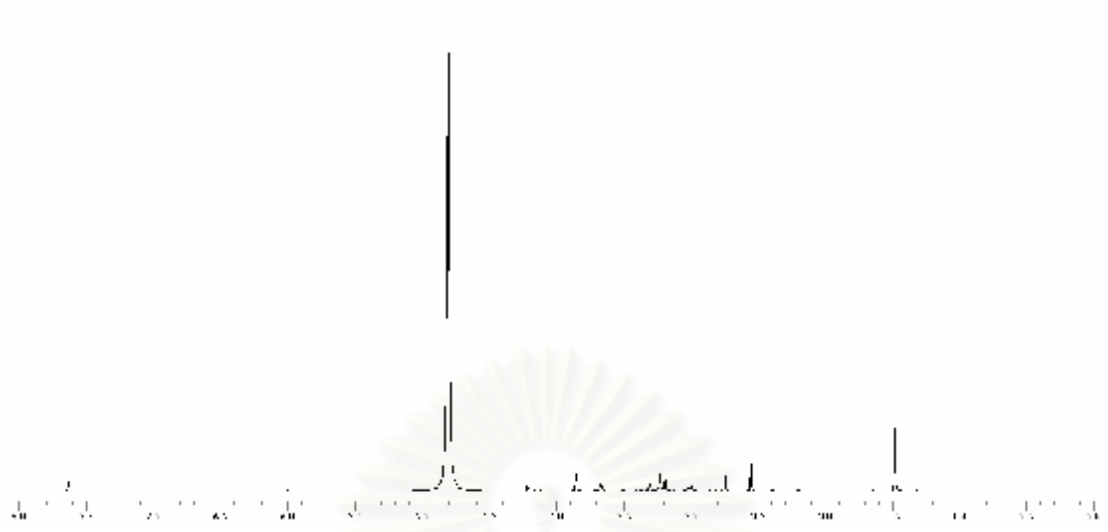

Figure B21 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 120 °C and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

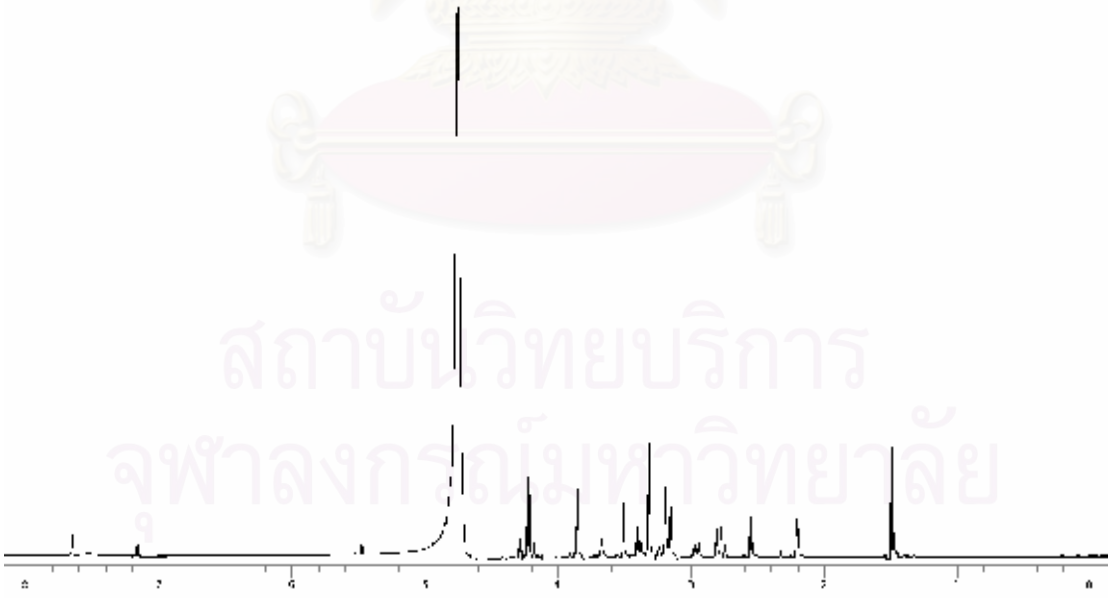

Figure B22 ^{1}H NMR spectrum of 200 mg the product mixture at 1 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

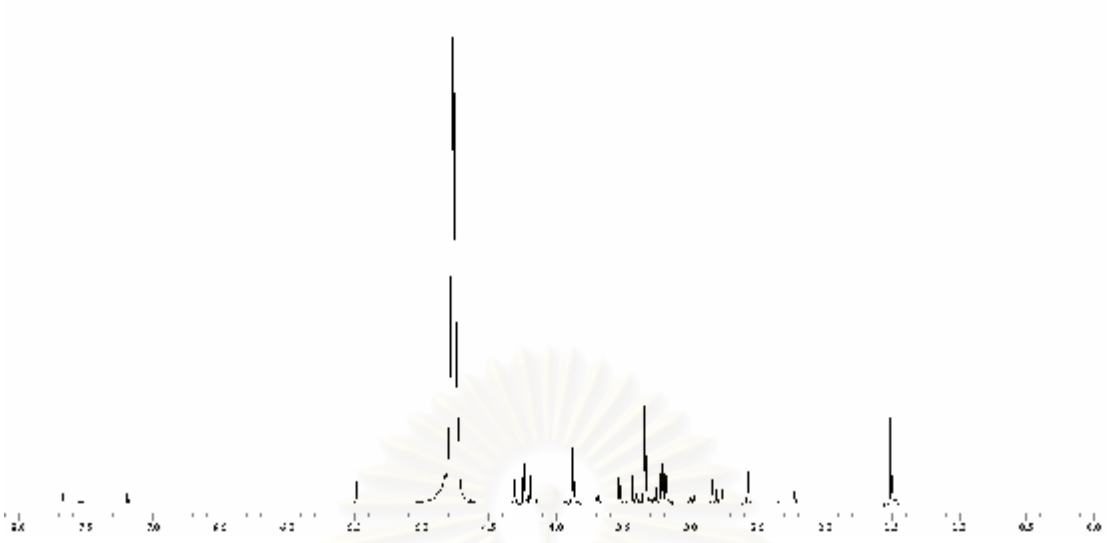

Figure B23 ^{1}H NMR spectrum of 200 mg the product mixture at 2 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

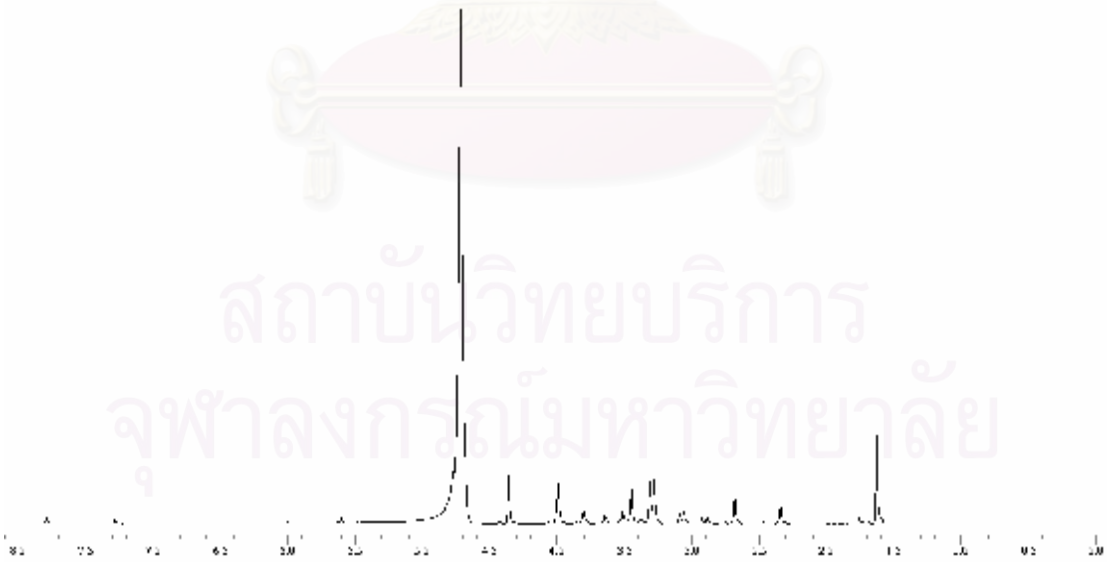

Figure B24 ^{1}H NMR spectrum of 200 mg the product mixture at 3 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

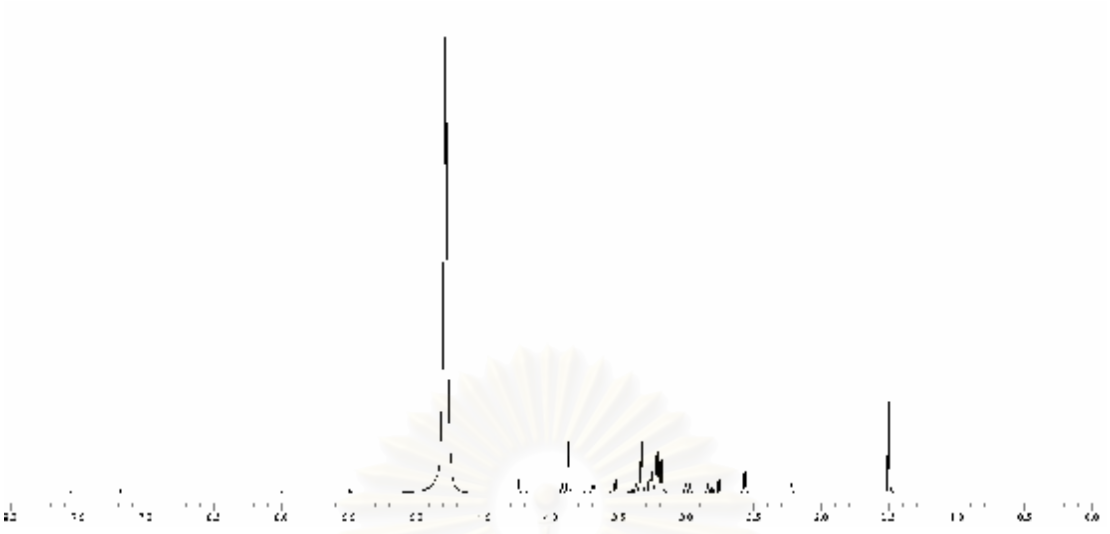

Figure B25 ^{1}H NMR spectrum of 200 mg the product mixture at 4 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

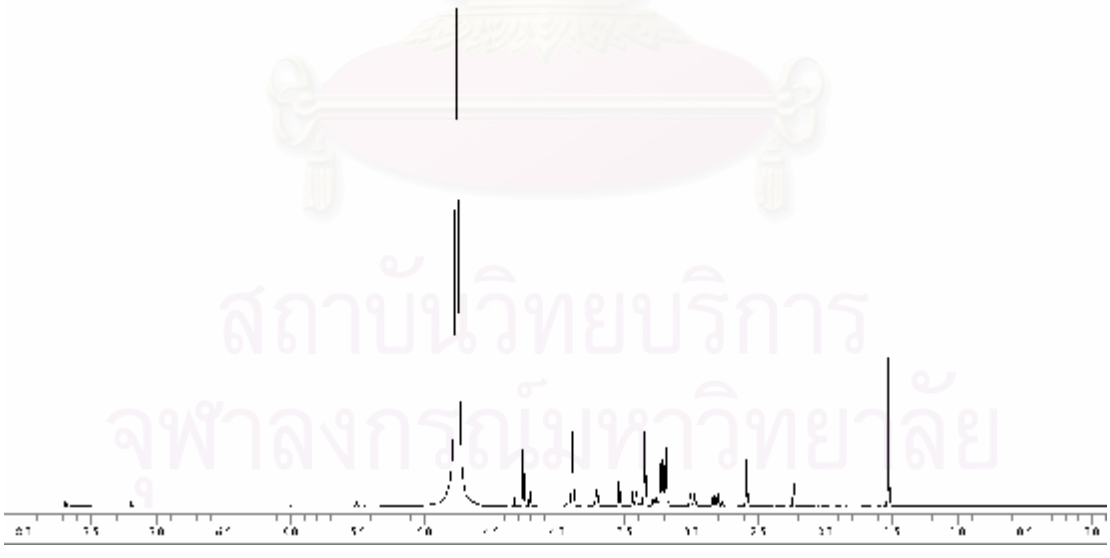

Figure B26 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 1 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

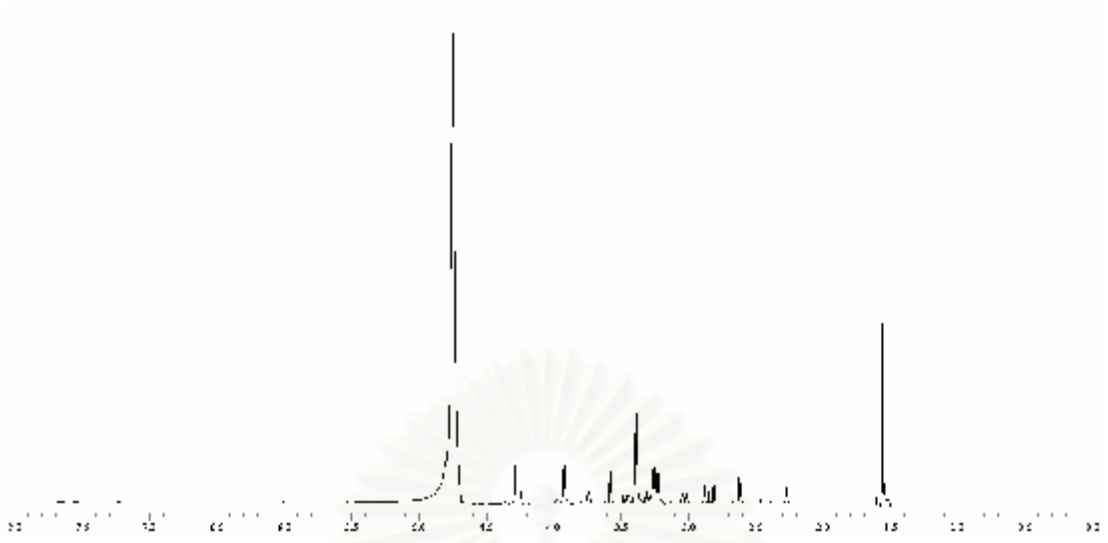

Figure B27 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 3 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

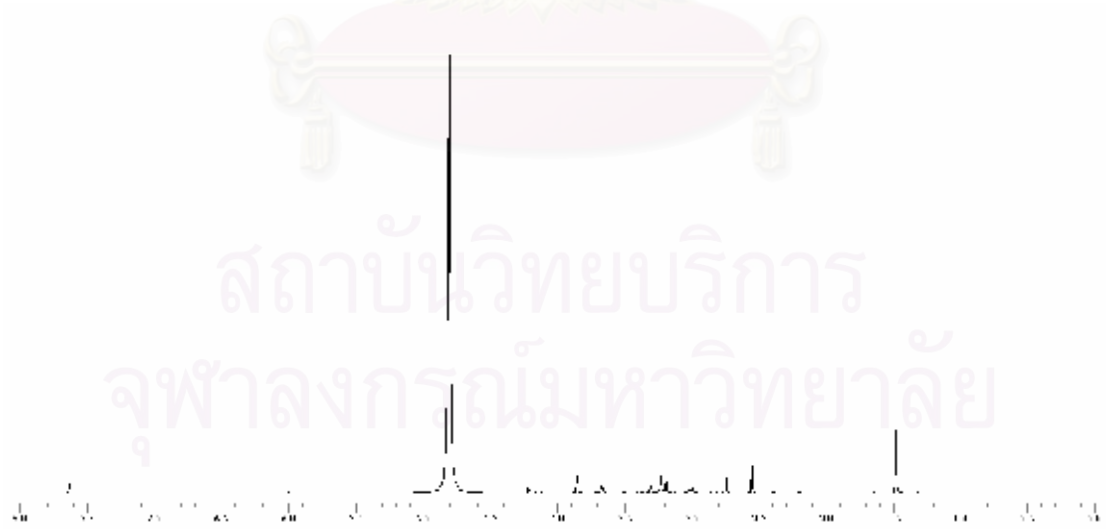

Figure B28 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 3A at 4 hour and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

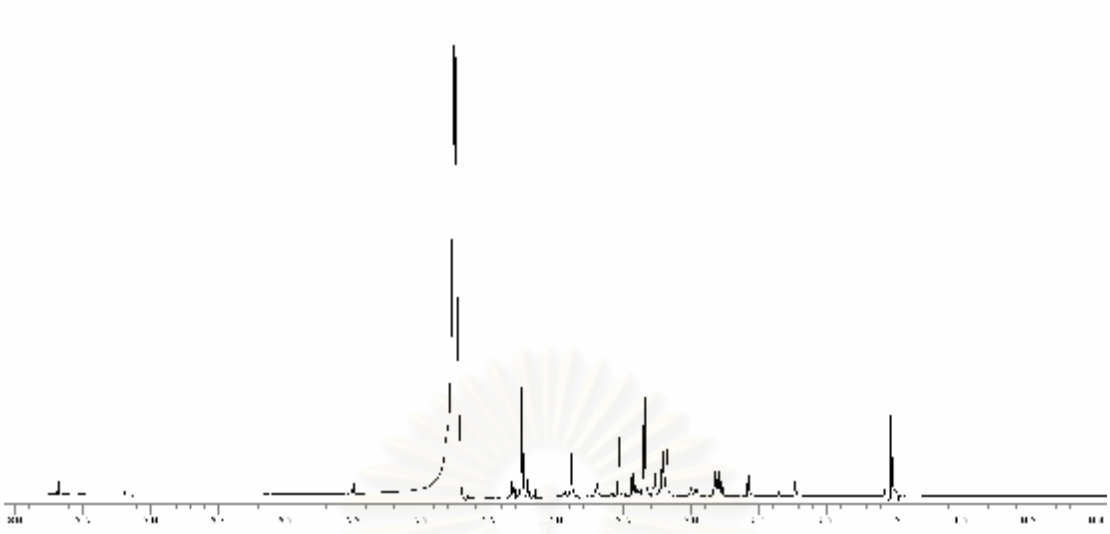

Figure B29 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 4A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

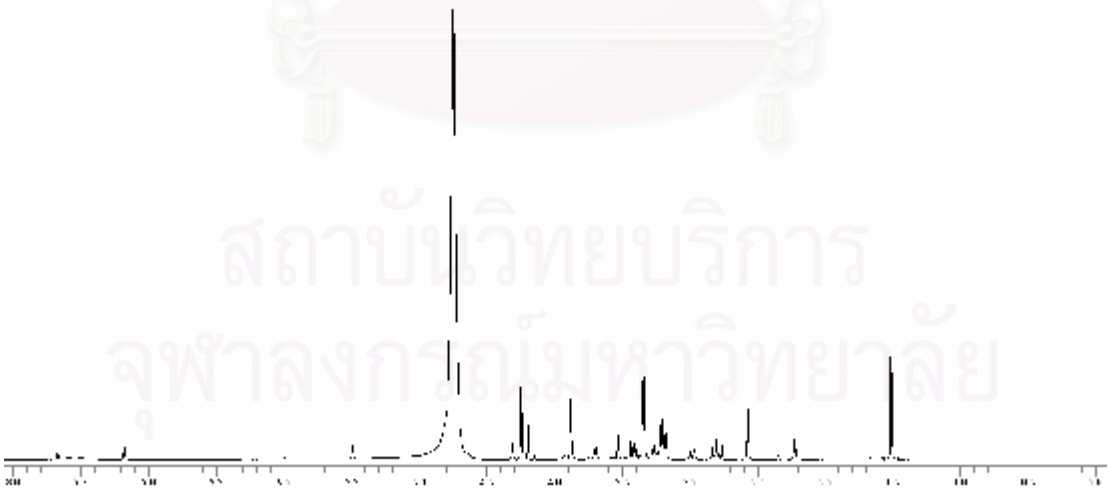

Figure B30 ^{1}H NMR spectrum of 200 mg the product mixture using 4 g (per glycine 1 mole) molecular sieve 5A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

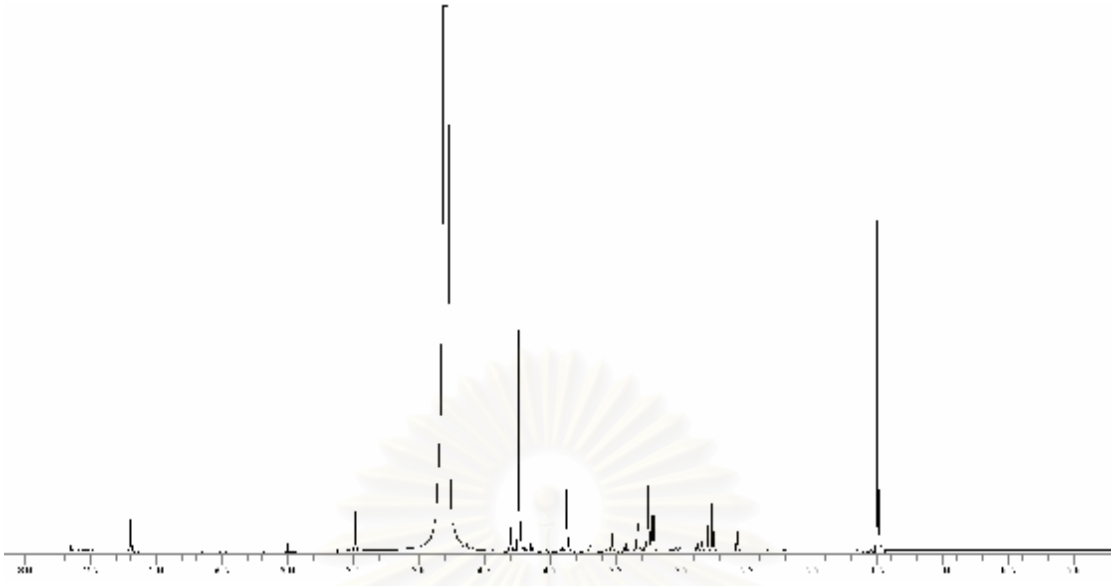

Figure B31 ^{1}H NMR spectrum of 200 mg the product mixture using 2 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

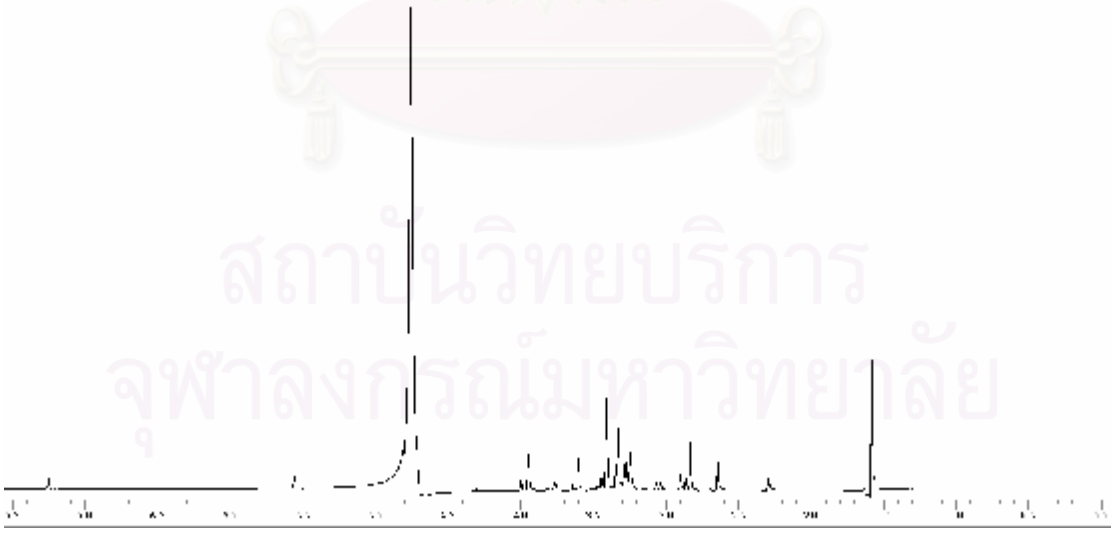

Figure B32 ^{1}H NMR spectrum of 200 mg the product mixture using 8 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

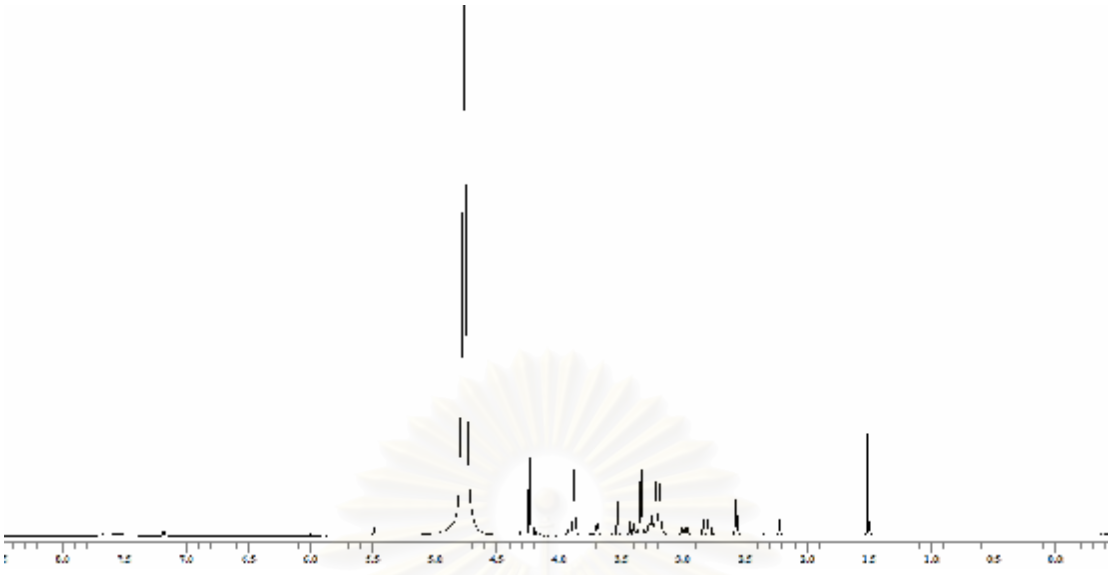

Figure B33 ^{1}H NMR spectrum of 200 mg the product mixture using 12 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

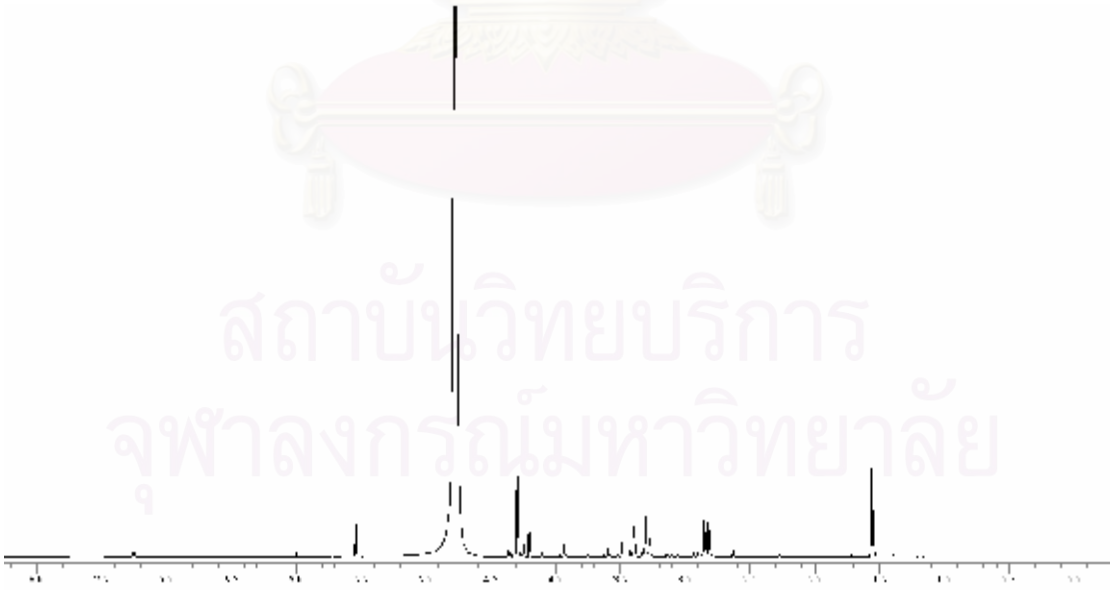

Figure B34 ^{1}H NMR spectrum of 200 mg the product mixture using 0.5 mole of phosphorous acid and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

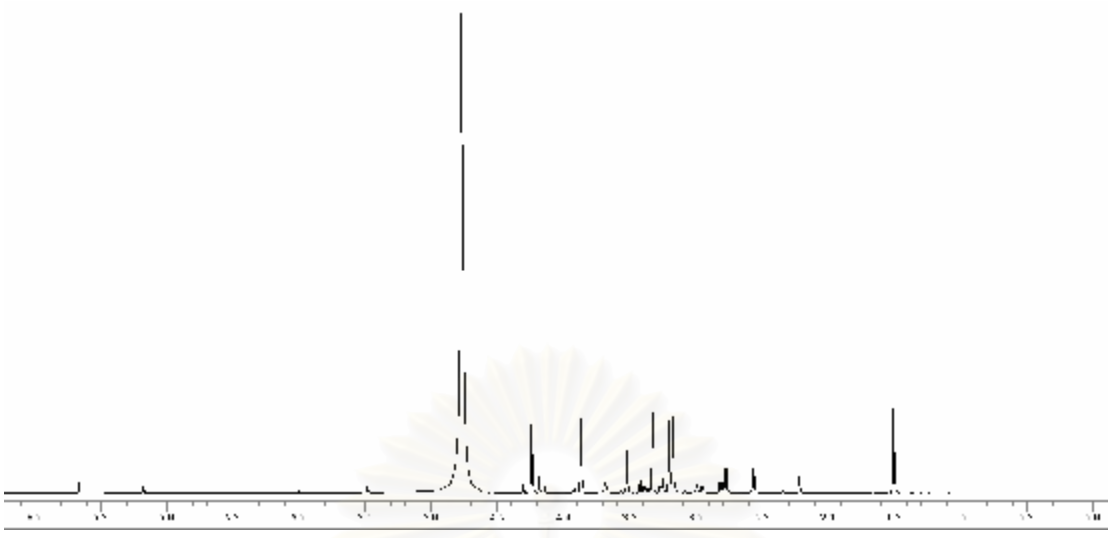

Figure B35 ^{1}H NMR spectrum of 200 mg the product mixture using 1.5 mole of phosphorous acid and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

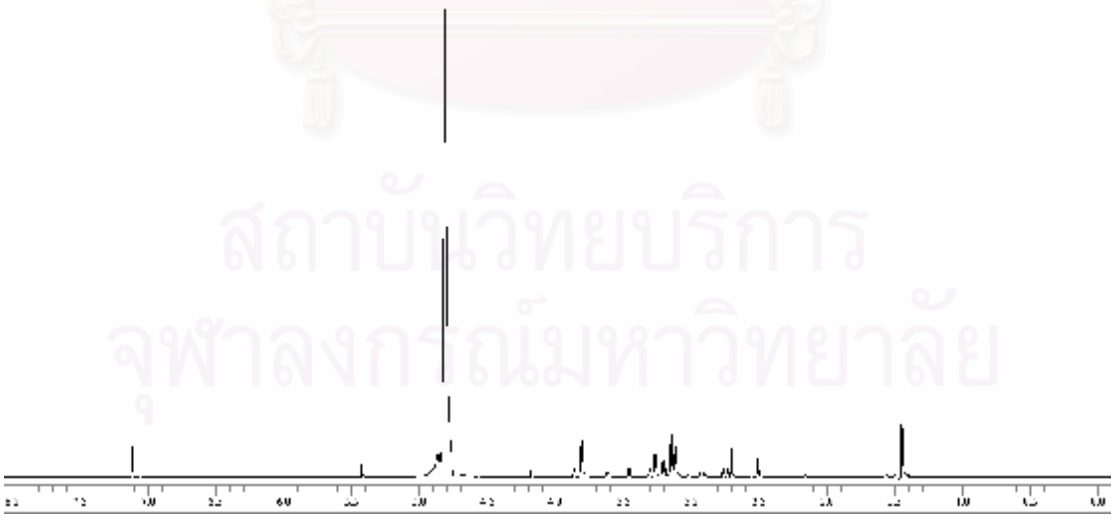

Figure B36 ^{1}H NMR spectrum of 200 mg the product mixture using 2 mole of phosphorous acid and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

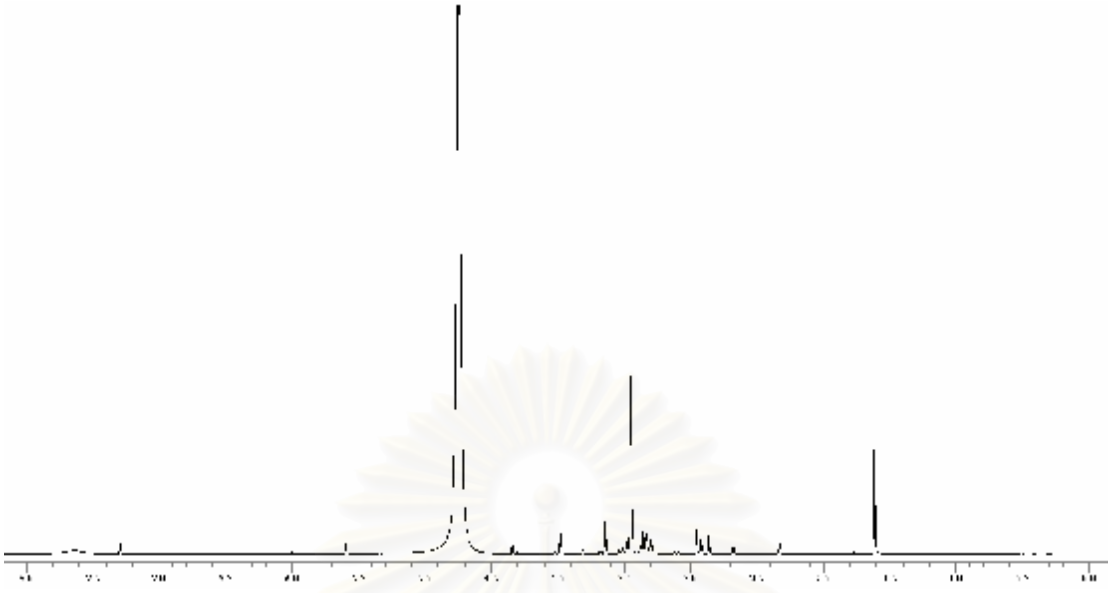

Figure B37 ^{1}H NMR spectrum of 200 mg the product mixture using 0.5 mole of phosphorous acid, 4 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

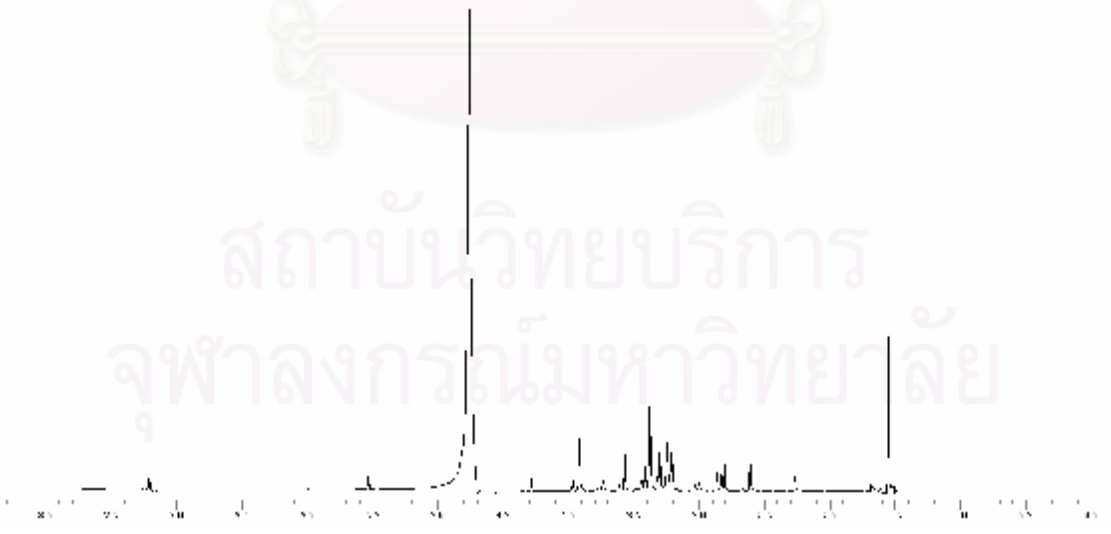

Figure B38 ^{1}H NMR spectrum of 200 mg the product mixture using 1.5 mole of phosphorous acid, 4 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

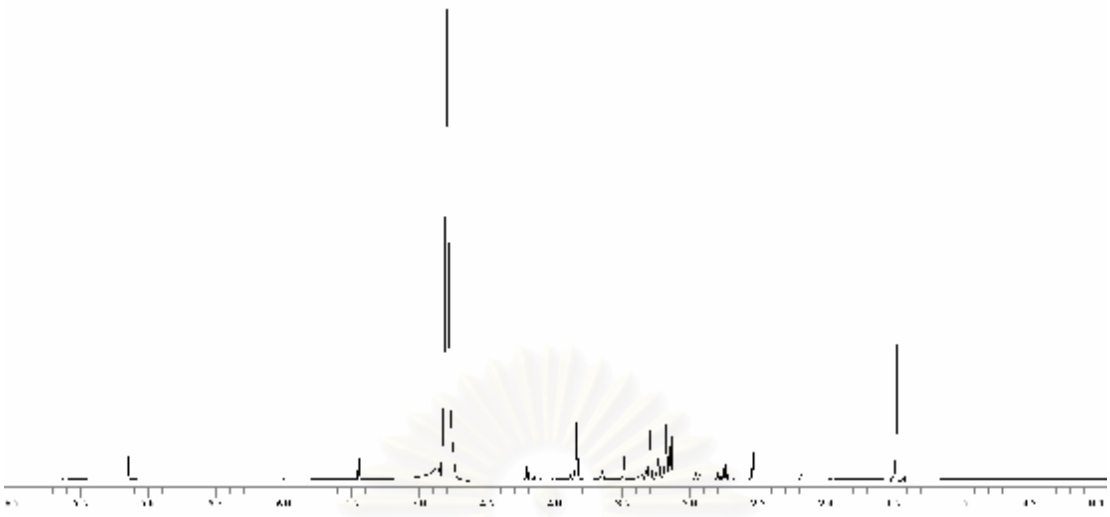

Figure B39 ^{1}H NMR spectrum of 200 mg the product mixture using 2 mole of phosphorous acid, 4 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

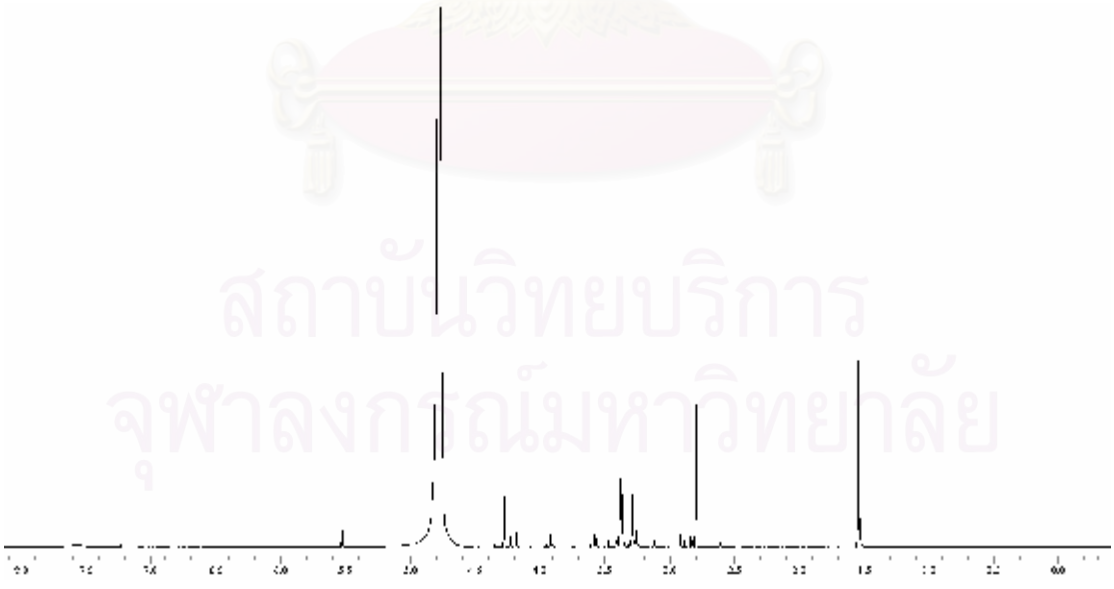

Figure B40 ^{1}H NMR spectrum of 200 mg the product mixture using 1 mole of formaldehyde and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

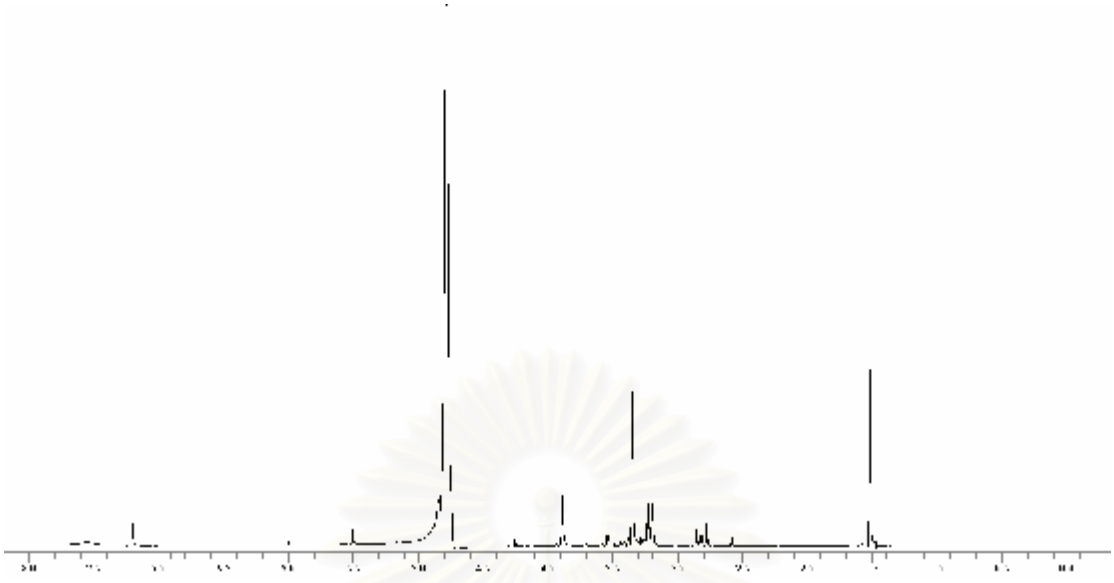

Figure B41 ^{1}H NMR spectrum of 200 mg the product mixture using 1 mole of formaldehyde, 4 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

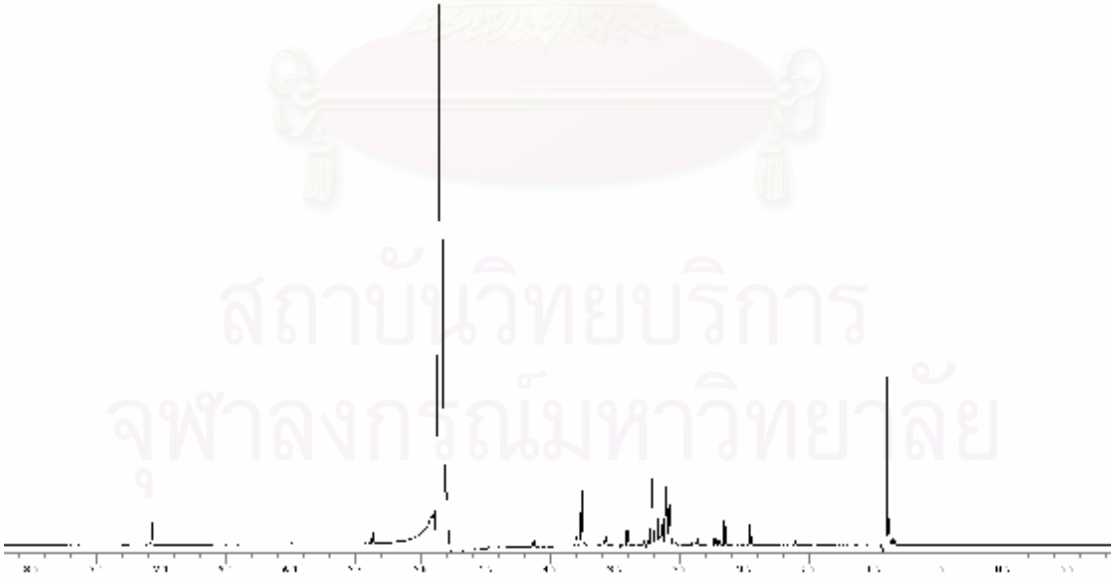

Figure B42 ^{1}H NMR spectrum of 200 mg the product mixture using 3 mole of formaldehyde and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

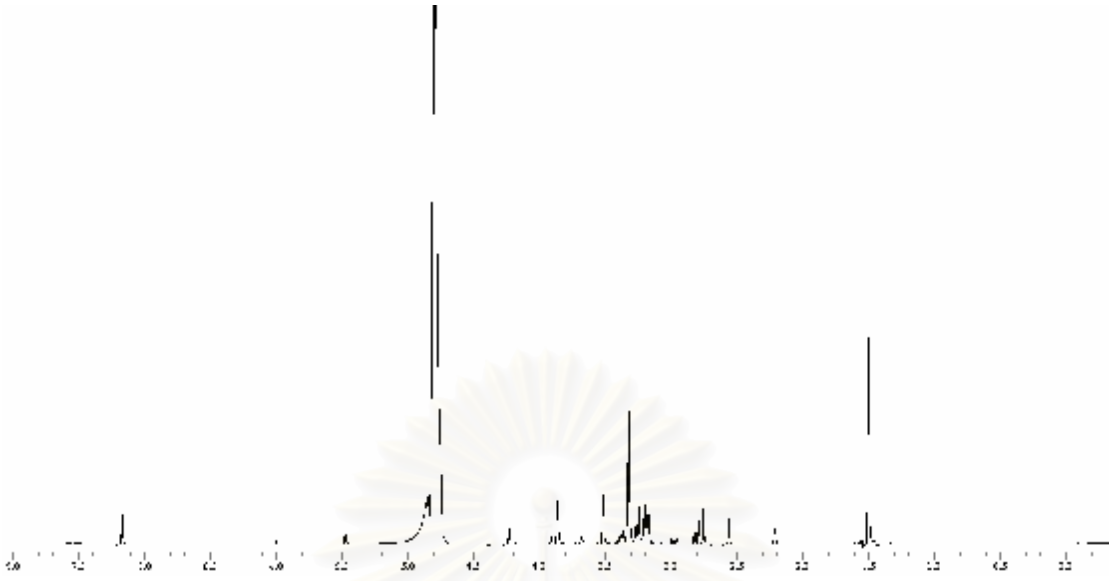

Figure B43 ^{1}H NMR spectrum of 200 mg the product mixture using 3 mole of formaldehyde, 4 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

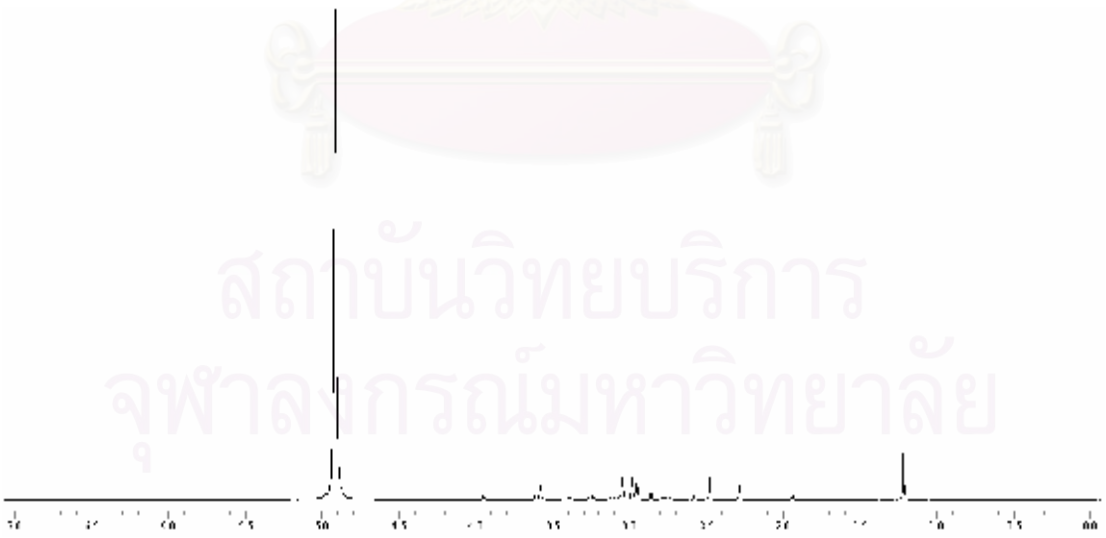

Figure B44 ^{1}H NMR spectrum of 200 mg the product mixture using concentrate sulfuric acid and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

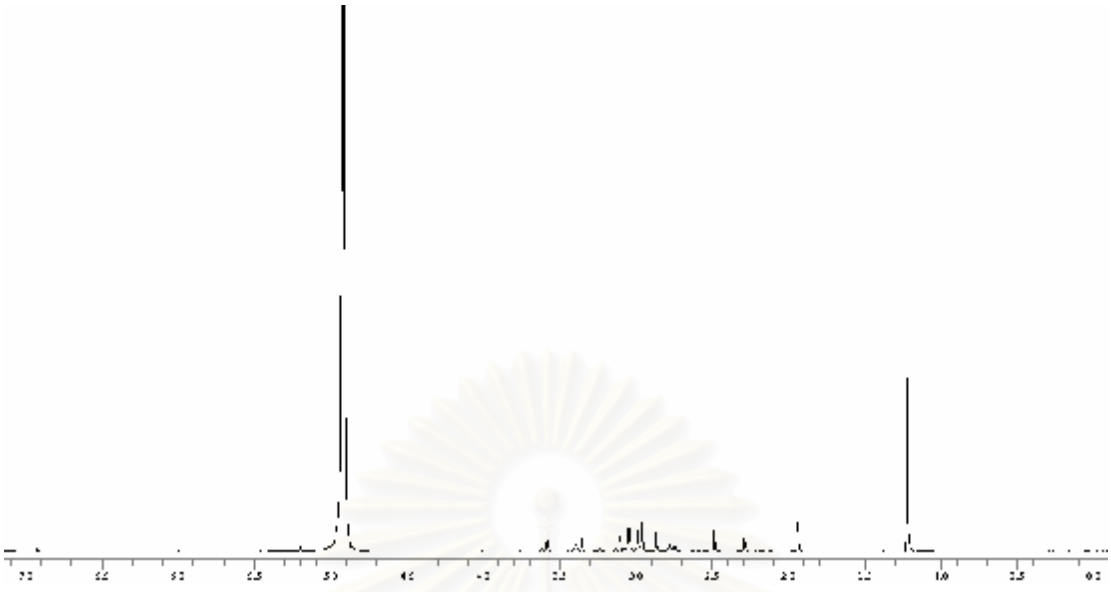

Figure B45 ^{1}H NMR spectrum of 200 mg the product mixture using concentrate sulfuric acid, 4 g (per glycine 1 mole) molecular sieve 3A and sodium acetate (25 mg) as internal standard in 0.5 ml of D_2O.

APPENDIX C

Calibration curve of *N*-phosphonomethylglycine salt

The ratio of peak intensity of CH_2-P (*N*-phosphonomethylglycine salt) and CH_3 (sodium acetate) in 0.5 ml D_2O with mole of *N*-phosphonomethylglycine salt are presented in Table C1. The standard curves of *N*-phosphonomethylglycine salt in D_2O are illustrated in Figure C1.

Table C1 The ratio of peak intensity of CH_2-P (*N*-phosphonomethylglycine salt) and CH_3 (sodium acetate) in 0.5 ml D_2O with mole of *N*-phosphonomethylglycine salt

Ratio of peak intensity of CH_2-P (glyphosate) and CH_3 (sodium acetate)	Mole of *N*-phosphonomethylglycine salt (mole)
0	0
0.0703	3.22×10^{-5}
0.1433	6.55×10^{-5}
0.2802	12.81×10^{-5}
0.4913	22.47×10^{-5}
1.0939	50.02×10^{-5}

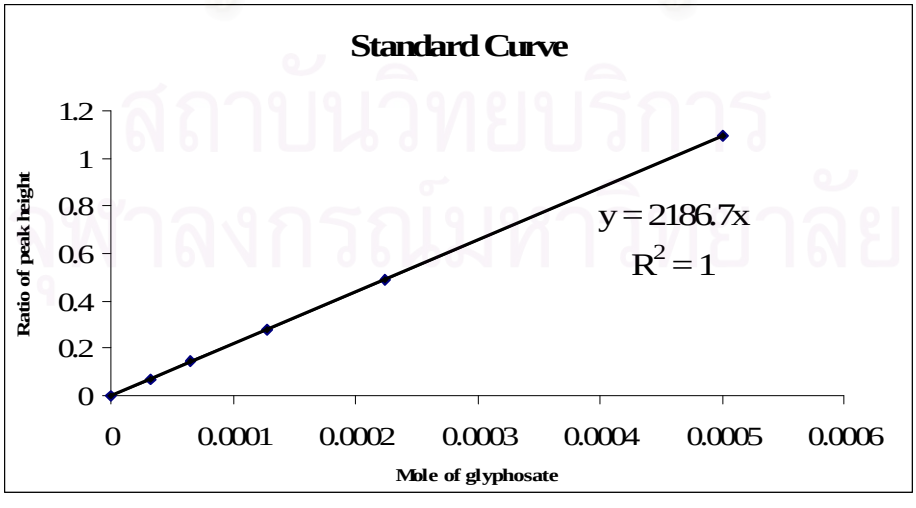

Figure C1 Calibration curve of *N*-phosphonomethylglycine salt in D_2O using sodium acetate as a catalyst.

Table C2 Effect of temperature on % yield of *N*-phosphonomethylglycine for 2 hours, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 and 37% w/v hydrochloric acid

Temperature (°C)	% Yield	
	Without molecular sieve	Acid treated molecular sieve 3A
30	0	0
60	14.66 ± 0.37	18.02 ± 1.78
70	31.01 ± 1.36	27.68 ± 1.09
80	21.16 ± 0.95	17.27 ± 1.53
100	14.59 ± 0.75	10.09 ± 0.18
120	9.98 ± 0.09	9.46 ± 0.25

Table C3 Effect of time on % yield of *N*-phosphonomethylglycine for 2 hours, mole ratio between glycine and phosphorous acid as 1:1, mole ratio between glycine and formaldehyde as 1:2 and 37% w/v hydrochloric acid

Time (hour)	% Yield	
	Without molecular sieve	Acid treated molecular sieve 3A
1	16.45 ± 0.2	13.38 ± 1.87
2	31.01 ± 1.36	27.68 ± 1.09
3	15.60 ± 0.64	10.07 ± 0.95
4	14.06 ± 0.54	10.72 ± 1.37

Table C4 Effect of mole ratio between glycine and phosphorous acid on % yield of *N*-phosphonomethylglycine for 2 hours, mole ratio between glycine and formaldehyde as 1:2 and 37% w/v hydrochloric acid

Ratio glycine : phosphorous acid	% yield	
	Without molecular sieve	Acid treated molecular sieve 3A
1:0.5	19.03 ± 1.92	39.47 ± 3.43
1:1	31.01 ± 1.36	27.68 ± 1.09
1:1.5	11.24 ± 0.05	18.42 ± 3.20
1:2	6.73 ± 0.15	5.96 ± 0.02

Table C5 Effect of mole ratio between glycine and formaldehyde on % yield of *N*-phosphonomethylglycine for 2 hours, mole ratio between glycine and phosphorous acid as 1:1 and 37% w/v hydrochloric acid

Ratio glycine : formaldehyde	% yield	
	Without molecular sieve	Acid treated molecular sieve 3A
1:1	19.78 ± 4.00	14.32 ± 2.20
1:2	31.01 ± 1.36	27.68 ± 1.09
1:3	9.74 ± 0.26	13.41 ± 1.24

Table C6 Effect of type of acid activated molecular sieve on % yield of *N*-phosphonomethylglycine for 2 hours, 70 °C, mole ratio between glycine and phosphorous acid, mole ratio between glycine and formaldehyde as 1:2 as 1:1 and 37% w/v hydrochloric acid

Type of acid activated molecular sieve	% yield
3A	27.68 ± 1.09
4A	15.64 ± 1.91
5A	14.04 ± 0.02

Table C7 Effect of content of acid activated molecular sieve 3A on % yield of *N*-phosphonomethylglycine for 2 hours, 70 °C, mole ratio between glycine and phosphorous acid, mole ratio between glycine and formaldehyde as 1:2 as 1:1 using 37% w/v hydrochloric acid

Content of acid activated molecular sieve 3A (gram per glycine 1 mole)	% yield
2	16.75 ± 3.10
4	27.68 ± 1.09
8	13.51 ± 0.71
12	11.61 ± 0.44

Table C8 Effect of hydrochloric acid and sulfuric acid on % yield of *N*-phosphonomethylglycine for 2 hours, 70 °C, mole ratio between glycine and phosphorous acid, mole ratio between glycine and formaldehyde as 1:2 as 1:1 using 37% w/v hydrochloric acid

Type of acid	% yield	
	Without molecular sieve	Acid treated molecular sieve 3A
Hydrochloric acid	31.01 ± 3.02	27.68 ± 0.89
Sulfuric acid	19.20 ± 0.58	7.657 ± 1.25

VITA

Mr. Pichate Hublee was born on Wednesday 4th November, 1981, in Bangkok, Thailand. In 2004, he graduated with a Bachelor's degree of Science in Chemistry, from Chulalongkorn University. After that, he has been studied for a Master's degree of science in Program of Petrochemistry and Polymer science, Faculty of Science, Chulalongkorn University, and completed the program in 2007.