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SYNTHESIS OF ZEOLITE FROM COAL FLY ASH AS WATER ADSORBENT

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งานวิจัยนี้ประกอบไปด้วยสองส่วนหลักด้วยกัน ในส่วนแรกเป็นการศึกษาความเป็นไปได้ในการนำเถ้าลอยถ่านหินมาใช้เป็นสารตั้งต้นเพื่อสังเคราะห์ซีโอไลท์ ซึ่งใช้ประโยชน์ในการดูดซับน้ำออกจากเอทานอลในกระบวนการผลิตเอทานอลบริสุทธิ์ โดยขั้นตอนการสังเคราะห์เริ่มจากการปรับปรุงคุณภาพของเถ้าลอย เพื่อกำจัดสิ่งเจือปน เช่น Fe2O3, CaO และสิ่งเจือปนอื่น ๆ ออกโดยใช้กรดชนิดต่างๆ (กรดไฮโดรคลอริก, กรดซัลฟิวริก และ กรดไนตริก) ทั้งนี้พบว่าสภาวะที่เหมาะสมที่สุดในการล้างสิ่งเจือปนออกจากเถ้าลอยถ่านหินคือการใช้กรดไฮโดรคลอริกเข้มข้น 20%โดยน้ำหนัก ที่สัดส่วน 20 มิลลิลิตรของกรดต่อกรัมของเถ้าลอย เพื่อล้างเถ้าลอยถ่านหินเป็นเวลา 2 ชั่วโมง ที่อุณหภูมิ 80oC โดยซีโอไลท์ที่สังเคราะห์จากเถ้าลอยถ่านหินที่ผ่านกระบวนการปรับปรุงคุณภาพภายใต้สภาวะดังกล่าวนั้นจะมีความบริสุทธิ์สูงได้ถึง 97% อีกทั้งยังมีค่าร้อยละความเป็นผลึกสัมพัทธ์ของซีโอไลท์เอ็กซ์สูงได้ถึง 88% และยังมีพื้นที่ผิวจำเพาะ 461 ตารางเมตรต่อกรัม อีกด้วย นอกจากนั้นยังมีการศึกษาการนำน้ำกรดที่ใช้ในกระบวนการปรับปรุงคุณภาพเถ้าลอยแล้วนั้นกลับมาใช้ใหม่เพื่อเป็นการลดผลกระทบที่เกิดขึ้นกับสิ่งแวดล้อม โดยพบว่าสิ่งเจือปนในเถ้าลอยถ่านหินถูกล้างออกโดยน้ำกรดที่นำกลับมาใช้ใหม่ได้อย่างมีประสิทธิภาพ และผลิตภัณฑ์ที่ได้นั้นยังคงมีความบริสุทธิ์สูงดังเดิม หลังจากปรับปรุงคุณภาพเถ้าลอยด้วยการล้างด้วยกรดแล้ว เถ้าลอยจะถูกแปรสภาพด้วยกระบวนการฟิวชั่นที่อุณหภูมิ 550°C เป็นเวลา 1 ชั่วโมง ด้วยสัดส่วนของโซเดียมไฮดรอกไซด์ 2.25 กรัมต่อกรัมของเถ้าลอย และปรับสัดส่วนโดยโมลของซิลิกอนต่ออะลูมิเนียม (Si/Al) ของเถ้าลอยให้มีค่าอยู่ในช่วง 0.54 ถึง 1.84 โดยการเติมอะลูมิเนียมออกไซด์โดยตรง หลังจากนั้นจึงนำเถ้าลอยที่แปรสภาพแล้วนี้มาตกผลึกที่อุณหภูมิ 80°C เป็นเวลา 4 ชั่วโมง ทั้งนี้พบว่าหากสัดส่วนโดยโมลของซิลิกอนต่ออะลูมิเนียมมีค่าน้อยกว่าหนึ่ง ซีโอไลท์ที่สังเคราะห์ได้จากสภาวะดังกล่าวจะเป็นซีโอไลท์ประเภทเอ และมีค่าผลได้อยู่ในช่วง 63-73% ในขณะที่ผลิตภัณฑ์ที่ได้จะเป็นซีโอไลท์ประเภทเอ็กซ์ ซึ่งจะมีค่าผลได้อยู่ในช่วง 28-33% หากสัดส่วนโดยโมลของซิลิกอนต่ออะลูมิเนียมมีค่ามากกว่าหนึ่ง

ในส่วนที่สองเป็นการทดสอบศักยภาพในการดูดซับน้ำของซีโอไลท์ที่สังเคราะห์ได้ดังกล่าวและเปรียบเทียบกับซีโอไลท์ที่มีขายในเชิงพาณิชย์ ทั้งนี้ซีโอไลท์ที่สังเคราะห์จากเถ้าลอยถ่านหินที่ปรับปรุงคุณภาพด้วยการล้างด้วยกรดภายใต้สภาวะที่เหมาะสมดังกล่าวและแปรสภาพเป็นซีโอไลท์ด้วยสัดส่วนของโซเดียมไฮดรอกไซด์ 2.25 กรัมต่อกรัมของเถ้าลอย และปรับสัดส่วนโดยโมลของซิลิกอนต่ออะลูมิเนียมเป็น 0.82 มีศักยภาพในการดูดซับน้ำออกจากเอทานอลได้มากกว่าซีโอไลท์ในเชิงพาณิชย์ที่ใช้ในระดับอุตสาหกรรม และจากการทดสอบการดูดซับน้ำออกจากเอทานอลที่อุณหภูมิ 90oC ด้วยซีโอไลท์ที่สังเคราะห์ได้ดังกล่าวพบว่าสามารถนำกลับมาใช้ใหม่ได้มากกว่า 10 ครั้ง และยังคงมีศักยภาพในการดูดซับที่มีประสิทธิภาพสูง โดยเอทานอลที่ผ่านกระบวนการดูดซับดังกล่าวแล้วจะมีความบริสุทธิ์สูงมากกว่า 99.5%โดยน้ำหนัก ทั้งนี้เมื่อทอสอบผลิตซีโอไลท์ดังกล่าวในระบบขนาดใหญ่ ผลิตภัณฑ์ที่ได้จะเป็นซีโอไลท์ประเภทเอ็กซ์และมีค่าผลได้ประมาณ 71-74% ในขณะที่ผลิตภัณฑ์ที่ได้จากการผลิตระดับห้องปฏิบัติการคือซีโอไลท์ประเภทเอ ทั้งนี้เนื่องมาจากความแตกต่างกันของเวลาในขั้นตอนการกรองแยก ซึ่งระบบขนาดใหญ่จะใช้เวลาในการกรองแยกมากกว่าทำให้ผลิตภัณฑ์ซีโอไลท์ที่ได้เปลี่ยนแปลงไป นอกจากนั้นจากการศึกษาศักยภาพการดูดซับน้ำของซีโอไลท์ที่ผลิตจากเถ้าลอยที่มีการปรับปรุงคุณภาพเถ้าลอยด้วยระบบต้นแบบขนาดใหญ่โดยล้างด้วยกรดไฮโดรคลอริกเข้มข้น 20%โดยน้ำหนัก พบว่าศักยภาพในการดูดซับน้ำของซีโอไลท์ที่สังเคราะห์จากระบบต้นแบบนี้จะมีค่าปริมาณการดูดซับสูงสุดมากกว่าตัวดูดซับในเชิงพาณิชย์ประเภท 3เอ แต่ยังคงมีค่าปริมาณการดูดซับน้ำสูงสุดน้อยกว่าตัวดูดซับในเชิงพาณิชย์ประเภท 4เอ แต่อย่างไรก็ตามเมื่อประเมินทางเศรษฐศาสตร์ พบว่าค่าใช้จ่ายในการผลิตซีโอไลท์ในระบบขนาดใหญ่มีค่าน้อยกว่าราคาของโมเลกูลาร์ซีฟที่ขายในปัจจุบัน

ภาควิชา วิศวกรรมเคมี

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ปีการศึกษา 2556

ลายมือชื่อนิสิต ....

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

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PANU PANITCHAKARN: SYNTHESIS OF ZEOLITE FROM COAL FLY ASH AS WATER ADSORBENT. ADVISOR: ASSOC. PROF. PRASERT PAVASANT, Ph.D.,ASSOC. PROF. NAVADOL LAOSIRIPOJANA, Ph.D., 110 pp.

This dissertation comprised two main parts. The first part is to evaluate the technical feasibility in the conversion of CFA to zeolite, which is widely employed in the ethanol purification unit. The synthesis began with the pretreatment of CFA to remove impurities (e.g., Fe2O3, CaO, etc.) under various acid types (HCl, H2SO4 and HNO3) and acid/CFA ratios (5 to 25 mlacid/gCFA). Due to the high purity (up to 97%), the high relative of zeolite X crystallinity (up to 88%), and the high specific area (461 m2/g), the use of 20%wt HCl with an L/S ratio of 20 mlHCl/gCFA to wash the CFA for 2 hr at 80°C were found to be the most suitable conditions for the acid-washing pretreatment. Furthermore, to reduce the environmental impact of the treatment process, the reuse of the acid was studied and found that most impurities in CFA could be removed effectively, and the products exhibited high purity. After acid-washing, the treated CFA was then converted to zeolite by fusion reaction at 550°C with a NaOH/CFA mass ratio of 2.25 and a Si/Al molar ratio in the range of 0.54 to 1.84. The Si/Al ratio was adjusted by mixing Al2O3 to the treated CFA. The fused product was further crystallized at 80°C for 4 hr. Zeolite type A was obtained with a yield in the range of 63-73% when the Si/Al molar ratios were lower than 1, whereas zeolite type X was formed with a yield in the range of 28-33% when the Si/Al molar ratio were higher than 1.

The second part is to investigate the water adsorption performance of the synthesized samples compared to the commercial grade molecular sieve. The zeolite synthesized using the most suitable conditions of acid-washing and zeolite synthesis (NaOH/CFA mass ratio of 2.25 and Si/Al molar ratio of 0.82), had a higher water adsorption performance than the commercial grade molecular sieve and under ten adsorption-testing cycles at 90°C, a high ethanol purity (>99.5%wt) can still be achieved without deactivation. Zeolite from the large scale production was always found to take the form of zeolite type X whereas that from the small scale was type A. This discrepancy occurred due to the inherited long filtration time in the large reactor which allowed further development of zeolite (from A to X). This gave a yield in the range of 71-74%. Regarding water adsorption performance, the maximum adsorption capacity of the sample treated with 20%wt using the large scale production were lower than the commercial molecular sieve type 4A, the maximum adsorption capacity of these samples were higher than the commercial molecular sieve type 3A. However, an economic analysis demonstrated that the total expense per batch of zeolite synthesized by large scale is relatively low when compared with the cost of commercial grade molecular sieve.

Department:	Chemical Engineering	Student's Signature	
Field of Study:	Chemical Engineering	Advisor's Signature	
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CHAPTER 1

INTRODUCTION

1.1 Motivations

The world energy crisis has become severe due to the depletion of fossil fuels. A blend of ethanol and gasoline (gasohol) can be used as an alternative fuel source for spark-ignition engines with an anhydrous ethanol content as low as 0.2%wt, which is sufficient to improve the octane number of petrol (Jako´biec and Marchut, 2000; Kornblit and Marchut, 1996; Richard and Bechtold, 1997). Moreover, ethanol can also be used as an additive to diesel fuels (Satgé D. C. et al., 2001). Biogenic ethanol is produced from the fermentation of feedstocks such as molasses, cassava and corn. These processes typically produce ethanol with approximately 30% concentration (by volume). Importantly, this ethanol solution must be concentrated by distillation and then dehydration to high purity ethanol prior to mixing with gasoline, because of the azeotrope formation at 78.2°C and 1.013 bar with 4.4% of water that cannot be removed by a simple distillation. Dehydration of the remaining water in ethanol solution by adsorption technique is therefore required to enhance the ethanol concentration to more than 95%wt. This is typically achieved through the use of molecular sieve water adsorption.

Coal fly ash (CFA) is an important by-product generated by the combustion of coal in power generation. It was reported that Thailand regularly generated more than 6 million tons of CFA per year (reported in year 2011) and is on a rising trend ("Energy Policy and Planning of Thailand," 2011). At present, many technologies have been developed for the disposal of CFA such as the use as a raw material substitute in cement production. As the major component of CFA is amorphous aluminosilicate glasses (about 80 %) (Molina and Poole, 2004), the conversion of CFA to zeolite has been proposed as a viable method. This is not only to generate a useful adsorbent but also to enhance the value of industrial waste CFA.

It has been reported that many types of zeolite can be synthesized (Moïse et al., 2001; Querol et al., 2002) from CFA, and among these, zeolite type A and faujasite are known as the most valuable forms as they have a uniform pore size and a high cation exchange capacity (CEC), which makes them an interesting adsorbent, molecular sieve, catalyst and a high cation exchange material (Querol et al., 2002). Large scale ethanol/water separation processes utilize zeolite A, or molecular sieve, that preferentially adsorbs water while ethanol molecules are excluded. Nevertheless, the reports relevant to water adsorption properties of zeolite A remain limited.

There are currently two potential zeolite production routes, i.e. hydrothermal and fusion methods (Breck, 1998; Querol et al., 2002). The fusion method gains advantages in terms of the short time requirement (Querol et al., 2002) and the achievement of high purity product (Jha et al., 2009; Rayalu et al., 2001), whereas the hydrothermal method benefits from the consistent pattern of zeolite product. Generally, the fusion method is preferable for the solid-phase reaction, while the hydrothermal method is more appropriate for the reaction in liquid phase. Hence, the fusion method is considered an appropriate technique for solid CFA conversion. For the fusion method, several researchers (Apiratikul and Pavasant, 2006, 2008; Jha et al., 2009; Mishra and Tiwari, 2006; Molina and Poole, 2004) have agreed that the preparing conditions, e.g. NaOH/CFA ratio, reaction time and temperature show significant impacts on the physical and chemical properties of zeolite products; hence, the zeolite synthesis conditions must be carefully controlled.

In this work, there is an effort underway to find an appropriate method of resource recovery and reuse of sub-bituminous CFA obtained from the pulping process in one of the commercial plantations in Thailand. Due to the presence of high impurities in raw CFA, the acid-washing pretreatment was proposed as a purification option prior to the fusion process. Various acid-washing pretreatment conditions were carried out in order to determine the suitable conditions for removing impurities from CFA. The influence of the Si/Al molar ratios of the CFA source on physical and chemical properties of synthesized zeolite were investigated. After converting CFA to zeolite, the synthesized samples were tested as water sorbent from ethanol solution. Its adsorption capacity was also compared to the commercial grade molecular sieve. Finally, the scaling up of such zeolite synthesis process was proposed and examined for its feasibility.

1.2 Objectives

The objectives of this work are to find the suitable conditions for the synthesis of zeolite from CFA using the fusion method followed by the hydrothermal method and to scale up the zeolite synthesis process. After the zeolite is completely synthesized, it is tested as water sorbent from ethanol solution.

1.3 Scopes of this work

This work is carried out based on some limitations as follows:

1.3.1 Pretreatment of CFA

- The acid categories used to remove the impurities from CFA are hydrochloric acid, nitric acid and sulfuric acid.

1.3.2 Zeolite synthesis

- The Si/Al molar ratio ranges from 0.54 to 1.84.

1.3.3 Water adsorption

- The synthesized zeolite are tested as water sorbent from 95%wt ethanol solution and compared with the commercial grade molecular sieve.

1.3.4 Scale up

- The synthesized zeolite process is scaled-up to large scale size, 1 kg CFA per batch.

CHAPTER 2

BACKGROUNDS AND LITERATURE REVIEW

2.1 Fly ash

2.1.1 Classification of fly ash

Fly ash is one of the residues generated in the combustion process. It is comprised of fine particles that rise with flue gases. Fly ash is generally captured by electrostatic precipitators (ESP) or other particle filtration equipments before it reaches the chimneys of coal-fired power plants.

Fly ash can be sub-divided into two major classes as specified in ASTM C 618 on the basis of their chemical composition resulting from the type of coal burned (ASTMC618, 2003).

1. Class F is fly ash normally produced from burning anthracite or bituminous coal,
2. Class C is fly ash normally produced from the burning of sub-bituminous coal and lignite.

The compositional similarity of fly ash to some volcanic material, precursor of natural zeolite, was the main reason to experiment with the synthesis of zeolite from the coal by-product (CFA) by Holler and Wirsching (Höller and Wirsching, 1985). The quality of the final zeolite product varies significantly because of the difference of raw fly ash properties.

Differences in coal impurity compositions, particularly those unburned minerals, mainly silica, alumina, calcium, magnesium and iron compounds dictate the quality of CFA, which has a direct effect on the quality of zeolite synthesized from CFA.

2.1.2 Chemical composition of coal fly ash

The components of CFA vary considerably. It is dependent on the source and makeup of the coal being burned, but all CFA includes substantial amounts of silicon dioxide (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), magnesium oxide (MgO) and iron oxide (Fe_2O_3). CFA also contains environmental toxins in significant quantities, including arsenic (As), barium (Ba), beryllium (Be), borom (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), fluorime (F), lead (Pb), manganese (Mn), nickel (Ni), vanadium (V) and zinc (Zn), etc. The concentrations of trace elements vary according to the type of coal.

2.2 Zeolite

In 1756, the Swedish mineralogist heated an unidentified silicate mineral and observed that it fused readily in a blowpipe flame with marked intumescence (Cronstedt, 1756). This result led him to call minerals that behaved in this manner “zeolite” (derived from the Greek words “zeo” (to boil) and “lithos” (stone)).

Zeolites are actually natural products. However, not all natural zeolites have been recreated in the laboratory, and conversely, many zeolites have been synthesized that do not occur in nature. Mineral or natural zeolite is a crystal of aluminosiligate group of mono or divalent base, which are mostly found in ore mining. Partial or full lose of water can occur during the process of crystallization, but the crystal structure remains the same. Mineral zeolites samples are faujasite, erionite, offreite, chabazite, gmelinite, mordernite, heulandite etc (Tongkam, 1999). Usually, synthesized zeolites are preferred over natural ones due to the possibility of adjusting their pore size through different synthesizing techniques. Many types of different zeolite synthesized from CFA, e.g. zeolite type A and faujasite, are more common because they are an interesting adsorbent having molecular sieve properties and can be used as catalysts, supports, and a high cation exchange material (Querol et al., 2002).

2.2.1 Zeolite structure

Structurally the zeolites are framework aluminosilicates, which are based on an infinitely extending three-dimensional network of $[AlO_4]^{-4}$ and $[SiO_4]^{-5}$ tetrahedra linked to each other by oxygen (Figure 2.1). The structural formula of a zeolite is based on the crystallographic unit cell, the smallest unit of structure, represented by:

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

where n is the valence of metal cation M, w is the number of water molecules per unit cell, x and y are the numbers of total tetrahedra per unit cell, and y/x usually has values of 1-5, in the case of high silica zeolite y/x is 10 to 100.

The primary unit is the structure of the zeolite, which consists of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral (Figure 2.1).each of which contains a silicon or aluminum atom in the center. The secondary building units are assembled by the primary structural units which may be simple polyhedra such as cubes, hexagonal prisms, or octahedral (Figure 2.2). The framework structures of the zeolite are composed of assembled secondary building units (Figure 2.3).

The framework structure contains channels or interconnected voids that are occupied by the cation and water molecules. The cations are quite mobile and usually are exchanged by other cations. The water in zeolite can be removed and is reversible. Dehydration and cation exchange of many zeolites may produce structural changes to the framework.

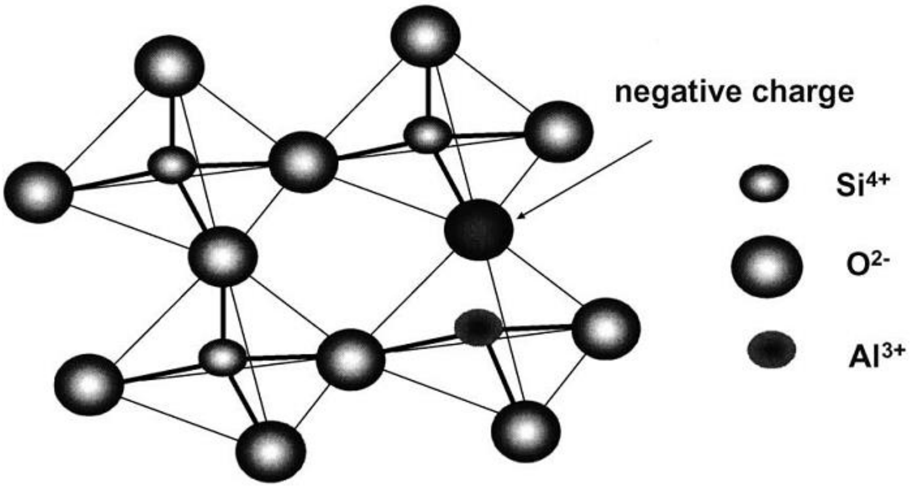


Figure 2. 1 Idealized structure of zeolite framework of tetrahedral [SiO4]4- with a Si/Al substitution ([AlO4]5-) yielding a negative charge, and consequently a cation exchange capacity.(Breck, 1998)

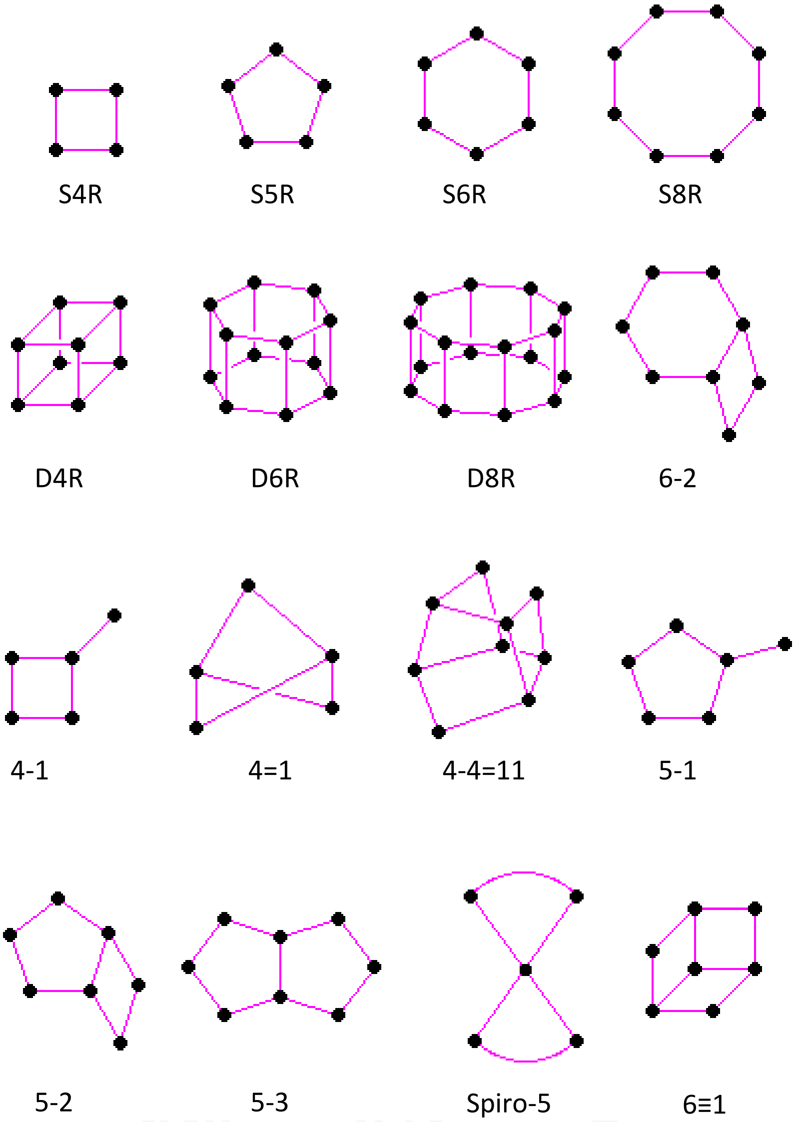


Figure 2. 2 Secondary Building Units (SBU) in zeolite

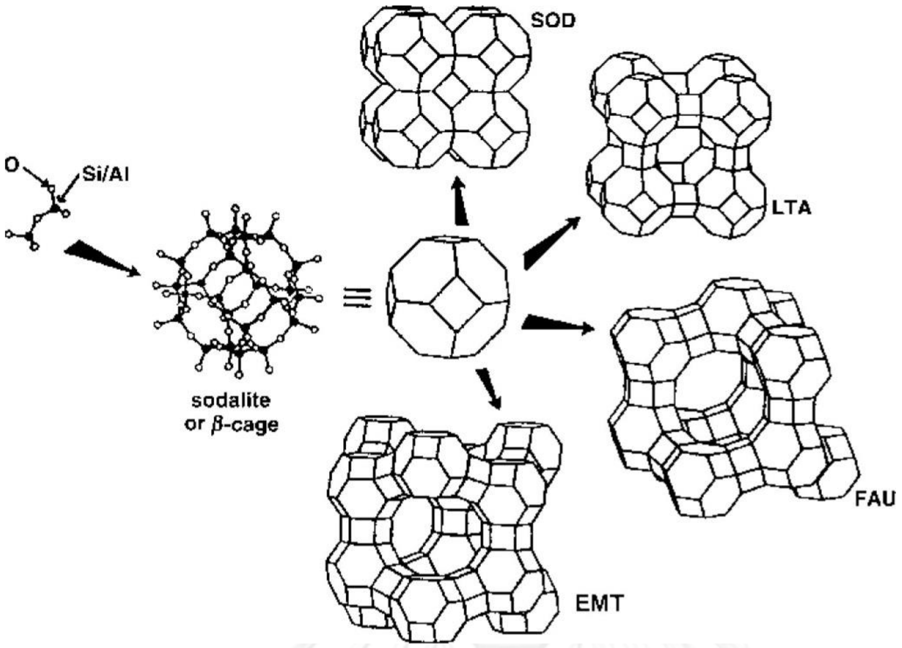


Figure 2. 3 Construction of four different zeolite frameworks (Auerbach et al., 2003)

Recent structural analyses of many zeolites have led to systems for the identification and classification of zeolites, which are based upon structural and physicochemical characteristics rather than external appearance. The classification based on the framework topology of zeolite consists of seven groups (Table 2.1). Although, in other classifications, each group has been named after a representative member, an arbitrary designation by number is preferable since no single member is more representative than any other.

The Structure Commission of the International Zeolite Association (IZA) identifies each framework with a three-letter mnemonic code (Auerbach et al., 2003). Table 2.2 lists the three-letter codes for zeolite framework types.

2.2.2Zeolite properties

Table 2.3 shows the properties of zeolite. Zeolite is porous in nature and their structure can accommodate a wide variety of cations. These positive ions can be easily exchanged for others. Zeolite belongs to the "molecular sieves" family of microporous solids. The ability to sort molecules based on size or the term molecular sieve refers to a particular property of these materials. This property arises due to the regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter or leave the pores of a zeolite is controlled by the dimensions of the channels.

However, it is important to note that the well established zeolite, i.e. A, X and Y are known as the most valuable zeolite forms, due to their superior performance and relatively low production cost, as they do not require the use of expensive or complex organic structure directing agents for their synthesis (Breck, 1998; Querol et al., 2002).

Zeolite type A is of most interest because its supercage structure is useful in catalysis. The inner cavity is large enough for structure changing reactions to take place, but the small pore means only a specific structure can get into the cavity for reaction, typically n-paraffins and olefins. One use is in paraffin cracking. Zeolite A is also widely used in molecular sieve.

Faujasite was described as a new mineral (Damour, 1842) for crystals previously considered apophyllite at Sasbach, Kaiserstuhl, Germany. Faujasite is a rare zeolite, but is well known, because it has the same framework topology as Linde X and Linde Y, synthetic counterparts used as sorbents and catalysts. There are several other types of zeolite where Table 2.3 summarizes the properties of some common ones.

2.3 Applications of zeolite

As a consequence of the peculiar structural properties of zeolite, they have a wide range of industrial applications (Breck, 1998). Table 2.4 shows the application of zeolite mainly based on:

- Ion exchange: High cation exchange capacity of zeolite allows them to be used as resin for exchanging cations of divalent.
- Adsorption and separation: The shape-selective properties of zeolite are also the basis for their use in molecular adsorption. The ability to adsorb certain molecules while excluding others, has opened up a wide range of molecular sieving applications.
- Catalysts: Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. This is exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Zeolite can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework.
- Others: The largest single use for zeolite is the global detergent market. The use of synthetic zeolite as builders in detergent formulation led to an increase on their production from 146 X 10^3 metric tons in 1978 to 720 X 10^3 metric tons in 1990 (De Lucas et al., 1992). Furthermore, zeolite can also be used in many applications such as construction, medical and agriculture.

2.4 Synthesis of zeolite

There are two main methods for the synthesis of zeolite, one is hydrothermal method and the other is fusion method (Breck, 1998; Querol et al., 2002). However, due to the presence of impurities in raw CFA, the acid washing pretreatment and the magmatic separator method were sometimes performed prior to the zeolite synthesis process as this was proven effective in removing several mineral compounds from CFA as shown in Table 2.5 (Molina and Poole, 2004; Shin et al., 1995; Wang et al., 2008).

The fusion method gains advantages in terms of the short time requirement (Querol et al., 2002) and the achievement of high purity product (Jha et al., 2009; Rayalu et al., 2001), whereas the hydrothermal method benefits from the consistent pattern of zeolite product. Generally, it is known that the fusion method is preferable for the solid phase reaction, while the hydrothermal method is more appropriate for the reaction in liquid phase. The properties of final zeolite product depend upon a complex interaction between many variables including SiO_2/Al_2O_3 ratio in the starting medium, fusion temperature, pH, water content, aging, stirring, and the presence of various inorganic and organic cations. Table 2.6 summarizes some of the part reports on how zeolites were being produced from CFA.

2.5 Literature review

As stated earlier, the properties of zeolite can be manipulated by varying several formation parameters. The tetrahedra ($[AlO_4]^{-4}$ and $[SiO_4]^{-5}$) make up a three dimensional network, with lots of voids and open spaces. These voids define many special properties of zeolite, such as the adsorption of molecules in the channels. The cation exchange capacity (CEC) is one of the most significant properties of zeolite for adsorption and ion exchange applications. The Silica and Alumina ratio of zeolite chemical components and several parameters of zeolite formation such as fusion temperature, concentration of the activation agent, crystallization temperature and crystallization time also have a very important influence on the zeolite types and the physical and chemical properties of zeolite obtained.

2.5.1 Synthesis

In this section, only the fusion method is considered because the speed of reaction is fast and it is often reported to yield a product with higher CEC than the hydrothermal product (Shigemoto et al., 1993). Literature regarding the effect of the various parameters on yield and the CEC properties of the zeolite can be summarized as follows.

Table 2.7 shows the effect of the ratio of activated reagent (e.g. NaOH) and the CFA. It demonstrates that the percent crystallinity and also the CEC increased with an increase in NaOH content. In addition, the change of ratio of NaOH and CFA would result in different types of zeolite produced, such as faujasite and zeolite type A. However, there seems to exist an appropriate proportion of the synthesized agents remaining, otherwise the quality of the final zeolite would be lowered (Ruen-ngam et al., 2009; Shigemoto et al., 1993).

The fusion temperature is also an important factor for the formation of zeolite. Table 2.8 shows that there was an increasing trend in CEC, surface area and percent of crystallinity of zeolite when the fusion temperature was increased. In addition, at too high a fusion temperature, negative effects would be exhibited on all of the properties of the zeolite produced. At high temperatures, the iron bearing components in the fly ash could be decomposed and incorporated into the framework of the zeolite during the fusion reaction (Vaughan et al., 1995). This limited the crystallization process, resulting in inferior zeolite properties such as low CEC value and surface area.

Table 2.9 demonstrates the effect of crystallization temperature: one of important factors for the formation of zeolite. Crystallization is the process that forms the crystal framework of the zeolite. It was reported that the crystal frameworks of the zeolite would occur faster at higher temperatures (Tsitsishuili et al., 1992). High crystallization temperatures led to a better CEC property (see Table 2.3). Conversely, at too high a crystallization temperature, the CEC decreased. However, there are only a few investigations on this aspect and so far there were no reports on the effect of crystallization temperature higher than 120°C which is perhaps due to the high evaporation loss at the boiling point temperature of water (Wajima and Munakata, 2011).

Table 2.10 demonstrates the effect of crystallization time, which illustrates that a higher crystallization time could lead to zeolite with higher CEC. However, it was reported that a long crystallization time could reduce the CEC of the final product (Ruen-ngam et al., 2009). Furthermore, Molina and Poole (2004) demonstrated that different types of zeolite were formed at different crystallization times, from a less stable to a more stable type. However, there were no reports relating to the stability of zeolite with CEC properties in this work.

The effect of the Si/Al ratio is also an important factor in the formation of many types of zeolite achieved. The summary in Table 2.11 illustrates that zeolite A and faujasite could form from CFA with Si/Al ratios in the range of 1–5. These results are consistent with the findings of Breck, 1998; Rabo and Schoonover, 2001; Somerset et al., 2005 .

2.5.2 Pilot plant scale

Zones presented a number of issues that need to be taken into account before considering a zeolite commercialization (Zones, 2011). Firstly, safety concerns with equipment and products must be addressed. Their price and their possible risks from an environmental and a health point of view have to be considered, if organic structure directing agent (SDA) molecules are used. Concerning the synthesis process itself, synthesis time, reaction temperature and post synthesis steps have to be carefully evaluated. Finally, the waste streams generated and their possible treatment must be taken into account.

Despite considerable laboratory research in this field, there is a lack of experimentation at pilot plant scale to confirm the results obtained. Table 2.12 presents a review on large scale zeolite synthesis. CFA has been used as a silica and alumina source for zeolite synthesis, and single phases of zeolite A, X, GIS, P1 and ZSM-5 have been described. General synthetic conditions may be inferred to synthesize different zeolites from CFA. It was reported that NaP zeolite synthesis from fly ash were highly reproducible (% NaP zeolite = 35-40%) at the pilot plant scale (started with CFA 1,100kg) (Querol et al., 2001). However, there are several technical and economical issues associated with the commercial production of synthesis zeolite. Generally, the long holding time and the time period for maintaining the reaction temperature (De Lucas et al., 1992; Kim et al., 1998; Rabo and Schoonover, 2001) and/or large amount of alkali metal hydroxide charge were needed to produce zeolite with a high yield (Querol et al., 2001). Some processes employed a relatively short holding time, but such processes still needed a large amount of alkali metal hydroxide charge (Moriyama et al., 2005). Another one of the main drawbacks is that a complete conversion of CFA into the crystalline zeolite could not be achieved. Moreover, CFA was usually processed without prior purification, and remaining coal and impurities such as Fe_2O_3 and CaO may contaminate the final zeolite product.

Table 2. 1 Classification of zeolite minerals based on the framework topology

Group	Secondary Building Unit	Nanme
Group 1	Single 4-ring, S4R	Analcime Philipsite Laumontite
Group 2	Single 6- ring, S6R	Erionite Sodalite
Group 3	Double 4-ring, D4R	A N-A ZK-4
Group 4	Double 6-ring, D6R	Faujasite Chabazite Gmelinite
Group 5	Complex 4-1, T_5O_{10} unit	Natrilite Thomosite
Group 6	Complex 5-1, T_8O_{16} unit	Mordanite Dachhiardite
Group 7	Complex 4-4-1, $T_{10}O_{20}$ unit	Heulandite Cinoptilolite

Table 2. 2 Nomenclature of zeolites and molecular sieves (Auerbach et al., 2003)

Structure	Code	Structure	Code
Li-A(BW)	ABW	Linde type A	LTA
Afghanite	AFG	Linde type L	LTL
Anaclime	ANA	Linde type N	LTN
Bikitaite	BIK	Mazzite	MAZ
Brewsterite	BRE	ZSM-11	MEL
Cancrinite	CAN	Melanophlogite	MEP
Chabazite	CHA	Merionite	MER
Dachiardite	DAC	ZSM-5	MFI
Deca-dodecasil-3R	DDR	Mordenite	MOR
Dodecasil-1H	DOH	ZSM-39	MTN
TMA-E(AB)	EAB	ZSM-23	MTT
Edingtonite	EDI	ZSM-12	MTW
Epistilbite	EPI	Natrolite	NAT
Erionite	ERI	Nonasil	NON
Faujasite	FAU	Offretite	OFF
Ferrierite	FER	Partheite	PAR
Gismondine	GIS	Paulingite	PAU
Gmelinite	GMF	Phillipsite	PHI
Goosecreekite	GOO	Rho	RHO
Heulandite	HEU	Roggianite	ROG
ZK-5	KFI	Sodalite	SOD
Laumonite	LAU	Stilbite	STI
Levyne	LEV	Thomsonite	THO
Liottite	LIO	Theta-1	TON
Losod	LOS	Wenkite	WEN
Lovdarite	LOV	Yugawaralite	YUG

Table 2. 3 Zeolite properties

Zeolite type	Structure group	Pore size (A°)	SBU	Void volume (mL/mL)	Framework density (g/mL)	Largest molecule adsorb
Analcime	1	2.6	S4R	0.18	1.85	NH_3
Philipsite	1		S4R	0.31	1.58	H_2O
P	1	2.6	S4R	0.41	1.57	H_2O
Sodalite	2	2.2	S6R	0.35	1.72	H_2O
A	3	4.2	D4R	0.5	1.3	C_2H_4
N-A	3	4.2 in **α-** cage	D4R	0.5	1.3	*n*-parafin
ZK-5	4	7.4	D6R	0.44	1.46	*n*-parafin
X	4	7.4	D6R	0.5	1.31	$(C_4H_9)_3N$
Y	4	7.4	D6R	0.48	1.25-1.29	$(C_4H_9)_3N$
Natrolite	5	2.6x3.9	Unit4-1	0.23	1.76	NH_3
Thomosite	5	2.6x3.9	Unit4-1	0.32	1.76	NH_3
Mordanite	6	6.7x7.0	Unit5-1	0.28	1.70	C_2H_4
Epistilbite	6	3.2x5.3	Unit5-1	0.25	1.76	H_2O
Heulandite	7	4.4x7.2	Unit4-4-1	0.39	1.69	NH_3
Cinoptilolite	7	-	-	0.34	1.71	O_2

Table 2. 4 Applications of zeolites

Applications	Source	Zeolite	Reference:
1 Adsorption and separation			
1.1 Ethanol purification	Coal fly ash	Sodium Aluminum Silicate Hydrate	(Klamrassamee et al., 2010)
1.2 Flue gas treatment (CO_2 capture)	Coal fly ash	Zeolite A and X	(Liu et al., 2010)
1.3 Flue gas treatment (SO_2 and NO_2)	Coal fly ash	NaP	(Srinivasan and Grutzeck, 1999)
1.4 Purification of acid mine water	Coal fly ash	NaP	(Moreno et al., 2001a)
2. Catalysts			
2.1 organic reactions	-	-	(Martínez and Corma, 2011)
2.2 crude oil cracking	-	-	(Martínez and Corma, 2011)
2.3 isomerization	Commercial	Zeolite A	(Fejes et al., 1984)
2.4 fuel reformation	Commercial	ZSM-5	(Lee, 2007)
2.5 NOx decomposition	Commercial	Fe-ZSM-5	(Prechtl et al., 2009)
3. Ion exchange			
3.1 Removal of Fe^{3+}, Al^{3+}, Cu^{2+}, Pb^{2+}, Cdl^{2+}, Ti^{+}, Zn^{2+}, Mn^{2+}, Ca^{2+}, $Sr^{2+}$and Mg^{2+} from wastewater	Coal fly ash	NaP	(Moreno et al., 2001b) (Querol et al., 2006)
3.2 Immobilization of heavy metal in contaminated soils	Coal fly ash	Na	(Shih and Chang, 1996)
3.3 Removal NH_4^+ and Cs^+ from wastewater	Coal fly ash	Zeolite A and Faujasite	(Zhang et al., 2011)
3.4 Removal of ammonium from aqueous solution	Coal fly ash	Faujasite, Zeolite A and P	
4. Others			
4.1 Detergents	Coal fly ash	NaP	(Kazemian et al., 2010)
4.2 Construction	Commercial	Natural Zeolite	(Ikotun and Ekolu, 2010)
4.3 Medical (haemostatic dressings)	-	Ag Zn Zeolite	(Li et al., 2009)
4.4 Agriculture	-	-	(Ramesh et al., 2011)

Table 2. 5 Pretreat method

Method	Conditions	Result	Reference:
Acid washing	10%wt HCl, L/S=25:1, 300 rpm, 100°C, 24 hr	Reduce iron oxide 76%	(Wang et al., 2008)
Magnetic separator	6,500 – 15,000g field intensity	Reduce iron oxide 58% - 71%	(Shin et al., 1995)
Magnetic separator	9,000g field intensity using an Eriez wet high intensity magnetic separator	Reduce iron oxide 65%	(Molina and Poole, 2004)

Table 2. 6 Synthetic methods of zeolite

Method	Conditions	Zeolite of type	Raw Mat.	Product	Reference:
Fusion follow by Hydrothermal	1. Fusion at 550°C for 2 hr with NaOH/CFA = 2:1 2. Hydrothermal at temp 100°C for 12 hr	Faujasite and Zeolite A	Coal fly ash	Yield = 30-60% Crystallinity = 20-60%	(Shigemoto, 1996; Shigemoto et al., 1993)
Fusion follow by Hydrothermal	1. Fusion at 550°C for 2 hr with NaOH/CFA = 2:1 2. Hydrothermal at temp 100°C for 12 hr	Zeolite P and Sodalite	Coal fly ash	Yield = 50% CEC 400 meq/100g	(Berkgaut and Singer, 1996)
Molten salt conversion	The molten mixture containing 0.7 g fly ash, 0.3 g base (KOH, NaOH and NH_4F), and 1 g salt (KNO_3, $NaNO_3$ and NH_4NO_3), heat at temp = 350±5°C for 24 hr	Sodalite and Cancrinite	Coal fly ash	CEC = 84-206 meq/100g Surface area = 86-276 m^2/g	(Park et al., 2000a, b)
Two step	1. Hydrothermal at 90°C for 24 hr with 2M of NaOH 2. Adjust Si/Al molar ratio to 0.8-2 and hydrothermal 90°C for 48 hr with 2M of NaOH	Zeolite X, Zeolite A and NaP	Coal fly ash	Yield = 50-80% CEC = 360-430 meq/100g	(Hollman et al., 1999)
Hydrothermal	80 -200°C, 3-48 hr	Up to 13 types of zeolite	Coal fly ash	CEC = 160-260 meq/100g	(Querol et al., 2002; Querol et al., 1997)

Table 2.6 Synthetic methods of zeolite (Continued)

Method	Conditions	Zeolite of type	Raw Mat.	Product	Reference:
Fusion follow by Hydrothermal	1. Fusion at 750°C for 1 hr with NaOH/CFA = 2:1 2. Stirring and aging for 2 hr at room temperature 3. Hydrothermal at temp 80°C for 6-24 hr	Zeolite X	Coal fly ash	CEC = 407 meq/100g Crystallinity = 68%	(Jha et al., 2009)
Fusion follow by Hydrothermal	1. Fusion at 500-600°C for 1-2 hr with NaOH/CFA = 1:1.2 2. Stirring and aging for 8 h at room temperature 3. Crystallization at 90-110°C for 2-24 hr	Zeolite X, Zeolite Y and Zeolite A	Coal fly ash	CEC = 400-450 meq/100g Surface area = 500-600 m^2/g	(Rayalu et al., 2000)
Fusion follow by Hydrothermal	1. Fusion at 600°C 2. Hydrothermal at temp 105°C for 20 hr	Zeolite 13X	Coal fly ash	Surface area = 500-430 m^2/g	(Mishra and Tiwari, 2006)
Fusion follow by Hydrothermal	1. Fusion at 250-550°C for 1 hr with NaOH/CFA = 0.5-3 2. Stirring and aging at 30°C for 12 hr 3. Crystallization at 60-120°C for 2-6 hr	Zeolite X	Coal fly ash	Yield = 79% CEC = 240 meq/100g Surface area = 305-325 m^2/g	(Ruen-ngam et al., 2009)
Hydrothermal	Fly ash 34.93g was mixed with 0.723-10.845g of NaOH in 80ml of DI water Hydrothermal at 100-160°C for 4-8hr	α-Quaz and Zeolite A	Coal fly ash	Crystallinity = 72% Surface Area = 41.2 m^2g^{-1} CEC = 377-400 meq/100g	(Chareonpanich et al., 2011)
Fusion follow by Hydrothermal	1. Fusion at 550°C for 1 hr with NaOH/CFA = 1:1.2 2. Hydrothermal use ultrasonic water bath at temp 25-30°C for 1 hr	Zeolite X	Coal fly ash	Crystallinity = 30%	(Belviso et al., 2011)

Table 2. 7 Effect of ratio of activation reagent

Activated reagent	Reagent/CFA ratio	CEC (meq/100g)	% Crystallinity	Yield (%wt)	Type of zeolite	References
NaOH	0.8			0	Zeolite X	(Shigemoto et al., 1993)
	1.2			60	Zeolite X	
	1.6			30	Zeolite X	
	2			0	Zeolite X	
NaOH	10	100			Zeolite X	(Molina and Poole, 2004)
	12	250			Zeolite X	
	14	230			Zeolite HS	
	16	200			Zeolite HS	
	20	100			Zeolite HS	
NaOH	11				No zeolite	(Somerset et al., 2005)
	12				Zeolite A	
	15				Zeolite A	
NaOH	1		10		Na-X zeolite	(Ojha et al., 2004)
	1.25		70		Na-X zeolite	
	1.3		80		Na-X zeolite	
	1.5		30		Na-X zeolite	

Table 2.7 Effect of ratio of activation reagent (Continued)

Activated reagent	Reagent/CFA ratio	CEC (meq/100g)	% Crystallinity	Yield (%wt)	Type of zeolite	References
NaOH	0	13		30	Zeolite X	(Ruen-ngam et al., 2009)
	0.5	32		23	Zeolite X	
	1.0	64		21	Zeolite X	
	1.25	101		22	Zeolite X	
	1.5	112		33	Zeolite X	
	1.75	129		61	Zeolite X	
	2.0	131		43	Zeolite X	
	2.25	153		43	Zeolite X	
	2.5	141		43	Zeolite X	
	3.0	75		38	Zeolite X	
NaOH	0.5				Zeolite P	(Kyung and Young, 2010)
	0.8				Sodalite	
	1.0				Sodalite	
	1.5				Sodalite	
	2.0				Sodalite	

Table 2. 8 Effect of fusion temperature

Fusion temperature (^{o}C)	Reagent/CFA ratio	CEC (meq/100g)	Surface area (m^2/g)	% Crystallinity	Type of zeolite	References
127				22	Zeolite X	(Shigemoto et al., 1993)
327				38	Zeolite X	
527				62	Zeolite X	
727				42	Zeolite X	
200				formation negligible	Zeolite Y	(Rayalu et al., 2000)
600				fully crystalline	Zeolite Y	
800				fully crystalline	Zeolite Y	
250	2.25	206	193		Zeolite X	(Ruen-ngam et al., 2009)
350	2.25	224	210		Zeolite X	
450	2.25	241	250		Zeolite X	
550	2.25	240	236		Zeolite X	

Table 2. 9 Effect of crystallization temperature

Crystallization temperature (^{o}C)	Reagent/CFA ratio	CEC (meq/100g)	Surface area (m^2/g)	Crystallinity	Type of zeolite	References
40		170		no crystallinity	Zeolite X	(Molina and Poole, 2004)
60		135		little crystallinity	Zeolite X	
90		250		maximum crystallinity	Zeolite X	
60	2.25	174	99		Zeolite X	(Ruen-ngam et al., 2009)
90	2.25	241	289		Zeolite X	
120	2.25	203	215		Zeolite X	
40	1.2				Zeolite X	(Belviso et al., 2010)
45	1.2				Zeolite X	
60	1.2				Zeolite X	
70	1.2				Zeolite A , Zolite ZK5	
90	1.2				Zeolite X, Sodalite	
80		120	12.5		Sodalite	(Wajima and Munakata, 2011)
120		70	14		Sodalite	
160		45	11		Katoite	

Table 2. 10 Effect of crystallization time

Crystallization time (Hour)	Reagent/CFA ratio	CEC (meq/100g)	Surface area (m^2/g)	Crystallinity	Type of zeolite	References
3		300			Zeolite A	(Rayalu et al., 2001)
3.5		430			Zeolite A	
0.5				no crystallinity	No zeolite	(Molina and Poole, 2004)
1				little crystallinity	Zeolite X	
2				maximum crystallinity	Zeolite X	
6				little crystallinity	Zeolite X, P	
2	2.25	241	275		Zeolite X	(Ruen-ngam et al., 2009)
4	2.25	305	230		Zeolite X	
6	2.25	216	236		Zeolite X	

Table 2. 11 Effect of Si/Al ratio

Si/Al molar ratio	CEC (meq/100g)	Surface area (m^2/g)	% Crystallinity	Yield (%wt)	Type of zeolite	References
2.22	250	236	57	55	Zeolite X	(Ruen-ngam et al., 2009)
4.06	240	325	79	68	Zeolite X	
4.63	221	283	65	57	Zeolite X	
0.5	62.5			-	Amorphous	(Ma et al., 2010)
1	260			61.3	Zeolite A	
1.5	286			79.6	Zeolite A	
2	275			70.3	Zeolite A	
2.6	254			46.6	Zeolite A	
3.2	245			-	Zeolite P	

Table 2. 12 Large scale zeolite synthesis

Reactor	Conditions	Type of zeolite	Raw Mat.	Product	References
Stirr Reactor Volume = 50L	1. Gel formation at 50-80°C for 0.5-3hr, Stirr at 125-750 rpm 2. Aging at 20-40 °C for 0-48hr 3. Crystallization at 50-90 °C	Zeolite 13X amd Zeolite A	Kaolin P. for silica, Spanish natural clay for Al_2O_3	48 kg of zeolite per batch Crystallinity = 94-95% Application: use in detergent	(De Lucas et al., 1992)
Stainless Reactor Volume = 30L	Hydrothermal at 100 °C for 72hr	ZSM-5	Reagent grade silica, Tetrapropylammonium bromide and Sodium aluminate	Crystallinity = 100% Surface Area = 371 m^2/g Yield > 70%	(Kim et al., 1998)
Stainless Reactor Volume = 10,000L CFA = 1,100kg NaOH = 352kg	Hydrothermal at 150 °C for 24Hr NaOH concentration = 2M 2L of NaOH /kg fly ash	Zeolite P	CFA	CEC = 160-260 meq/100g %NaP Zeolite = 35-40%%	(Querol et al., 2001)
Volume = 600L CFA = 130kg	Hydrothermal at 420K for 150min NaOH = 2.5-3.5 mol/dm^3 Liquid/Solid = 0.88-1.1 dm^3/kg of CFA	Zeolite GIS	4 Types of CFA	CEC = 145-200 meq/100g	(Moriyama et al., 2005)
CFA = 0.5kg	Hydrothermal at 120 °C for 4Hr	Zeolite A	1. CFA was used to prepare sodium silicate solution 2. sodium aluminate	Crystallinity = 72% Surface Area = 41.2 m^2/g CEC = 377-400 meq/100g	(Chareonpanich et al., 2011)

CHAPTER 3

MATERIALS AND METHODS

3.1 Sources of CFA

CFA was collected for 9 times (between December 2010 to December 2011) from the pulping process in a commercial plantation area in Prachinburi province of Thailand.

3.2 Acid-washing pretreatment procedures

Various acid-washing pretreatment conditions were carried out in order to determine the suitable conditions for removing impurities from CFA.

3.2.1 Effect of acid categories

1. Mix 20 g of CFA with 500 mL (to make the acid to CFA ratio (L/S ratio) of 25:1) of HCl acid (20%w/w or 6M) in flask (1 L)
2. Stir constantly (300 rpm) on the magnetic stirrer at 80°C for 2 hr
3. Filter off the solid sample using Glass micro fiber filter (Whatman GF/C) and wash the sample repeatedly with DI water until the solution reaches neutral pH
4. Dry the solid sample overnight at 105°C in the kiln
5. Repeat Steps 1-4 with H_2SO_4 (20%w/w or 2.4M) and HNO_3 (20%w/w or 3.6M) under the same L/S ratio

3.2.2 Effect of acid to CFA ratio

1. Mix 20 g of CFA with 100 mL (to make the acid to CFA ratio (L/S ratio) of 5:1) of HCl acid (20%w/w or 6M) in flask (1 L)
2. Stir constantly (300 rpm) on the magnetic stirrer at 80°C for 2 hr
3. Filter off the solid sample using Glass micro fiber filter (Whatman GF/C) and wash the sample repeatedly with DI water until the solution reaches neutral pH
4. Dry the solid sample overnight at 105°C in the kiln
5. Repeat Steps 1-4 with different L/S ratio (10:1 15:1, 20:1 and 25:1)

3.2.3 Effect of reusing acid

1. Mix 20 g of CFA with 500 mL (to make the acid to CFA ratio (L/S ratio) of 20:1) of HCl acid (20%w/w or 6M) in flask (1 L)
2. Stir constantly (300 rpm) on the magnetic stirrer at 80°C for 2 hr
3. Filter off the solid sample using Glass micro fiber filter (Whatman GF/C) and wash the sample repeatedly with DI water until the solution reaches neutral pH
4. Dry the solid sample overnight at 105°C in the kiln
5. Repeat Steps 1-4 with 20 mL of filtered HCl from Step 3, add fresh HCl (20%w/w or 6M) to yield HCl (mL):CFA (g) ratio of 20:1

3.3 Zeolite synthesis procedure

For this part, the method developed by Ruen-ngam et al. (2009) (the fusion method followed by the hydrothermal method) was employed. Zeolite synthesis procedure is diagrammatically shown in Figure 3.1. A stainless steel reactor with the length of 25 cm and the diameter of 5 cm was used as the zeolite synthesis reactor.

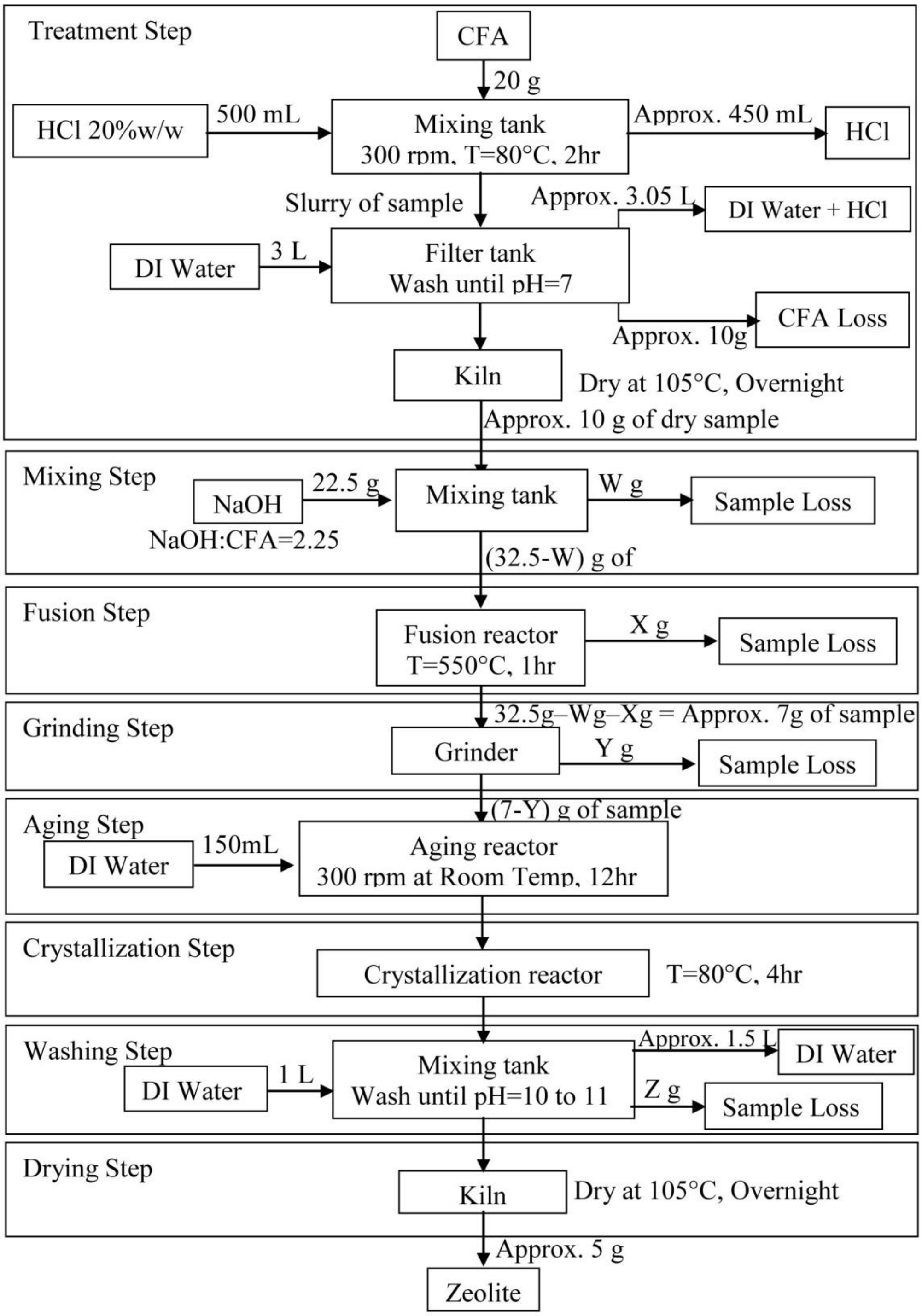
The schematic diagrams of zeolite synthesis experimental setup at the lab scale are shown in Figure 3.2. In this work, the batch composition refers to the batch preparation stated in ratios of oxides. The basis is a singular formula mole of Al_2O_3.

3.3.1 Effect of raw material

1. Mix 10 g of CFA (from Section 3.2) with 22.5 g of NaOH (NaOH anhydrous, Sigma-Aldrich) to make the NaOH/CFA mass ratio of 2.25 (Ruen-ngam et al., 2009) (Note: The batch composition is shown in Table 3.1)
2. Grind the mixture until homogeneous using mortar and pestle
3. Load the mixture in the zeolite synthesis reactor (Figure 3.2) and burn the mixture at 550°C for 1 hr using furnace
4. Remove the solid sample from the reactor and grind it using mortar and pestle
5. Mix the product with 100 mL of DI water in flask (1 L) and stir the mixture constantly on the magnetic stirrer at 300 rpm at room temperature for 12 hr
6. Crystallize under static condition of 80°C for 4 hr
7. Recover the crystal by filtration using Glass micro fiber filter (Whatman GF/C) and wash thoroughly with DI water (until the filtrate reaches pH 10-11)
8. Dry the solid sample overnight at 105°C in the kiln
9. Repeat Steps 1-7 with CFA collected from different times
10. Compare the results with the untreated CFA (repeat Steps 1-7 with untreated CFA)

3.3.2 Effect of Si/Al ratio

1. Analyze the CFA chemical compositions using XRF and adjust the Si/Al molar ratio of CFA to be 1.00 by adding Al_2O_3 (99.9% Al_2O_3 powder, Sigma-Aldrich) directly to the CFA (Note: The batch composition is shown in Table 3.1)
2. Mix 10 g of CFA (from Section 3.2) with 22.5 g of NaOH (NaOH anhydrous, Sigma-Aldrich) to make the NaOH/CFA mass ratio of 2.25 (Ruen-ngam et al., 2009)
3. Grind the mixture until homogeneous using mortar and pestle
4. Load the mixture in the zeolite synthesis reactor (Figure 3.2) and burn the mixture at 550°C for 1 hr using furnace
5. Remove the solid sample from the reactor and grind it using mortar and pestle
6. Mix the product with 100 mL of DI water in flask (1 L) and stir the mixture constantly on the magnetic stirrer at 300 rpm at room temperature for 12 hr
7. Crystallize under static condition of 80°C for 4 hr
8. Recover the crystal by filtration using Glass micro fiber filter (Whatman GF/C) and wash thoroughly with DI water (until the filtrate reaches pH 10-11)
9. Repeat Steps 1-7 with CFA that is adjusted the Si/Al molar ratio to 0.82, 0.67 and 0.54



Note : W = Sample loss from mixing step (g) X = Sample loss from fusion step (g)
Y = Sample loss from grinding step (g) Z = Sample loss from washing step (g)

Figure 3. 1 Zeolite synthesis process

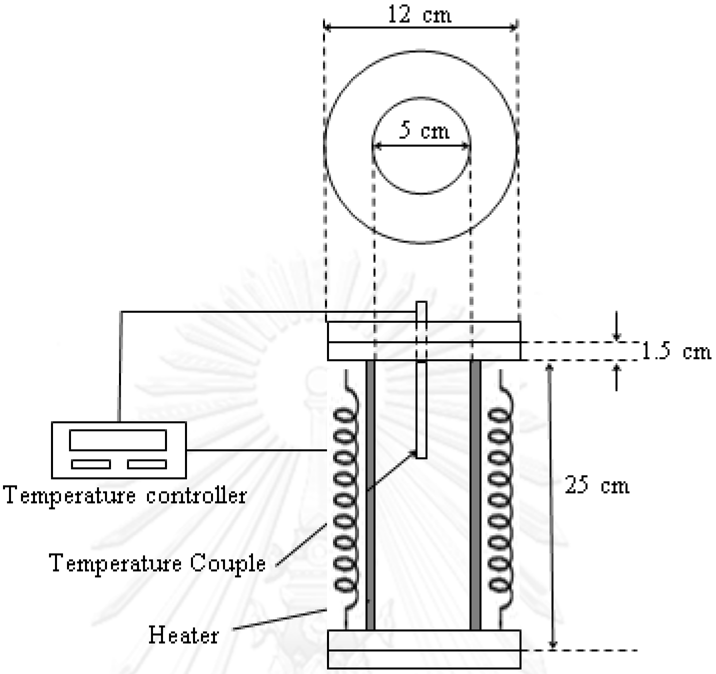


Figure 3. 2 Zeolite synthesis experimental set-up and schematic diagram of fusion reactor at lab scale

3.4 Adsorption method procedure

The schematic diagram of the adsorption testing experiment system is shown in Figure 3.3.

1. Dry the zeolite sample in the kiln at 105°C overnight
2. Pack zeolite in the fix-bed adsorption reactor (use glass wool as a bed support) and set the equipment as shown in Figure 3.3
3. Activate the zeolite sample at 250°C for 4 hr and flow nitrogen gas at the same time to drive off the water within the sample
4. Prepare the ethanol solution at the concentration of 95%wt

5. Cool the adsorption reactor to 90°C and flow nitrogen gas at the same time to be a medium carrier through the bed
6. Feed ethanol vapor at the flow rate of 36 mL/hr into the top of the adsorption reactor
7. Collect sample products by condensation every 1 minute
8. Analyze for water content in the sample by Karl Fischer Method

3.5 Zeolite regeneration procedure

1. Dry the zeolite sample in the kiln at 105°C overnight
2. Pack zeolite in the fix-bed adsorption reactor (use glass wool as a bed support) and set the equipment as shown in Figure 3.3
3. Activate the zeolite sample at 250°C for 4 hr and flow nitrogen gas at the same time to drive off the water within the sample
4. Prepare the ethanol solution at the concentration of 95%wt
5. Cool the adsorption reactor to 90°C and flow nitrogen gas at the same time to be a medium carrier through the bed
6. Feed ethanol vapor at the flow rate 36 mL/hr into the top of the adsorption reactor
7. Collect sample products by condensation every 1 minute
8. Analyze the water in sample by Karl Fischer Method
9. Regenerate zeolite in the adsorption reactor at 250°C for 4 hr and flow nitrogen gas at the same time to drive off the water within the zeolite sample
10. Repeat Steps 4-9 with the same zeolite for 10 times of regeneration cycle

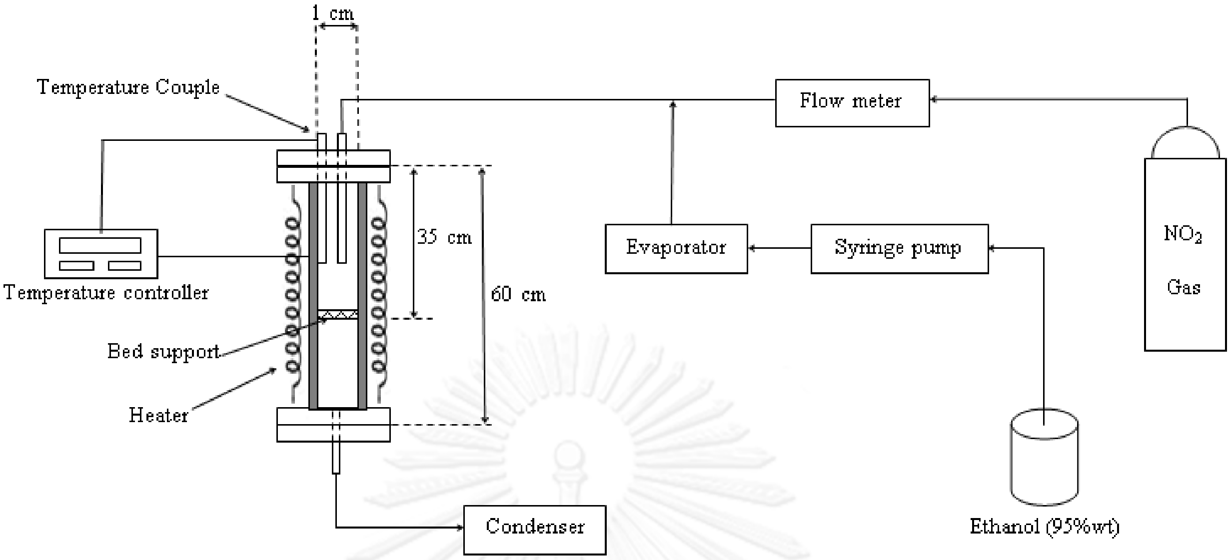


Figure 3. 3 Adsorption experimental set-up and schematic diagram of adsorption reactor

3.6 Large scale of zeolite synthesis experiment

1. Set the equipment as illustrated in Figures 3.4 and 3.5
2. Mix 1 kg of CFA with 20 L of HCl acid (20%w/w or 6M) in the mixing reactor
3. Stir at 300 rpm constantly at 80°C for 2 hr
4. Transfer the mixture to the separation reactor and filter off the solid sample using Glass micro fiber filter (Whatman GF/C)
5. Wash the sample repeatedly with DI water until the solution reaches neutral pH
6. Dry the solid sample overnight at 105°C in the kiln
7. Mix the sample from Step 5 with NaOH and Al_2O_3 (to make the Si/Al molar ratio of 0.82; the batch composition of $12.89NaOH : 0.06K_2O : 0.47CaO : Al_2O_3 : 1.64SiO_2 : 127.19H_2O$) in the ceramic container (in this work, the flowerpot as shown in Figure 3.6 was used for this purpose)
8. Burn the mixture at 550°C for 1 hr in the furnace

9. Remove the solid sample from the reactor and grind it using mortar and pestle
10. Mix the product with 10 L of DI water in the mixing reactor and stir the mixture constantly at 300 rpm at room temperature for 12 hr
11. Crystallize under static condition of 80°C for 4 hr
12. Transfer the mixture to the separation reactor and recover the crystal by filtration using Glass micro fiber filter (Whatman GF/C)
13. Wash thoroughly with DI water (until the filtrate reaches pH 10-11)
14. Dry the product overnight at 105°C in the kiln

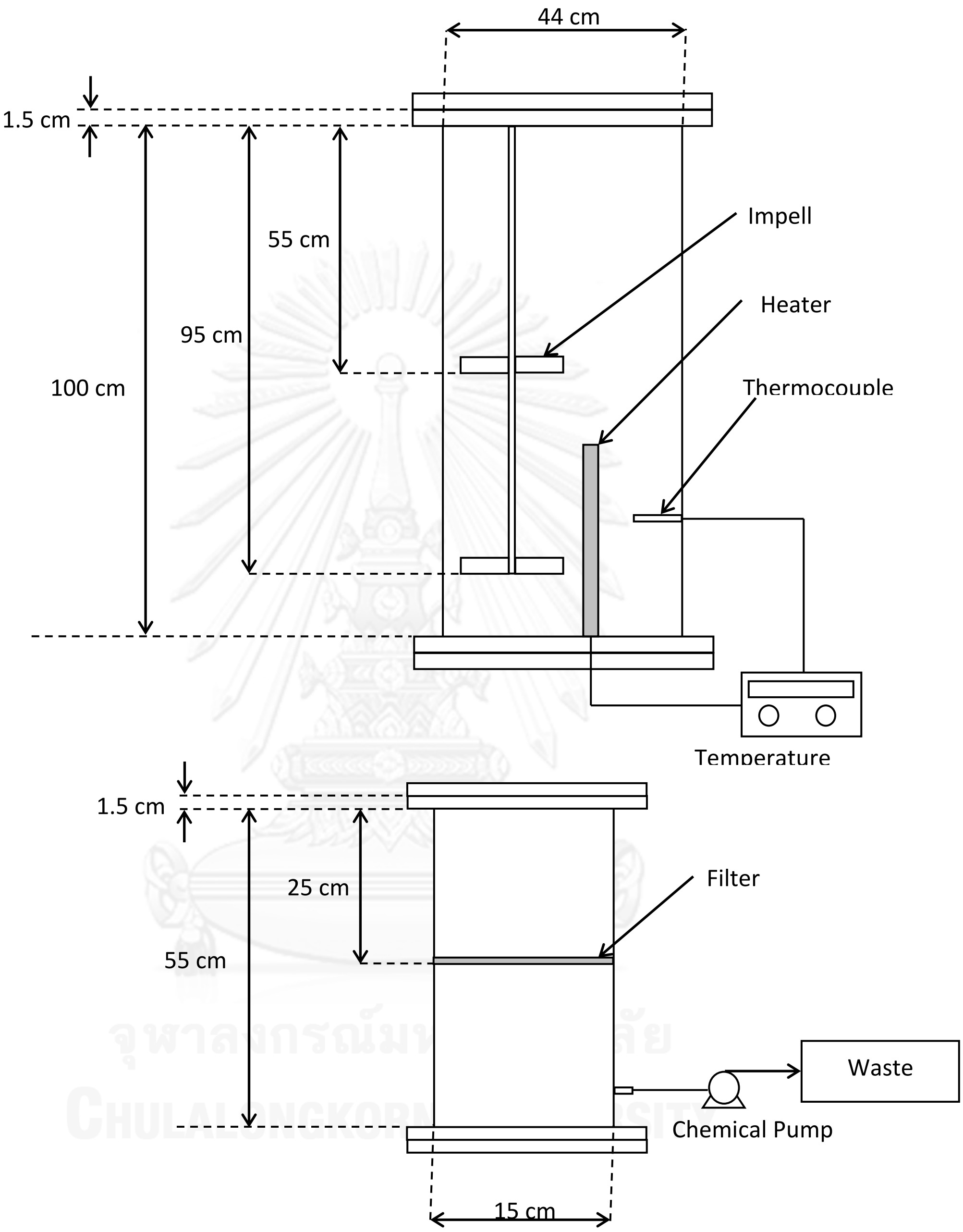


Figure 3. 4 Large scale experimental set up and schematic diagram of mixing and separation reactor

Figure 3. 5 Photograph of large scale experimental set up

Figure 3. 6 Photograph of the container using in the fusion step at large scale experiment

3.7 Analyses of sample

Several physical characterizations of the synthesized zeolite samples were observed using a variety of conventional techniques.

3.7.1 X-Ray Fluorescence Spectrophotometer (XRF) analysis

The XRF data (Philips, model PW2400 the Netherlands) was used to determine the overall mineral composition of the CFA and zeolite samples.

3.7.2 X-Ray Diffraction Spectroscopy (XRD) analysis

X-ray (XRD) analysis is performed with Bruker AXS D8 Discover, Germany accurately in the 5-60° 2θ. It was used to determine the phase identification and calculate the degree of the relative crystallinity of zeolite samples.

3.7.3 Scanning Electron Microscope (SEM) analysis

The morphology of the synthesized zeolite samples such as the shape and the size distribution of crystal products were observed by Scanning Electron microscope (Jeol, model Jsm5410lv Japan).

3.7.4 BET Surface Area analysis

The BET surface area analyzer (Quantachrome Instruments, model NOVA 2200e) was used to determine the specific surface area, pore size and pore volume of synthesized zeolite samples by Nitrogen physisorption technique (at 77.4K, relative pressure in a range of 10^{-6} to 0.35) using the HK method.

3.7.5 Karl Fischer Titration analysis

Karl Fischer (Mettler Toledo, C20 Compact KF Coulometer) was used to determine the water content from ethanol samples. It can be used to determine the water content from ppm up to 100% reliability and accuracy.

3.7.6 Percent yield

The percent yield, which is one of the important parameters, is calculated in order to demonstrate the efficiency of the zeolite synthesis process.

$$\mathrm{Y} = \left(\frac{\mathrm{W_{zeolite}}}{\mathrm{W_{CFA}}}\right) \times 100 \qquad (3.1)$$

where $W_{zeolite}$ is the weight of synthesized zeolite product (g) and W_{CFA} is the weight of raw CFA (g).

3.7.7 Adsorption performance in fixed bed column

The water adsorption capacity is the mass of water (g_{water}) that was adsorbed by the synthesized zeolite ($g_{zeolite}$ per synthesis batch). The water adsorption capacity is calculated using the following equation:

$$\mathrm{A} \quad = \mathrm{a_{sp}Y} \qquad (3.2)$$

and

$$\mathrm{a_{sp}} = (\mathrm{E_{out}} - \mathrm{E_{in}})\frac{\mathrm{G_{ETOH}}}{\mathrm{G_{zeolite}}} \qquad (3.3)$$

where a_{sp} is the specific water adsorption capacity ($g_{water}/g_{zeolite}$). Y is the percent yield (%) of synthesized zeolite product. E_{in} and E_{eq} are the initial and the equilibrium concentrations of ethanol solution (%wt), G_{ETOH} the mass of the ethanol fed through the adsorption system in the liquid phase (g), and $G_{zeolite}$ is the mass of the adsorbent (1 g of the synthesized zeolite or the commercial molecular sieve). The zeolite sample was activated (or regenerated) at 250°C for 4 hr prior to each adsorption testing experiment.

The total amount of water (Q) adsorbed on the pack bed from ethanol is measured by applying the following equation to the breakthrough curves:

$$q_{\max} = \frac{F\rho_{ETOH} E_{in}}{G_{zeolite}} \int_0^{t_{eq}} (1 - \frac{E_t}{E_{in}}) dt \qquad (3.4)$$

where *F* is the flow rate of ethanol (36 mL/hr), ρ_{ETOH} is the density of ethanol (0.789 g/mL), t_{eq} is the equilibrium time and E_t is the concentrations of ethanol solution at the exit of the adsorption system (%wt).

Table 3. 1 Batch composition of zeolite synthesis experiment

	Parameter studied	Batch composition
Effect of raw material	CFA1	$38.75NaOH : 0.23K_2O : 2.22CaO : Al_2O_3 : 3.07SiO_2 : 308.41H_2O$
	CFA2	$28.68NaOH : 0.14K_2O : 0.98CaO : Al_2O_3 : 3.62SiO_2 : 282.98H_2O$
	CFA3	$30.35NaOH : 0.17K_2O : 1.20CaO : Al_2O_3 : 3.68SiO_2 : 299.45H_2O$
	CFA4	$35.85NaOH : 0.23K_2O : 1.42CaO : Al_2O_3 : 3.65SiO_2 : 353.73H_2O$
	CFA5	$32.59NaOH : 0.24K_2O : 1.57CaO : Al_2O_3 : 3.64SiO_2 : 321.57H_2O$
	CFA6	$38.49NaOH : 0.22K_2O : 2.73CaO : Al_2O_3 : 3.59SiO_2 : 379.84H_2O$
	CFA7	$30.67NaOH : 0.13K_2O : 1.28CaO : Al_2O_3 : 3.46SiO_2 : 302.65H_2O$
	CFA8	$27.44NaOH : 0.12K_2O : 0.99CaO : Al_2O_3 : 3.49SiO_2 : 270.80H_2O$
	CFA9	$27.58NaOH : 0143K_2O : 1.04CaO : Al_2O_3 : 3.45SiO_2 : 272.10H_2O$
Effect of Si/Al ratio	Si/Al = 0.54	$8.49NaOH : 0.04K_2O : 0.31CaO : Al_2O_3 : 1.08SiO_2 : 83.76H_2O$
	Si/Al = 0.67	$10.53NaOH : 0.05K_2O : 0.38CaO : Al_2O_3 : 1.34SiO_2 : 103.93H_2O$
	Si/Al = 0.82	$12.89NaOH : 0.06K_2O : 0.47CaO : Al_2O_3 : 1.64SiO_2 : 127.19H_2O$
	Si/Al = 1.00	$15.72NaOH : 0.07K_2O : 0.57CaO : Al_2O_3 : 2.00SiO_2 : 155.11H_2O$

CHAPTER 4

ZEOLITE SYNTHESIS AND CHARACTERIZATION

4.1 Characterization of coal fly ash

Chemical compositions of the CFA samples analyzed by X-Ray fluorescence are reported in Table 4.1. The results showed that the main components of the original CFA were silicon and aluminium oxides and that the impurities were of metallic oxides such as Fe and Ca. Other elements were presented in trace amounts, i.e. MgO, K_2O and TiO_2. High amorphous aluminosilicate (approx. 80%) content suggested a potential conversion to zeolite (Molina and Poole, 2004). Figure 4.1 is a picture of the original CFA before treatment by acid process. The colors of CFA are a loose indicator of its chemical contents. The collected CFA samples were sub-bituminous fly ashes, which are usually light tan to grey color. The light grey color indicated relatively low amounts of carbon as well as the presence of lime or calcium, while a brownish color is typically associated with the iron content. Similar results were reported by Zaeni et al. (2010). To produce high purity zeolite, the quality of CFA raw material was subjected to a certain pretreatment process, i.e. acid-washing, for the removal of such impurities and to enhance Si and Al compositions.

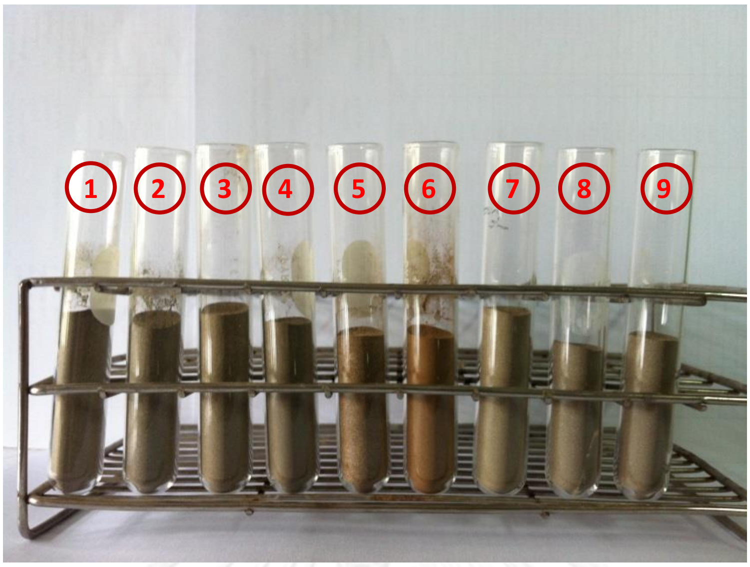


Figure 4. 1 Photograph of the original CFA collected from the power plant in Prachinburi Province of Thailand

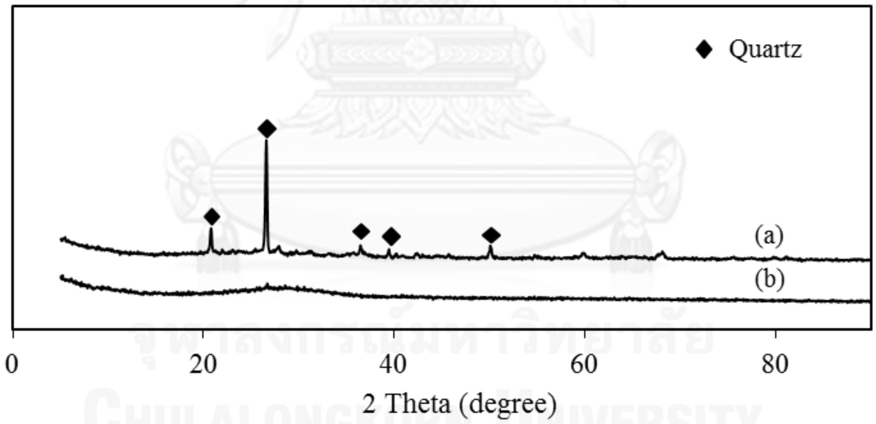


Figure 4. 2 X-ray diffraction of original CFA (a), and CFA after fusion with NaOH (b)

Figure 4.2 (a) shows the XRD pattern of the original CFA, which indicates that the original CFA is of amorphous phase and the diffraction peak corresponds to the presence of quartz (JCPDF no. 01-079-1906). The quartz crystal phases are difficult to dissolve into alkali solution to form a zeolite structure by hydrothermal reaction (Shigemoto et al., 1993). To produce zeolite in pure form with a high crystallinity, the crystal phase of CFA raw material has to be converted to soluble phase (amorphous phase) prior to the hydrothermal reaction using the alkali fusion process.

An alkali fusion pretest reveals that there was a possibility that quartz in CFA be converted to be amorphous form. For the alkali treatment process, the original CFA was treated with NaOH by fusion at 550°C for 1 hr with a NaOH/CFA mass ratio of 2.25 (Ruen-ngam et al., 2009). Figure 4.2 (b) shows the XRD pattern of the original CFA after alkali fusion treatment which indicates that this alkali treatment successfully led to the transformation of CFA into an amorphous material. The alkali fusion method decomposed and converted the quartz phase into soluble phase, the conditions necessary for the formation of zeolite. The results agree with that of Wajima et al. (2011) who reported the use of the alkali fusion method to convert the crystalline to soluble phase and to transform CFA into various zeolite products by varying the experimental conditions. From these results, it can be concluded that the alkali fusion method is a suitable method to convert a crystalline phase of raw CFA to soluble phase prior to the zeolite synthesis process.

4.2 Acid-washing pretreatment

To study the effect of acid-washing pretreatment on the removal of impurities in CFA, various pretreatment conditions were carried out. Figure 3.1 shows the flow diagram of the acid-washing pretreatment and the subsequent zeolite synthesis process.

4.2.1 Effect of acid categories

Figure 4.3a presents the chemical components of CFA raw material and zeolite synthesized from CFA with and without acid-washing pretreatment. The results show that most of the impurities (Fe_2O_3, CaO and other impurities) in CFA could be removed by treatment with 20%w/w concentration (HCl, H_2SO_4 and HNO_3) and at the liquid (acid solution)/solid (CFA) ratio of 25 mL_{acid}/g_{CFA}. Furthermore, higher specific surface area and higher pore size diameter were observed from the pretreated sample, according to the BET measurement as presented in Table 4.2. Zeolite synthesized from the non-treated CFA had a purity of 59% (Na_2O, SiO_2 and Al_2O_3), a specific area of 58 m^2/g, and a pore size of 3.42 Å. Among the various acid species (HCl, H_2SO_4 and HNO_3), zeolite synthesized from CFA treated with HCl provided the highest purity material (87% of Na_2O, SiO_2 and Al_2O_3), with the specific area of 261 m^2/g, pore size of 4.34 Å and pore volume of 0.8 mL/g, whereas zeolite synthesis from CFA treated with HNO_3 only achieved the purity of 69% with the specific area of 139 m^2/g and pore volume of 0.12 mL/g.

The XRD diffraction peak of all zeolite products (with and without acid-washing) corresponded to the presence of sodium aluminum silicate hydrate as shown in Figure 4.4a. Sodium aluminum silicate hydrate is referred to as sodium aluminosilicate material, and is composed of sodium, aluminum, silica, and oxygen, in many different forms, e.g. zeolite type analcime, Na-A, Na-X, etc. From the results, the major phase formation of all zeolite products (with and without acid-washing) was found to be zeolite type X (JCPDF no. 01-089-8235).

The relative of zeolite X crystallinity of zeolite samples were determined. Table 4.2 shows that zeolite synthesized from CFA treated with HCl provided the highest relative of zeolite X crystallinity (30%), whereas zeolite synthesis from CFA treated with H_2SO_4, HNO_3 and the non-treated CFA achieved the relative of zeolite X crystallinity of 29%, 13% and 21%, respectively.

The percent yield of zeolite synthesis from the non-treated CFA was 55%, while the percent yield of zeolite synthesis from samples treated with acids were in the range of 32-34% as indicated in Table 4.2. The impurities contained in the treated CFA were washed away before the conversion of CFA to zeolite, therefore, providing a lower yield, but higher purity. Hence, due to the highest purity, the highest relative of zeolite X crystallinity, and the highest specific area obtained from CFA after treatment with acids, HCl was considered to be the most suitable acid for acid-washing pretreatment.

4.2.2 Effect of acid to CFA ratio

After pretreatment with 10%w/w and 20%w/w HCl, the CFA products showed higher purity percentage of 78%wt and 85%wt, respectively. Nevertheless, this positive effect became less pronounced when the acid concentration increased to 30%w/w (83%wt of purity). It was observed that there was a gradual decrease in Al_2O_3 percentage (15%wt, 14%wt and 13%wt of Al_2O_3) at a higher acid concentration (10%w/w, 20%w/w and 30%w/w, respectively). The results agree with that of Nayak and Panda who reported that the aluminum extraction efficiency by direct acid leaching increased gradually with an increasing acid concentration (Nayak and Panda, 2010). Hence, based on the purity of the zeolite product, the acid concentration at 20%w/w is considered to be a suitable concentration for acid-washing pretreatment.

Figure 4.3b shows the chemical components of zeolite synthesized from CFA treated with 20%w/w HCl under various L/S ratios. There were differences in the quality of zeolite products depending on the L/S ratio. Most of the impurities of CFA were removed and attained their maximum values of purity (86%wt of Na_2O, SiO_2 and Al_2O_3) at L/S = 10 mL_{acid}/g_{CFA} and no significant improvement in the purity (approximately 84-85%wt) at other range of acid/CFA ratio was observed. Furthermore, the percent yield of all zeolite products was quite similar, all in the range of 28–33%. However, the highest specific surface area (227 m^2/g), total pore volume (0.22 mL/g) and pore size (4.09 Å) was observed from the pretreated sample with L/S ratio of 20 mL_{Lcid}/g_{CFA}, whereas the specific area and pore size of the sample with L/S ratio of 10 mL_{acid}/g_{CFA} were 72 m^2/g and 3.62 Å, according to the BET measurement, as presented in Table 4.2.

The main phase formation of zeolite product synthesized from pretreated CFA, with various L/S ratios analyzed by XRD was sodium aluminum silicate hydrate, in which the diffraction peak corresponded to the presence of zeolites type X (JCPDF no. 01-089-8235) as illustrated in Figure 4.4b. The diffraction peak intensity of zeolite samples increased with L/S ratio meaning a better crystallinity of zeolites. The highest relative zeolite X crystallinity (88%) was observed from the pretreated sample of 20 mL_{Lcid}/g_{CFA}. However, the relative zeolite X crystallinity decreased to 22% when the L/S ratio increased to 25 mL_{acid}/g_{CFA}. Hence, a L/S =20 mL_{acid}/g_{CFA} (at 20% wt/wt HCl) is considered to be a suitable ratio for acid-washing pretreatment.

4.2.3 Effect of reusing acid

From the results above, high purity zeolite could be produced from CFA treated with a concentrated HCl (20%w/w) at a high ratio of acid volume to CFA (20 mL_{acid}/g_{CFA}). To reduce the environmental impact of the treatment process, the reuse of the acid was studied. Furthermore, this also proposes significant financial rewards throught the reduction in the demand for virgin HCl.

Figure 4.3c shows the chemical components of zeolite synthesized from CFA treated with 20%w/w concentration of reused HCl under an L/S of 20 mL_{acid}/g_{CFA}. The results indicated that there were no significant differences in the quality of the zeolite products when compared with that obtained from the use of fresh medium. This test was repeated four consecutive times and the reused acid seemed to give satisfactory results where most impurities could be removed effectively, and the products exhibited high purity (77-81%wt, with reasonable specific surface area (200-210 m^2/g) and pore volume (0.21-0.37 mL/g) as indicated in Table 4.2. The percent yield of zeolite products were in the range of 28-32%.

The main phase formation of all zeolite products synthesized from CFA treated with the reused acid was sodium aluminum silicate hydrate, in which the diffraction peak corresponded to the presence of zeolites type X (JCPDF no. 01-089-8235) as shown in Figure 4. The relative of zeolite crystallinity of zeolite products were in the range of 21-28%. Note that the acid volume decreases by approximately 10% after the acid-washing process, yet the concentration of the reused acid remained unchanged. Fresh HCl with 20%w/w concentration was added to yield the L/S of 20 mL_{acid}/g_{CFA} prior to the next pretreatment. The color of the acid solution changed from colorless (transparent liquid) to green-yellow after pretreatment as shown in Figure 4.5. This suggests that impurities were leached out of the CFA raw material. Furthermore, some of the precipitation of the reusing acid was observed as shown in Figure 4.5b.

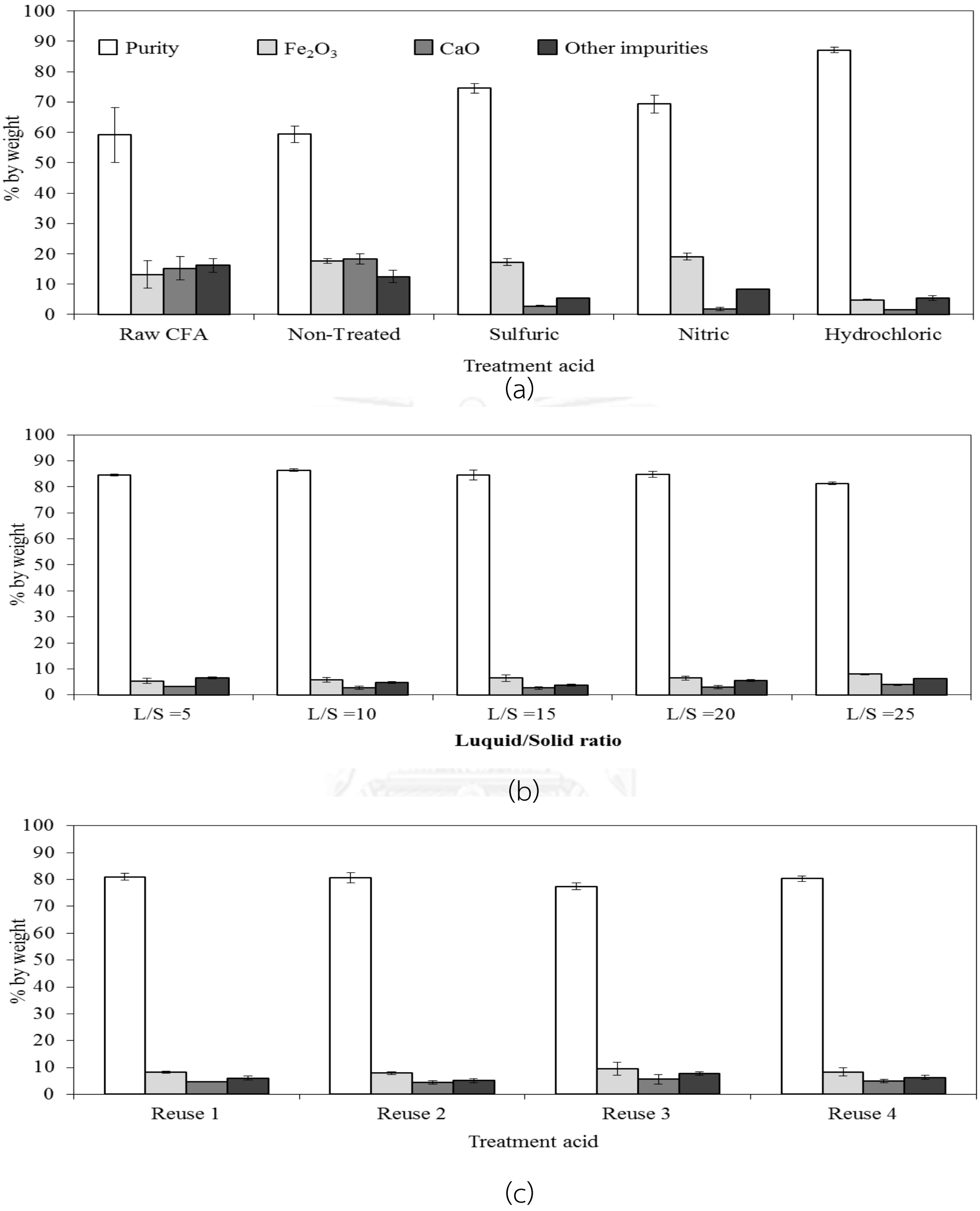


Figure 4. 3 Chemical compositions of zeolite products, synthesized from CFA treated with various acids (a), various L/S ratios (b) and reused acid (c)

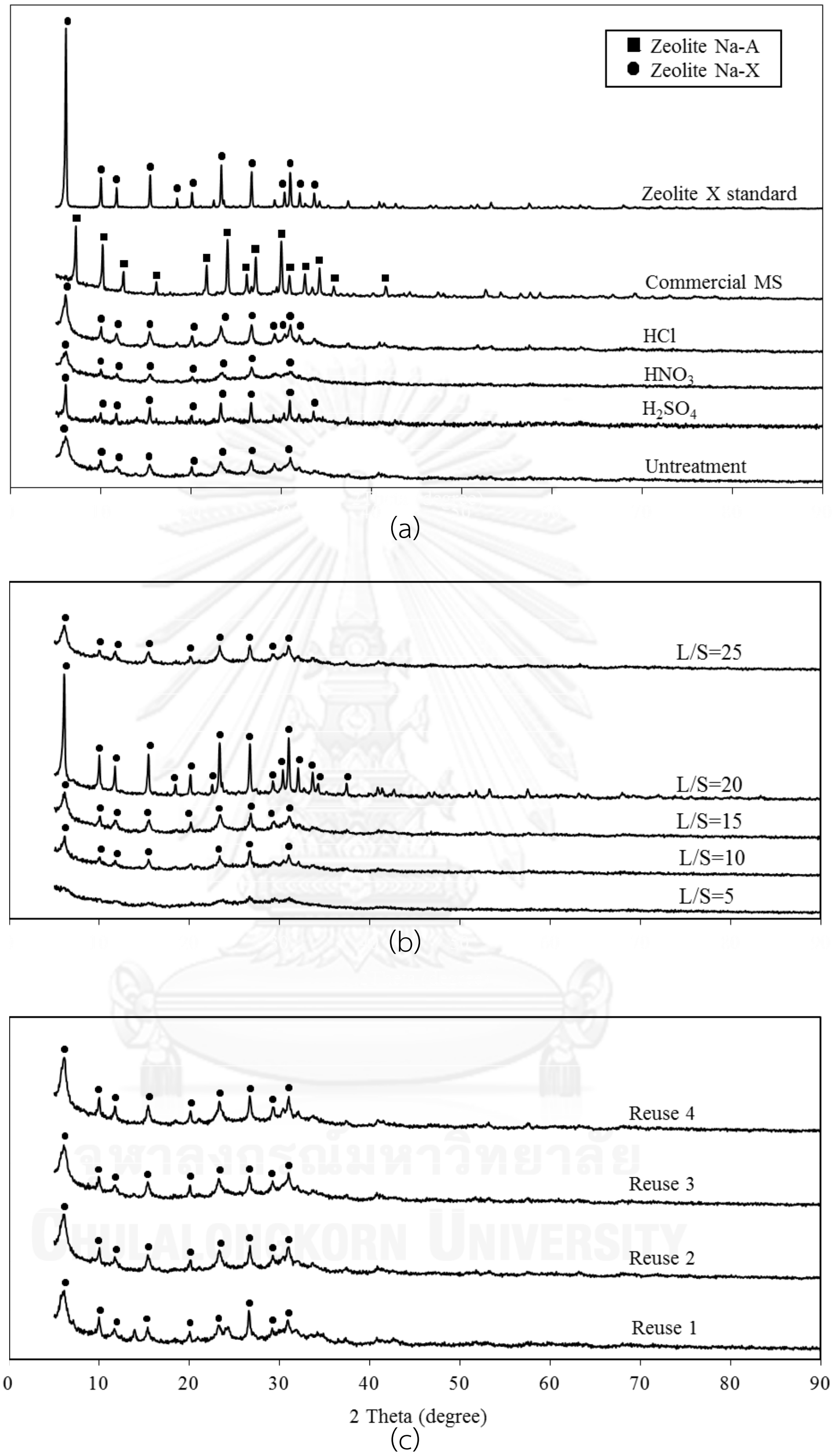


Figure 4. 4 X-ray diffraction of zeolite products synthesized from CFA treated with various acids (a), various L/S ratios (b), and reused acid (c)

(a) (b)

Figure 4. 5 Photographs of hydrochloric acid solution before and after acid-washing process

4.3 Zeolite synthesis

4.3.1 Effect of chemical compositions of raw material

The chemical compositions of the CFA (Table 4.1) were not fixed but vary due to the composition of coal used in the combustion process, and this led to a difference in Si to Al ratio in the fly ash. Furthermore, the differences in coal impurity compositions, particularly those unburned minerals, (mainly silica, alumina, calcium, and iron compounds) dictated the quality of CFA. This then had a direct effect on the quality of zeolite synthesized from the CFA. To remove the impurities of CFA and to make a higher purity of zeolite product, acid-washing pretreatment was carried out prior to using the fusion method with 20%w/w HCl under the L/S ratio of 20 mL/g at 80°C for 2 hr. The pretreated CFA was converted to zeolite using the fusion temperature of 550°C with NaOH/CFA mass ratio of 2.25 for 1 hr followed by crystallization at 80°C for 4 hr. Acid-washing pretreatment and zeolite synthesis procedure are diagrammatically shown in Figure 3.1. Chemical compositions of zeolite products synthesized from various CFAs are shown in Figure 4.6. These results show that most of the impurities were removed and a higher purity (75-87%wt of purity) of zeolite product was achieved. Note that zeolite synthesized from non-treated CFA had a purity of 59%wt as shown in Section 4.3.1. The percent yields of the products were all in the range of 21-32%, as shown in Table 4.2.

The XRD patterns of all zeolites were demonstrated to be that of sodium aluminum silicate hydrate which the major phase formation of all zeolite products was found to be zeolite type X (JCPDF no. 01-089-8235). The Si/Al molar ratio of CFA raw materials were in a range of 1.54-1.84, which favored the formation of zeolite type faujasite (i.e. zeolite type X or type Y). Similar results were obtained from Purnomo et al. and Tanaka et al. (Purnomo et al., 2012; Tanaka et al., 2002). Moreover, the morphological analysis of the zeolite samples synthesized from various CFAs, performed by SEM (shown in Figure 4.7a) also demonstrates that the zeolite samples were all in the phase of sodium aluminum silicate hydrate. The relative of zeolite X crystallinity of all zeolite products was quite similar, in the range of 62–75% as shown in Table 4.2.

The BET surface area, pore size and the pore volume of the synthesized zeolite from various CFA raw materials were determined as shown in Table 4.2. The values of the specific surface area for the zeolite products were in a range of 301-461 m^2/g. while the pore sizes were in a range of 4.43-4.89 Å and with the pore volume in a range of 0.24-0.32 mL/g.

These results demonstrate that a high purity and similar physical properties of the synthesized zeolite products could be obtained despite the differences in the quality of the CFA raw material.

Due to the large pore size of the synthesized zeolite products (4.43-4.89 Å) and in order to use the synthesized zeolite products as water adsorbent from ethanol solution, it is possible that ethanol (molecule size is approx. 4.4 Å) can be adsorbed within the zeolite pores, which results in a low water adsorption performance. The water adsorption performance of zeolite samples can be improved by creating suitable conditions for zeolite synthesis, including a suitable Si/Al ratio of CFA in order to improve the zeolite products' physical properties (e.g. framework type, specific surface area and pore size) and chemical properties (e.g. ion-exchange, affinity for water adsorption).

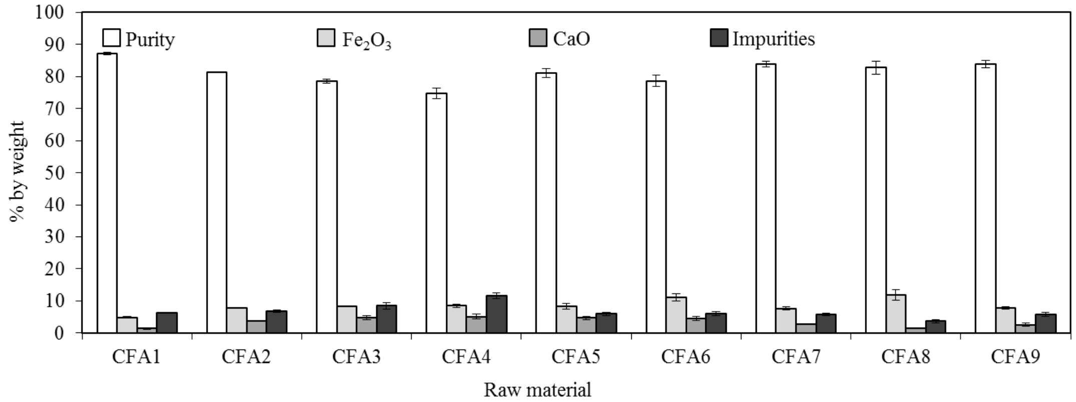
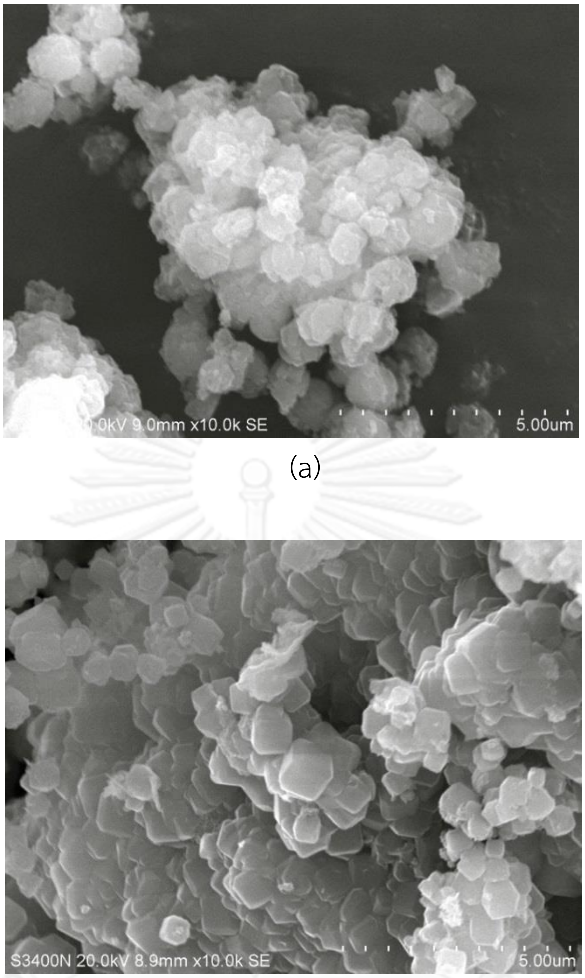


Figure 4. 6 Chemical compositions of zeolite products synthesized from various CFA



(a)

(b)

Figure 4. 7 SEM photographs of the zeolite samples synthesized from CFA without the Si/Al ratio adjustment (a) with Si/Al ratio adjustment (b) at lab scale experimentation

4.3.2 Effect of Si to Al ratio

For this investigation, CFA was pretreated with acid prior to fusion with HCl 20%w/w concentration under the L/S ratio of 20 mL/g at 80°C for 2 hr to remove the impurities. The Si/Al molar ratio of the treated CFA was then adjusted in the range of 0.54 to 1 before the fusion at 550°C with NaOH/CFA mass ratio of 2.25 for 1 hr. This was followed by crystallization at 80°C for 4 hr. The adjustment of Si/Al molar ratios in the fusion reaction mixture was achieved by adding alumina powder (Al_2O_3) as a source of aluminum. Acid-washing pretreatment and zeolite synthesis procedure with the Si/Al adjustment are diagrammatically shown in Figure 4.8.

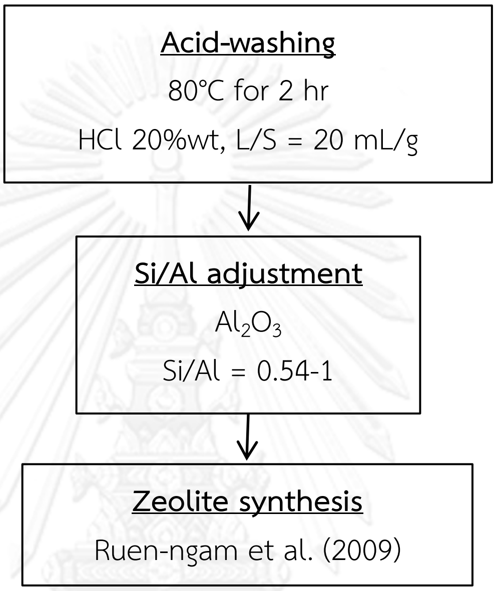


Figure 4. 8 Process flow diagram for acid-washing pretreatment and zeolite synthesis with Si/Al adjustment

XRF shows that, with this technique, most of the impurities were removed and a higher purity (96-97%wt of purity) of zeolite product was achieved. The yields of the products were all in the range of 63-73% as shown in Table 4.2. A much too high Si/Al molar ratio was not found to have positive effects on the purity.

The BET surface area, the pore size and the pore volume of the synthesized zeolite samples from CFA with adjusted Si/Al molar ratio prior to the fusion step were calculated, and displayed in Table 4.2. All zeolite samples showed a high surface area, which were in a range of 406-418 m^2/g, while the pore sizes of the samples were quite similar (4.08-4.28 Å). Based on these results of these experiments, the zeolite synthesized from CFA with adjusted Si/Al of 0.82 had the highest surface area (418 m^2/g) and the largest pore volume (0.76 mL/g). Furthermore, it had the pore size at 4.08 Å, which is smaller than ethanol molecule size. It is possible to improve the water adsorption of the zeolite produced by controlling the Si/Al of the raw material before hydrothermal process at 0.82, as ethanol cannot be adsorbed within the pores.

The XRD patterns in Figure 4.9 suggest that all zeolite samples matched the pattern of zeolite A (JCPDF no. 01-089-3142). From the results, the relative zeolite A crystallinity of zeolite samples increased when the Si/Al molar ratio decreased from 1 to 0.82 (211% and 214%, respectively). However, the relative zeolite A crystallinity decreased when Si/Al molar ratio lower than 0.82. The relative zeolite A crystallinity of zeolite samples with the Si/Al molar ratio of 0.67 and 0.54 were 169% and 139%, respectively. This finding leads to a conclusion that pure zeolite type A was synthesized when the Si/Al ratios in the reaction mixture were less than or equal to 1, whereas zeolite type X was obtained at the Si/Al molar ratio in a range of 1.54 to 1.84. These results agree with that of Tanaka et al. and Purnomo et al. who reported that a single phase zeolite type A was formed at the Si/Al molar ratio of not more than one, while the other phases of zeolite (e.g. Na-X, Na-Y and NaP) was slightly formed at the Si/Al molar ratio of more than one (Purnomo et al., 2012; Tanaka et al., 2002).

SEM of zeolite samples (Figure 4.7b) revealed the presence of crystal with the cubic morphology and with even crystal size distribution. The average diameter of the zeolite cubic crystal was approximately 1 μm. No considerable amounts of amorphous material were detected with this technique, which indicates a high degree of crystallization.

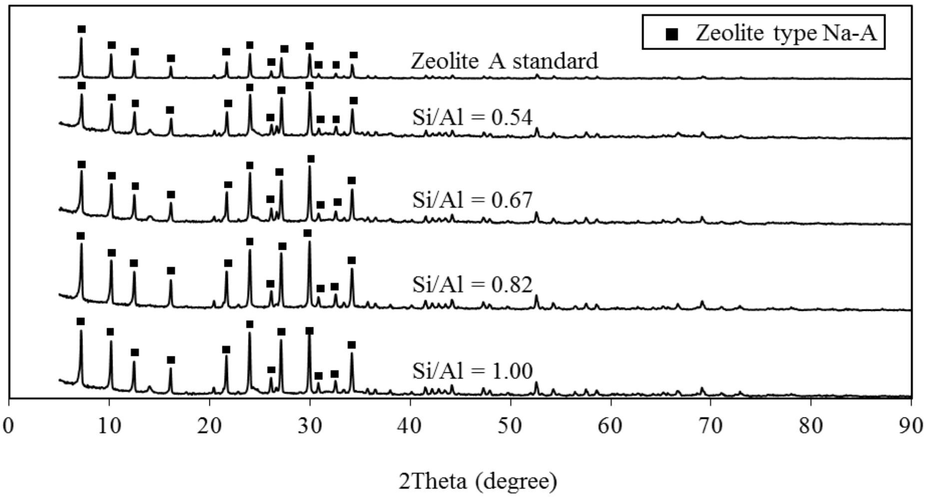


Figure 4. 9 X-ray diffraction of zeolite products, synthesized from CFA with the Si/Al ratio adjustment

4.4 Concluding remarks

This chapter evaluated the technical feasibility of the conversion of industrial waste CFA to zeolite. Due to the presence of high impurities in raw CFA, various conditions of acid-washing pretreatment have been proposed as a purification option prior to the synthesis process. Experimental results suggest that there were conditions which yielded some specific zeolite type with certain quality and yield. These zeolites are tested as water sorbent from ethanol solution which is discussed in the next chapter.

Table 4. 1 Chemical compositions of original CFA samples analyzed by XRF

Chemical composition	CFA1 (%wt)	CFA2 (%wt)	CFA3 (%wt)	CFA4 (%wt)	CFA5 (%wt)	CFA6 (%wt)	CFA7 (%wt)	CFA8 (%wt)	CFA9 (%wt)
Na_2O	-	3.6	3.9	4.7	3.8	-	3.3	3.2	2.6
Si_2O	26.8	42.7	41.0	34.4	37.8	31.5	38.1	43.0	42.3
Al_2O_3	14.8	20.0	18.9	16.0	17.6	14.9	18.7	20.9	20.8
Fe_2O_3	25.1	13.4	13.0	16.5	13.2	19.3	15.0	10.8	11.2
TiO_2	2.2	3.5	3.1	3.0	2.8	2.0	2.6	2.3	2.3
MgO	1.5	2.4	2.7	2.7	3.1	3.4	2.1	2.0	2.0
CaO	18.1	10.8	12.5	17.0	15.2	22.4	13.2	11.4	11.9
K_2O	3.2	2.5	3.0	3.4	3.9	3.0	2.2	2.4	2.6
SO_3	7.3	-	-	-	2.1	3.2	2.8	2.6	2.6
NiO	0.3	-	-	-	-	-	-	-	-
Rb_2O	0.1	-	-	-	-	-	-	-	-
SrO	0.2	-	-	-	0.5	0.4	1.1	0.9	0.1
Y_2O_3	0.2	-	-	-	-	-	-	-	-
ZrO_2	0.3	0.03	-	-	-	-	-	-	-
P_2O_5	-	0.7	1.5	1.8	-	-	0.9	0.5	0.6

Note: CFA = coal fly ash

Table 4. 2 Properties of zeolite products synthesized from CFA with various conditions

Conditions					Results					
Parameter studied	Raw CFA	Acid Types	L/S (mL/g)	Si/Al (molar ratio)	XRD Analysis	Yield (%)	Surface Area (m^2/g)	Pore Size (Å)	Pore Volume (mL/g)	Zeolite Crystallinity (% zeolite)
Effect of acid types	CFA8	Non-treated	25	1.73	Na-X	55	58	3.42	0.25	21% zeolite X
	CFA8	H_2SO_4	25	1.73	Na-X	33	226	4.17	0.29	29% zeolite X
	CFA8	HNO_3	25	1.73	Na-X	34	139	4.30	0.12	13% zeolite X
	CFA8	HCl	25	1.73	Na-X	33	261	4.34	0.80	30% zeolite X
Effect of L/S ratio	CFA8	HCl	5	1.73	Na-X	32	35	3.61	0.16	-
	CFA8	HCl	10	1.73	Na-X	31	72	3.62	0.17	17% zeolite X
	CFA8	HCl	15	1.73	Na-X	28	75	3.02	0.12	21% zeolite X
	CFA8	HCl	20	1.73	Na-X	33	227	4.09	0.22	88% zeolite X
	CFA8	HCl	25	1.73	Na-X	29	117	3.79	0.21	22% zeolite X
Effect of reusing acid	CFA8	HCl(Reuse1)	20	1.73	Na-X	32	301	4.43	0.27	21% zeolite X
	CFA8	HCl(Reuse2)	20	1.73	Na-X	33	319	4.61	0.37	24% zeolite X
	CFA8	HCl(Reuse3)	20	1.73	Na-X	28	317	4.39	0.21	22% zeolite X
	CFA8	HCl(Reuse4)	20	1.73	Na-X	31	306	4.62	0.24	28% zeolite X
Effect of raw CFA	CFA1	HCl	20	1.54	Na-X	23	461	4.79	0.32	78% zeolite X
	CFA2	HCl	20	1.81	Na-X	29	371	4.65	0.29	74% zeolite X
	CFA3	HCl	20	1.84	Na-X	27	363	4.54	0.29	75% zeolite X
	CFA4	HCl	20	1.82	Na-X	32	381	4.72	0.32	75% zeolite X
	CFA5	HCl	20	1.83	Na-X	32	301	4.43	0.25	62% zeolite X
	CFA6	HCl	20	1.80	Na-X	28	372	4.86	0.24	66% zeolite X
	CFA7	HCl	20	1.73	Na-X	21	360	4.89	0.26	71% zeolite X
	CFA8	HCl	20	1.75	Na-X	31	301	4.85	0.27	66% zeolite X
	CFA9	HCl	20	1.73	Na-X	31	322	4.54	0.28	70% zeolite X
Effect of Si/Al ratio	CFA8	HCl	20	0.54	Na-A	73	406	4.27	0.49	140% zeolite A
	CFA8	HCl	20	0.67	Na-A	67	413	4.28	0.61	169% zeolite A
	CFA8	HCl	20	0.82	Na-A	65	418	4.08	0.76	214% zeolite A
	CFA8	HCl	20	1.00	Na-A	63	408	4.10	0.57	211% zeolite A

Note: CFA: coal fly ash, SAS: Sodium aluminum silicate hydrate

CHAPTER 5

ADSORPTION PERFORMANCE AND SCALING UP

5.1 Performance of synthesized zeolite as water sorbent

After converting CFA to zeolite by the method shown in Figure 3.1, the adsorption performance of synthesized zeolite was investigated by testing it as water adsorbent from ethanol solution (95%wt). Its adsorption capacity was also compared to the commercial grade molecular sieve. The schematic diagram of the adsorption testing experiment system is shown in Figure 3.3. Finally, the scaling up of such zeolite synthesis process was proposed and examined for its feasibility.

5.1.1 Effect of acid-washing treatment

5.1.1.1 Effect of acid categories

To study the effect of acid-washing treatment, various pretreatment conditions were carried out for the treatment of CFA. Firstly, the effect of acid categories on water adsorption of zeolite samples was investigated. Figure 5.1 shows the flow diagram of the effect of acid categories experimentation.

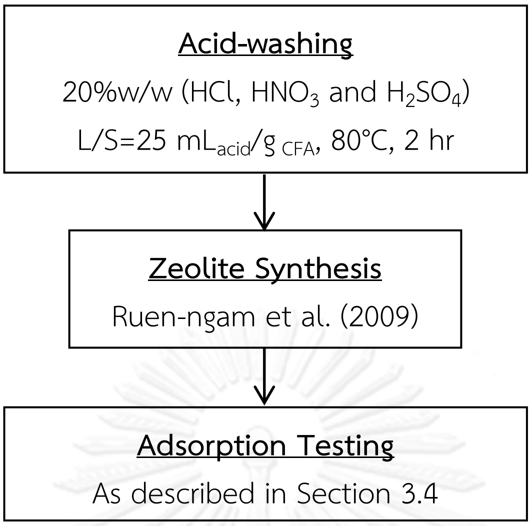


Figure 5. 1 Flow diagram of the effect of acid categories experimentation

The breakthrough curve of water adsorption on commercial molecular sieve and zeolite products synthesized from treated and non-treated CFA was plotted as demonstrated in Figure 5.2a. The acid-washing pretreatment process had a positive effect on the water adsorption performance of the synthesized zeolite products. In other words, the samples pretreated by acid-washing prior to the fusion process demonstrated a greater adsorption performance than the samples without pretreatment. A good adsorption performance was indicated by a higher adsorption capacity, specific adsorption capacity and outlet ethanol concentration. The zeolite with acid-washing pretreatment had a higher specific surface area and pore size than the sample without pretreatment (see Table 4.2), which was the main reason for a better water adsorption performance.

From these studies, the highest ethanol concentration achieved at the outlet of the adsorption process observed using the sample treated with HCl (at 98.3%wt).

The samples pretreated with H_2SO_4 and HNO_3 and the sample without pretreatment produced the highest ethanol concentration of 98.1%wt, 97.7%wt and 96.6%wt, respectively. In this comparison, the adsorption capacity was calculated based on the initial weight of CFA used to produce zeolite. The water adsorption capacity (*A*), the specific water adsorption capacity (a_{sp}) and the maximum water adsorption capacity (q_{max}) of the zeolite samples with and without pretreatment are calculated from Eqs. 3.2 - 3.4, and the results are shown in Table 5.1. The highest value of the adsorption capacity and the specific adsorption capacity were observed using the sample pretreated with HCl (5.08×10^{-3} g_{water}/g_{CFA} and 1.54×10^{-2} $g_{water}/g_{zeolite}$ respectively), which was higher than the sample pretreated with HNO_3 (5.01×10^{-3} g_{water}/g_{CFA} and 1.47×10^{-2} $g_{water}/g_{zeolite}$) and H_2SO_4 (4.22×10^{-3} g_{water}/g_{CFA} and 1.28×10^{-2} $g_{water}/g_{zeolite}$) and the sample without pretreatment (4.03×10^{-3} g_{water}/g_{CFA} and 7.32×10^{-3} $g_{water}/g_{zeolite}$), respectively. Furthermore, it is seen that the time required to reach a plateau value varies as a function of acid-washing pretreatment conditions. The time needed to reach a plateau value in the case of using zeolite synthesized from the CFA treated with HCl was approximately 7mins, which is comparable to the commercial molecular sieve. This is longer than that of zeolite synthesized from CFA treated with H_2SO_4, HNO_3 and the zeolite synthesized from untreated CFA.

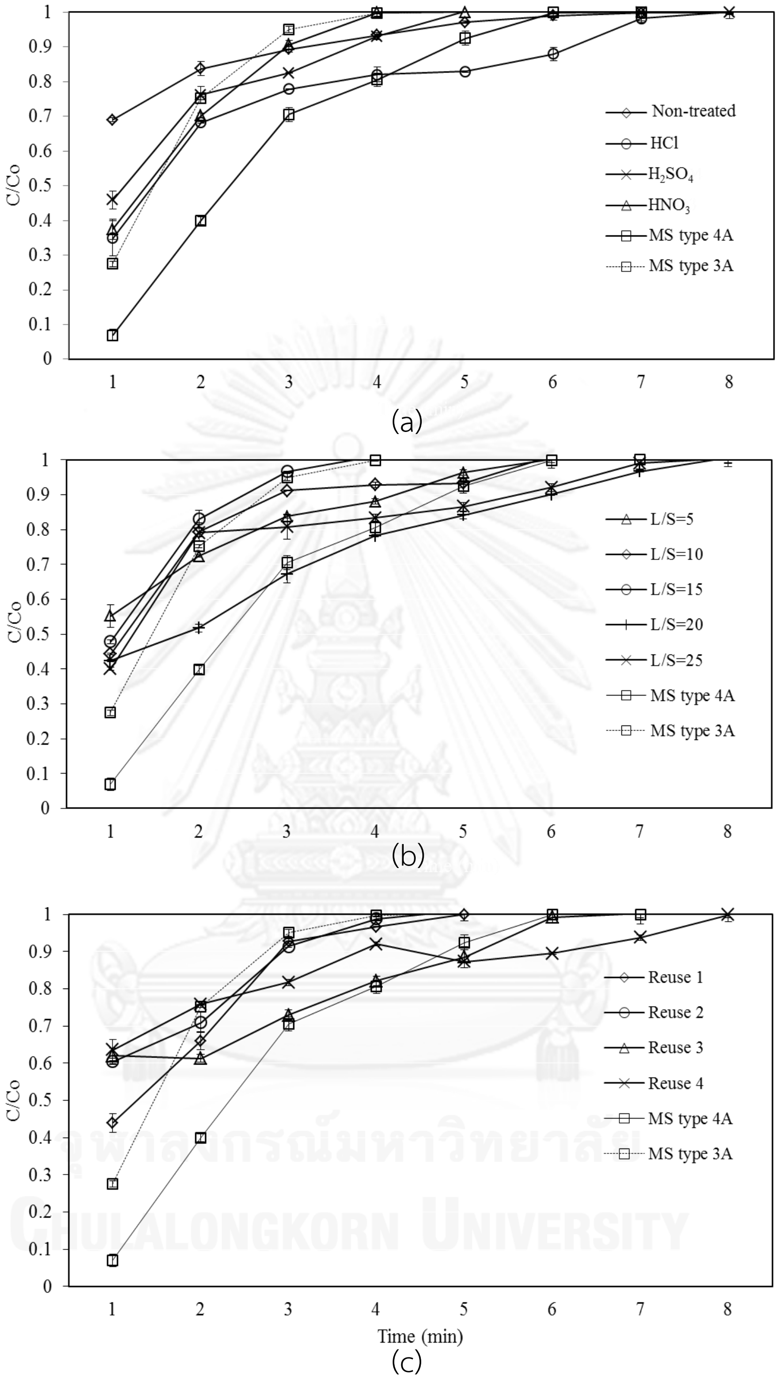


Figure 5. 2 Breakthrough curves of water adsorption on the zeolite products synthesized from CFA treated with various acid types (a), with various L/S ratios (b), and with reused acid (c)

From these preliminary results, due to the purity (as described in section 4.3) and the water adsorption capacity of the synthesized zeolite sample, it was recommended to perform the acid-washing process prior to the fusion process. Furthermore, among the three acid types, HCl was selected as the preferred CFA pretreatment. The commercial molecular sieve type 4A showed a higher value of the outlet ethanol concentration (99.7%wt) and the maximum water adsorption capacity (6.15×10^{-2} $g_{water}/g_{zeolite}$) than the commercial molecular sieve type 3A (98.7%wt and 3.61×10^{-2} $g_{water}/g_{zeolite}$, respectively) and the zeolite sample treated with HCl (98.3%wt and 5.16×10^{-2} $g_{water}/g_{zeolite}$, respectively). However, the zeolite sample treated with HCl showed a higher value of the maximum water adsorption than the commercial molecular sieve type 3A and the water adsorption performance of the synthesized zeolite could be improved by adjusting conditions of acid-washing pretreatment (e.g. acid concentration, acid/CFA ratio) and/or zeolite synthesis (e.g. Si/Al ratio of CFA) as illustrated in the following subsections.

5.1.1.2 Effect of acid to CFA ratio

The effect of acid (acid solution, L)/solid (CFA, S) ratios on water adsorption of zeolite samples was investigated. Figure 5.3 shows the flow diagram of the effect of L/S ratios experimentation. The water adsorption from ethanol solution using zeolite synthesized from CFA treated with 20%w/w concentration of HCl under various L/S ratios and commercial molecular sieve is plotted in Figure 5.2b. The L/S ratio of acid-washing pretreatment showed a significant effect on the water adsorption performance of the zeolite products. Table 5.1 demonstrates that the zeolite synthesized from CFA treated with HCl at L/S ratio of 20 mL_{acid}/g_{CFA} had the largest specific surface area, pore size, and also the highest value of the water adsorption capacity, the specific water adsorption capacity and the maximum water adsorption capacity (4.51×10^{-3} g_{water}/g_{CFA}, 1.42×10^{-2} $g_{water}/g_{zeolite}$ and 5.69×10^{-2} $g_{water}/g_{zeolite}$, respectively). The highest ethanol concentration at the outlet of the adsorption process using zeolite synthesized from CFA treated with HCl at L/S ratio of 20 mL_{acid}/g_{CFA} was 98.9%wt, which was higher than that from the commercial molecular sieve type 3A (98.7%wt). However, it was still lower than that from the commercial molecular sieve types 4A (99.7%wt).

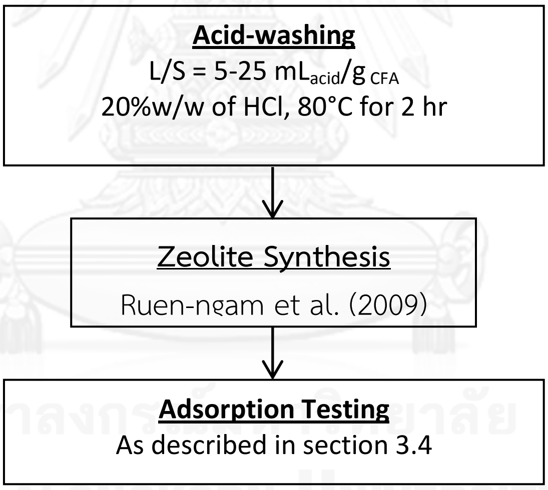


Figure 5. 3 Flow diagram of the effect of L/S ratios experimentation

5.1.1.3 Effect of reusing acid

The effect of reusing acid on water adsorption of zeolite samples was investigated. The flow diagram of the effect of reusing acid experimentation is shown in Figure 5.4. After pretreating CFA with fresh HCl (20%w/w) under the L/S of 20

mL_{acid}/g_{CFA}, the solid sample was filtered off and then used as raw material for synthesizing zeolite. The acid solution, once the solid sample was filtered off, was used in next pretreatment batches.

The breakthrough curve of water adsorption on commercial molecular sieve and zeolite synthesized from the CFA treated with the reused acid are plotted as shown in Figure 5.2c. The zeolite samples synthesized from CFA treated with reused acid had quite a similar value of the outlet ethanol concentration (97-98%) to that from the commercial. The maximum water adsorption capacity were in the range 3.05×10^{-2} to 4.35×10^{-2} of and the time required to reach a plateau value of the samples were in a range of 6-8 min as shown in Table 5.1. However, when considered the adsorption capacity, the specific adsorption capacity and the maximum adsorption capacity of zeolite samples, the sample treated with fresh acid showed a higher adsorption performance than the samples treated with reused acid. Furthermore, the adsorption capacity and the specific adsorption capacity of zeolite samples decreased when the acid solution was used repeatedly as shown in Table 5.1.

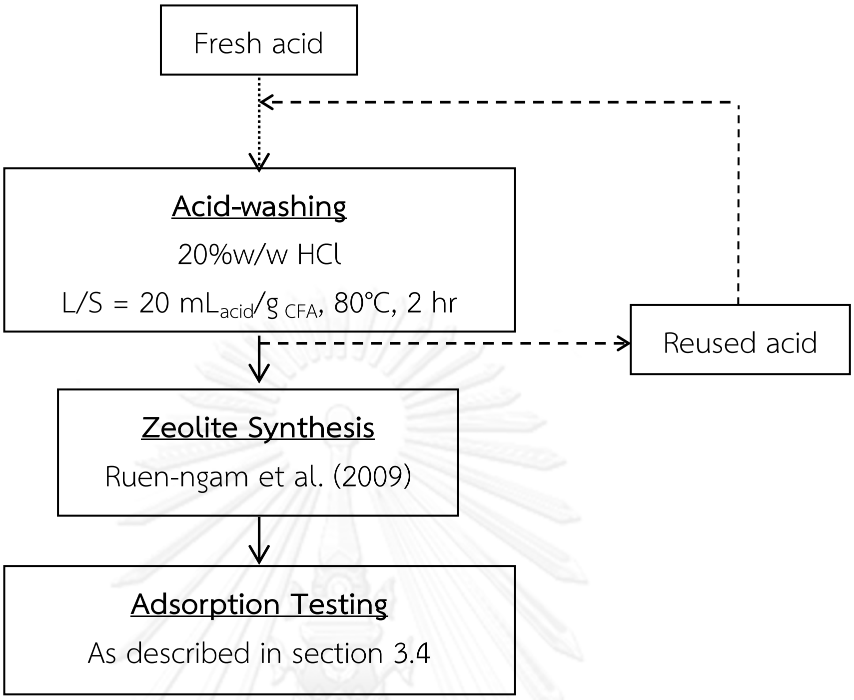
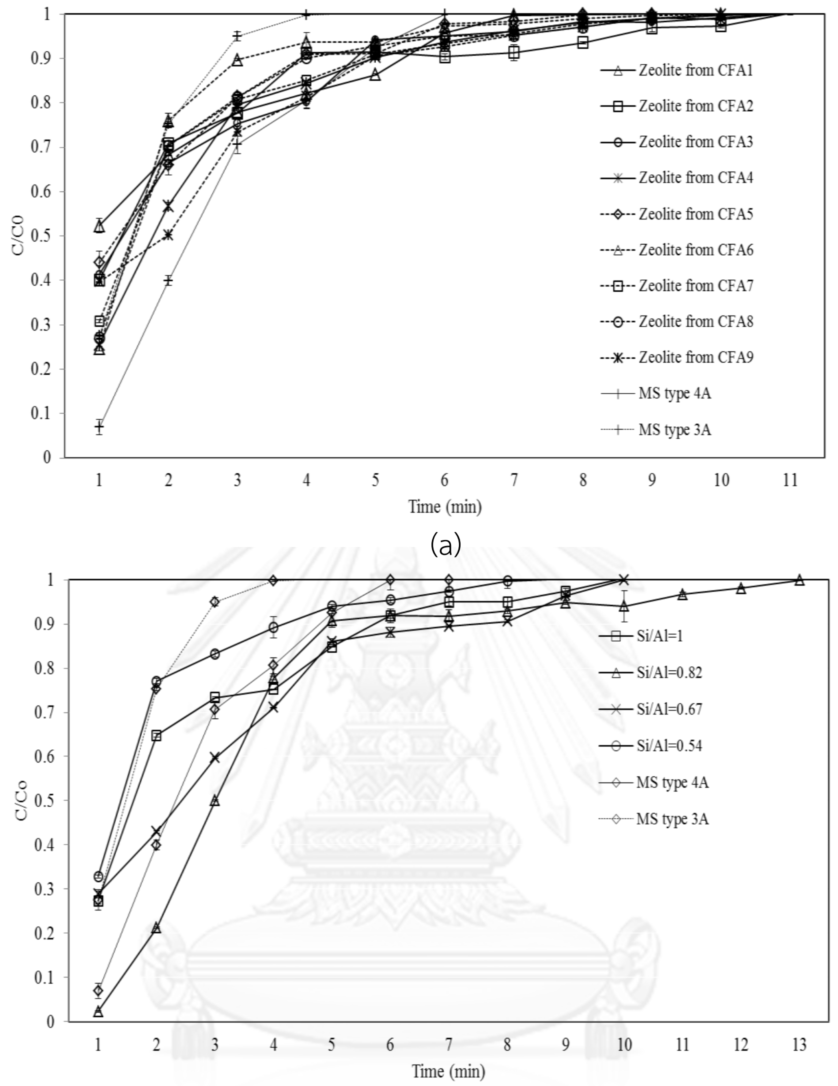


Figure 5. 4 Flow diagram of the effect of reusing acid experimentation

5.1.2 Effect of chemical compositions of raw material

The impurities in the CFA as listed in Table 4.1 illustrates that each CFA could have a variety of contaminants and that each CFA would contain various quantities of Si and Al. This will then have a direct effect on the quality of zeolite synthesized from the CFA. To remove the impurities of CFA and to make a higher purity of zeolite product, the acid-washing pretreatment was carried out prior to using the fusion method with HCl 20%w/w concentration under the L/S ratio of 20 mL/g at 80°C for 2 hr. The pretreated CFA was converted to zeolite using the fusion temperature of 550°C with NaOH/CFA mass ratio of 2.25 for 1 hr followed by crystallization at 80°C for 4 hr (See Figure 3.1 for the experiment procedures).

Figure 5.5a shows the breakthrough curve of water adsorption on zeolite samples synthesized from various CFAs and commercial molecular sieve. From the results, all zeolite samples showed quite similar adsorption performance as shown in Table 5.1. The highest ethanol concentration at the outlet of the adsorption process in the case of using the synthesized zeolite samples was in a range of 97-98%wt (shown in Table 5.1), which was lower than in the case of using commercial molecular sieve types 3A and 4A. When considered a maximum adsorption capacity of zeolite, the commercial molecular sieve also gave a higher value than the synthesized zeolite samples as shown in Table 5.1. Due to the large pore size of the synthesized zeolite sample (4.43-4.89 Å), it is possible that ethanol (molecule size is approx. 4.4 Å) can be adsorbed within the zeolite pores, which results in a low water adsorption performance.



(a)

(b)

Figure 5. 5 Breakthrough curves of ethanol-water system, during water adsorption by synthesized zeolite samples, without the Si/Al ratio adjustment at lab scale (a), with Si/Al ratio adjustment at lab scale and pilot scale (b)

From these results, it can be concluded that although the chemical compositions of raw CFA were different each time they were collected, the zeolite type produced was identical when employing similar synthetic conditions as shown in Figure 3.1. However, the water adsorption performance of zeolite samples can be improved by creating suitable conditions for zeolite synthesis, including a suitable Si/Al ratio of CFA in order to improve the zeolite products physical properties (e.g. framework type, specific surface area and pore size) and chemical properties (e.g. ion-exchange, affinity for water adsorption).

5.1.3 Effect of Si to Al ratio

For this investigation, CFA was pretreated with acid prior to fusion with HCl 20%w/w concentration under the L/S ratio of 20 mL/g at 80°C for 2 hr to remove the impurities. The Si/Al molar ratio of the treated CFA was then adjusted in the range of 0.54 to 1 before the fusion at 550°C with NaOH/CFA mass ratio of 2.25 for 1 hr. This was followed by crystallization at 80°C for 4 hr. The adjustment of Si/Al molar ratios in the fusion reaction mixture was achieved by adding alumina powder (Al_2O_3) as a source of aluminum. The flow diagram of the effect of Si/Al ratio experimentation was shown in Figure 5.6.

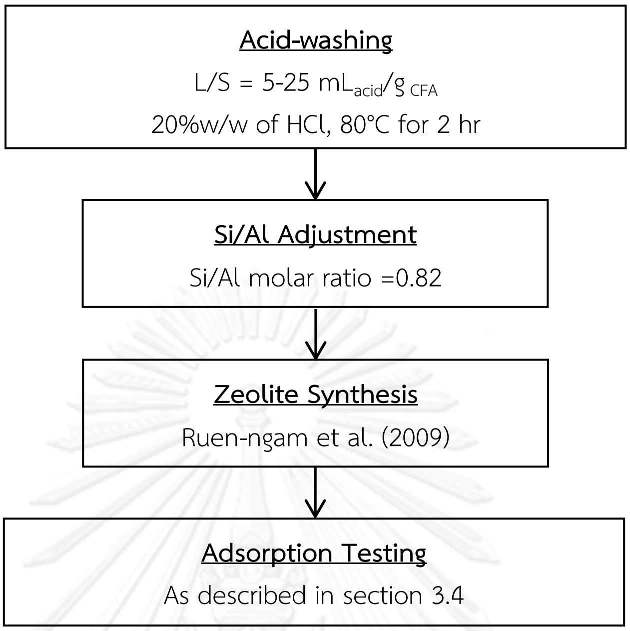


Figure 5. 6 Flow diagram of the effect of Si/Al ratio experimentation

The breakthrough curves of water adsorption on zeolite products with various Si/Al and commercial molecular sieve were plotted in Figure 5.5b. The process to improve the Si/Al ratio, by adding alumina prior to the fusion process, not only strongly affected the structure formation of the zeolite samples (described in Section 4.3), but also dramatically affected the water adsorption performances of the products. All of the zeolites undergoing the Si/Al improvement process prior to the fusion process exhibited a higher water sorption performance, i.e. a higher ethanol concentration and a higher value of the specific water adsorption capacity than the commercial molecular sieve. Among these samples, the zeolite product with a Si/Al ratio of 0.82 displayed the highest adsorption performance. The water adsorption capacity of the above sample was 1.50×10^{-2} g_{water}/g_{CFA} and the specific water adsorption capacity and the maximum water adsorption capacity were 8.23 x 10^{-2} $g_{water}/g_{zeolite}$ and 2.31 x 10^{-2} $g_{water}/g_{zeolite}$, which were higher than the maximum water adsorption and the specific water adsorption of the commercial molecular sieve (8.23 x 10^{-2} $g_{water}/g_{zeolite}$ and 2.20 x 10^{-2} $g_{water}/g_{zeolite}$, respectively) (see Table 5.1). Furthermore, ethanol concentration at the outlet of the adsorption process using the synthesized zeolite sample with Si/Al molar ratio of 0.82 was approximately 99.9%wt, which was higher than that obtained from the commercial molecular sieve (99.7%) as illustrated in Table 5.1. The time needed to reach a plateau value in the case of using zeolite with Si/Al improvement process prior to the fusion process was in a range of 9-11mins. From these results, due to the physical properties improvement of (as described in Section 4.3) and the water adsorption performance of the synthesized zeolite sample, Si/Al molar ratio of 0.82 was considered to be the most suitable Si/Al molar ratio for zeolite synthesis.

5.1.4 Effect of regeneration cycle

In this experiment, the zeolite was regenerated using Thermal Swing method where the temperature was raised to 250°C for 4 hr in order to remove moisture from the sample. It should be noted that temperatures higher than 270°C was not recommended as this could cause extensive structural damage to zeolite (Simo et al., 2009). After that the system was cooled down to the operating adsorption temperature (90°C). The entire adsorption cycle test was investigated without removing the sample from the bed to avoid the influence of moisture in the air. The zeolite sample synthesized from CFA treated with 20%w/w of HCl (80°C, 2 hr) and with Si/Al molar ratio of 0.82 prior to the fusion process (NaOH/CFA=2.25, 550°C, 1 hr) was used to study the breakthrough behavior of the regenerated zeolite.

Figure 5.7 shows the breakthrough curve of water adsorption on zeolite product. The results illustrate that zeolite deactivation was not observed under ten adsorption-testing cycles. A similar behavior of water adsorption performance was observed in all adsorption cycles. Similar behavior with the finding in the last section was found where the highest ethanol concentration at the outlet of the adsorption process was more than 99.9%wt for all adsorption cycles, which was higher than that using the commercial molecular sieve type 3A (98.7%wt) and type 4A (99.7%wt). The maximum adsorption capacity of zeolite sample in ten adsorption cycles were all in the range of 7.79×10^{-2} to 9.26×10^{-2} g_{water}/g_{CFA}.

Based on these results, it can be concluded that the zeolite synthesized by the method shown in Figure 3.1 with a Si/Al molar ratio adjustment can be used as a water adsorbent in the ethanol-water system, with a higher performance than using the commercial molecular sieve. This process can be repeated more than ten times with no observable deactivation.

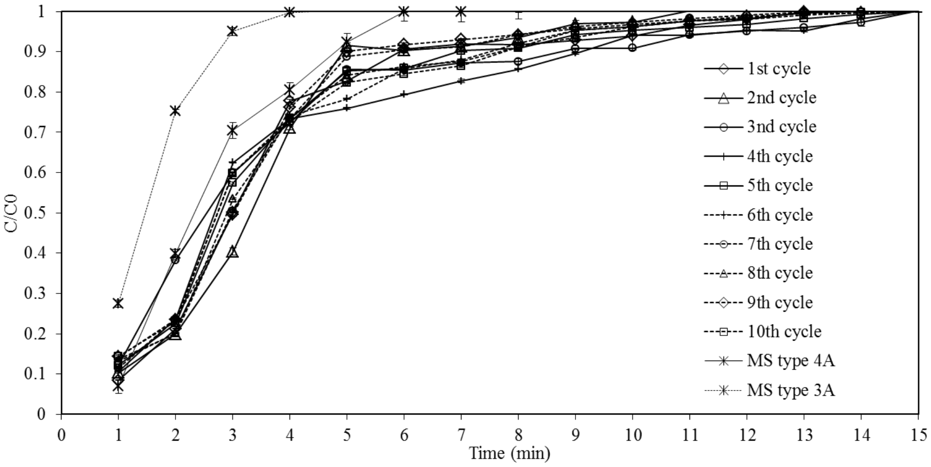


Figure 5. 7 Breakthrough curves of water adsorption on zeolite product

5.2 Large scale of zeolite synthesis

This section focuses on the synthesis of zeolite from industrial waste CFA using larger scale equipment (Figures 3.4-3.6). The synthetic conditions at large scale were selected from the best results obtained at lab scale experimentation to synthesize zeolite molecular sieve. The experimental conditions at large scale are summarized in Table 5.2.

XRF results show that the chemical compositions of zeolite product obtained at large scale were similar to that obtained at laboratory scale. Most of the impurities (Fe_2O_3, CaO and others) of CFA could be removed and a greater purity of zeolite achieved (approx. 92%wt of purity), by pretreatment with HCl. High purity synthetic zeolite has a large application in a range of industries. The zeolite synthesis from CFA treated with 20%wt of HCl provided a higher specific area (478 m^2/g) than the zeolite synthesized from CFA treated with 5%wt of HCl (411 m^2/g) while the pore size

(3.73Å) and pore volume 0.17mL/g) were lower than the zeolite synthesized from CFA treated with 5%wt of HCl (4.35 Å and 0.36 mL/g, respectively).

From the XRD studies, the main phase formation of zeolite product is zeolite type X. Moreover, the morphological analysis by SEM (Figure 5.8) demonstrates that the zeolite crystal formed conglomerates. Additionally, no considerable amount of amorphous materials was detected by this technique. Based on these results, under the same operating conditions, the main difference in the phase formation found from large and laboratory scale experiments was that zeolite type X was detected using the large scale, whilst only zeolite type A was detected using laboratory scale (Table 4.2). This can be due to the unavoidable long filtration time for the large scale system which allowed zeolite to develop further from zeolite A to zeolite X. This long filtration time was inherited from the setup employed in this system as the solid precipitates blocked the outlet channel of the reactor. Note that the results of this study achieved high synthesis yields in a range of 70 % to 75 % of zeolite.

Figure 5. 8 SEM photograph of the zeolite sample synthesized from CFA at large scale

This process has some disadvantages, however, such as a high water consumption and the need for high filtration periods. High water volumes were used for the acid-washing pretreatment and the zeolite synthesis processes. From the point of view of production costs, the high water consumption used during the washing and filtering will be an important consideration. By decreasing the acid concentration from 20%w/w to 5%w/w of HCl, the use of water volumes in acid-washing and filtering processes decreased (approx. 55 L/batch and approx. 25 L/batch, respectively).

The water adsorption performance of the samples synthesized using large scale was evaluated by comparing them with the commercial molecular sieve. Figure 5.5b shows the breakthrough curves of ethanol-water system during water adsorption by the zeolite synthesized using large scale. The results showed that the acid concentration used in the acid-washing pretreatment process strongly affected the water adsorption performance of synthesized zeolite products as shown in Table 5.1. The zeolite synthesized from CFA treated with 20%wt of HCl had a better adsorption performance than the zeolite synthesized from CFA treated with 5%wt of HCl. The highest ethanol concentration at the outlet of the adsorption process, using the sample treated with 20%wt and 5%wt (98.3%wt and 96.6%wt, respectively) of HCl were lower than using the commercial molecular sieve type 4A (99.7%wt) and 3A (98.7%wt), respectively. Although the maximum adsorption capacity of the sample treated with 20%wt (6.38×10^{-2} g_{water}/g_{CFA}) and 5%wt (3.55×10^{-2} g_{water}/g_{CFA}) of HCl were lower than the commercial molecular sieve type 4A, the maximum adsorption capacity of these samples were higher than the commercial molecular sieve type 3A.

From these results, it can be concluded that although the water adsorption performance of the samples synthesized at the large scale were lower than those of the commercial molecular sieve, the zeolite samples synthesized by the method shown in Table 5.2 are still suitable for water adsorption. However, this is only a preliminary study, which needs further investigation. Furthermore, while zeolite synthesis process at lab scale can be carried out under suitable conditions, at large scale there are many other variables (e.g. the time required to reach the operating conditions etc.) that can impact on zeolite properties (e.g. zeolite type and water adsorption performance).

5.3 Economic analysis

A rough cost estimate of the synthesis is given in Tables 5.3 - 5.4, which demonstrates that the total expense per batch using lab scale (approx. 13 g of zeolite product per batch) and large scale (approx. 1.5 kg of zeolite product per batch) were approximately US$6.52 (US$501.43 per kilogram of zeolite) and US$38.57 (US$19.74 per kilogram of zeolite), respectively. The large scale production can be carried out at a considerably lower cost and this looks to be commercially viable when compared with the current global price of zeolite type 4A at US$83.87 per kg (UOP: Changxing Molecular Sieves Group). Moreover, actual industrial scenarios would allow the use of waste heat in the acid-washing and synthesis processes, which might also lower the production cost.

Table 5. 1 Properties of zeolite products synthesized from CFA with various conditions

Conditions					Results								
Parameter studied	Raw CFA	Acid Types	L/S (mL/g)	Si/Al (molar ratio)	XRD Analysis	Yield (%)	Surface Area (m^2/g)	Pore Size (Å)	Pore Volume (mL/g)	The highest Ethanol Conc. (%wt)	A (mg_{water}/g_{CFA})	a_{sp} ($mg_{water}/g_{zeolite}$)	q_{max} (($mg_{water}/g_{zeolite}$))
Effect of acid types	CFA8	Non-treated	25	1.73	Na-X	55	58	3.42	0.25	96.6	7.32×10^{-3}	7.32×10^{-3}	2.82×10^{-2}
	CFA8	H_2SO_4	25	1.73	Na-X	33	226	4.17	0.29	97.7	4.22×10^{-3}	1.28×10^{-2}	3.62×10^{-2}
	CFA8	HNO_3	25	1.73	Na-X	34	139	4.30	0.12	98.1	5.01×10^{-3}	1.47×10^{-2}	3.62×10^{-2}
	CFA8	HCl	25	1.73	Na-X	33	261	4.34	0.80	98.3	5.08×10^{-3}	1.54×10^{-2}	5.16×10^{-2}
Effect of L/S ratio	CFA8	HCl	5	1.73	Na-X	32	35	3.61	0.16	97.2	3.39×10^{-3}	1.06×10^{-2}	3.66×10^{-2}
	CFA8	HCl	10	1.73	Na-X	31	72	3.62	0.17	97.8	4.09×10^{-3}	1.32×10^{-2}	3.53×10^{-2}
	CFA8	HCl	15	1.73	Na-X	28	75	3.02	0.12	97.6	2.23×10^{-3}	1.24×10^{-2}	2.95×10^{-2}
	CFA8	HCl	20	1.73	Na-X	33	227	4.09	0.22	98.9	4.51×10^{-3}	1.42×10^{-2}	5.69×10^{-2}
	CFA8	HCl	25	1.73	Na-X	29	117	3.79	0.21	97.9	4.12×10^{-3}	1.37×10^{-2}	4.46×10^{-2}
Effect of reusing acid	CFA8	HCl(Reuse1)	20	1.73	Na-X	32	301	4.43	0.27	97.8	4.25×10^{-3}	1.33×10^{-2}	3.58×10^{-2}
	CFA8	HCl(Reuse2)	20	1.73	Na-X	33	319	4.61	0.37	97.0	3.09×10^{-3}	9.37×10^{-3}	3.05×10^{-2}
	CFA8	HCl(Reuse3)	20	1.73	Na-X	28	317	4.39	0.21	96.8	2.39×10^{-3}	8.52×10^{-3}	4.35×10^{-2}
	CFA8	HCl(Reuse4)	20	1.73	Na-X	31	306	4.62	0.24	96.8	2.68×10^{-3}	8.63×10^{-3}	3.95×10^{-2}
Effect of raw CFA	CFA1	HCl	20	1.54	Na-X	23	461	4.79	0.32	97.4	2.59×10^{-3}	1.13×10^{-2}	4.45×10^{-2}
	CFA2	HCl	20	1.81	Na-X	29	371	4.65	0.29	98.0	4.11×10^{-3}	1.41×10^{-2}	4.96×10^{-2}
	CFA3	HCl	20	1.84	Na-X	27	363	4.54	0.29	97.9	3.75×10^{-3}	1.39×10^{-2}	4.87×10^{-2}
	CFA4	HCl	20	1.82	Na-X	32	381	4.72	0.32	98.7	5.64×10^{-3}	1.76×10^{-2}	5.37×10^{-2}
	CFA5	HCl	20	1.83	Na-X	32	301	4.43	0.25	97.8	4.25×10^{-3}	1.33×10^{-2}	4.28×10^{-2}
	CFA6	HCl	20	1.80	Na-X	28	372	4.86	0.24	98.8	4.99×10^{-3}	1.78×10^{-2}	4.22×10^{-2}
	CFA7	HCl	20	1.73	Na-X	21	360	4.89	0.26	98.5	3.44×10^{-3}	1.64×10^{-2}	4.90×10^{-2}
	CFA8	HCl	20	1.75	Na-X	31	301	4.85	0.27	98.6	5.35×10^{-3}	1.73×10^{-2}	4.81×10^{-2}
	CFA9	HCl	20	1.73	Na-X	31	322	4.54	0.28	98.0	4.42×10^{-3}	1.43×10^{-2}	5.49×10^{-2}
Effect of Si/Al ratio	CFA8	HCl	20	0.54	Na-A	73	406	4.27	0.49	98.4	1.16×10^{-2}	1.59×10^{-2}	4.29×10^{-2}
	CFA8	HCl	20	0.67	Na-A	67	413	4.28	0.61	98.5	1.13×10^{-2}	1.68×10^{-2}	7.02×10^{-2}
	CFA8	HCl	20	0.82	Na-A	65	418	4.08	0.76	99.9	1.50×10^{-2}	2.31×10^{-2}	8.23×10^{-2}
	CFA8	HCl	20	1.00	Na-A	63	408	4.10	0.57	98.6	1.08×10^{-2}	1.72×10^{-2}	5.81×10^{-2}
Large scale	CFA8	HCl(5%w/w)	20	1.73	Na-X	75	411	4.35	0.37	96.6	9.87×10^{-3}	1.37×10^{-2}	3.55×10^{-2}
	CFA8	HCl(20%w/w)	20	1.73	Na-X	70	478	3.73	0.17	98.3	1.40×10^{-2}	1.86×10^{-2}	6.38×10^{-2}
Commercial M.S. type 3A										98.7	-	1.72×10^{-2}	3.61×10^{-2}
Commercial M.S. type 4A										99.7	-	2.20×10^{-2}	6.15×10^{-2}

Table 5. 2 Zeolite synthesis conditions of the large scale experiment

Raw CFA	**Lab scale** : 20g per batch **Large scale :** 2 kg per batch
Conditions	**Acid-washing pretreatment** 5-20%w/w HCl, L/S=20 mL_{HCl}/g_{CFA}, 80°C, 2 hr, 300 rpm **Fusion** NaOH/CFA = 2.25 (mass ratio), Si/Al = 0.82 (molar ratio), 550°C, 1 hr **Aging** Room temperature, 12 hr, 300 rpm **Crystallization** 80°C, 4 hr without agitation
Filtration	Glass microfiber filters, Whatman GF/C diameter 47 mm
Washing	**After pretreatment** Room temperature, until pH reaches 7 **After crystallization** Room temperature, until pH reaches 10-11

Table 5. 3 Estimated electrical production cost of zeolite

Electrical Process Requirement	Lab scale				Large scale			
	Electrical Power (kW)	Time Used (hr)	Electricity Consumed (Unit)	Electricity Charge (US$)	Electrical Power (kW)	Time Used (hr)	Electricity Consumed (kwh)	Electricity Charge (US$)
Heater	0.415	2.5	1.04	0.09	1.00	2.5	2.50	0.21
Motor	0.415	12.0	4.98	0.42	0.44	44.5	19.58	1.65
Fan	-	-	-	-	0.37	44.5	16.467	1.39
Acid/Alkali Chemical Pump	0.12	6.0	0.72	0.06	0.03	30.0	0.90	0.08
Kiln	1.60	28.0	44.8	3.77	1.60	28.0	44.8	3.77
Furnace	2.00	2.0	4.0	0.34	3.10	2.0	6.2	0.52
Total (US$/Batch)				4.68				7.61
Total (US$/kg of zeolite)				359.68				5.08

Note 1. Electrical process requirements and time used based on the synthesis condition in Table 5.1.

2. The Electricity tariff (2.61 THB/kW or approx. 0.084 US$/kW for ≥69kW) based on the Electricity Generating Authority of Thailand (EGAT), 2011.

3. The productivity of zeolite product in the case of using the lab scale and large scale are approx. 13 g/batch and 1.5 kg/batch, respectively.

Table 5. 4 Estimated material production cost of zeolite

Materials	Lab scale			Large scale		
	Amount Used	Cost (US$/Unit)	Cost (US$)	Amount Used	Cost (US$/kwh)	Cost (US$)
HCl, 37%	0.27 L	4.90 US$/L	1.33	27.03 L	1.05 US$/L	28.33
Tap water	4.38 L	3.48×10^{-2} US$/L	1.4148×10^{-3}	107.97 L	3.48×10^{-2} US$/L	0.03
NaOH anhydrous pellet	22.50 g	10.32 US$/kg	0.23	2.25 kg	0.97 US$/kg	2.18
Al_2O_3 powder	6.77 g	41.94 US$/kg	0.28	0.34 kg	1.26 US$/kg	0.43
Total (US$/Batch)			1.84			30.97
Total (US$/kg of zeolite)			141.75			20.65

Note 1. Amount of materials used based on the synthesis condition in Table 5.1.

2. Material cost based on the commercial price in Thailand, 2012.

3. The Water tariff (0.01 THB/L or approx. 3.23x10-4 US$/L) based on The Metropolitan Waterworks Authority of Thailand (MWA), 2012.

4. The productivity of zeolite product in the case of using the lab scale and large scale are approx. 13 g/batch and 1.5 kg/batch, respectively.

CHAPTER 6

CONCLUSIONS AND ACHIEVEMENTS

6.1 Conclusions

The investigation in this study can be summarized as follows:

1. Coal fly ash can be used as a raw material for the synthesis of zeolite molecular sieve.
2. Most of the impurities (Fe_2O_3, CaO and other impurities) in CFA can be removed by acid-washing pretreatment method.
3. The most suitable conditions for removing impurities were found to be the use of 20%wt HCl with an L/S ratio of 20 mL_{HCl}/g_{CFA} to wash the CFA for 2 Hr at 80°C.
4. The reused acid test was repeated four consecutive times with satisfactory results where most impurities could be removed effectively, and the products exhibited high purity (77-81%).
5. Alkali fusion method can convert the crystalline phase CFA to an amorphous phase, which then can be transformed into various zeolite products by varying the experimental conditions.
6. Si/Al molar ratio of raw material (CFA) has a significant effect on the chemical and physical properties of the synthesized zeolite products.
7. The most suitable conditions for converting CFA to zeolite molecular sieve were fusion reaction at 550ºC with a NaOH/CFA mass ratio of 2.25, Si/Al molar

ratio of 0.82 (adjusted by mixing Al_2O_3 to the treated CFA) followed by crystallization reaction at 80°C for 4 hr.

8. Despite the differences in chemical compositions of raw CFA, the type of zeolite (zeolite type A or X) can be formulated by employing suitable conditions of acid-washing and zeolite synthesis.
9. The zeolite synthesized using the most suitable conditions of acid-washing (20%wt of HCl, an L/S ratio of 20 mL_{HCl}/g_{CFA}, at 80°C for 2 Hr) and zeolite synthesis (NaOH/CFA mass ratio of 2.25 and Si/Al molar ratio of 0.82), had a higher water adsorption performance than the commercial grade molecular sieve and under ten adsorption-testing cycles at 90°C, a high ethanol purity (>99.5%) can still be achieved without deactivation.
10. Chemical compositions of the zeolite product obtained from the large scale process were similar to those obtained at laboratory scale under the same synthesis conditions.
11. Under the same operating conditions, the main difference in the phase formation found from large and laboratory scale experiments was that zeolite type X was detected in the product obtained from the large scale, whilst only zeolite type A was detected using the laboratory scale system.
12. The commercial molecular sieve showed a higher performance than the zeolite synthesized at large scale. The highest ethanol concentration at the outlet of the adsorption process, using the sample treated with 20%wt and 5%wt of HCl were 98.3%wt and 96.6%wt, respectively, while using the

commercial molecular sieve type 4A and 3A were 99.7%wt and 98.7%wt), respectively.

13. The maximum adsorption capacity of the sample treated with 20%wt and 5%wt of HCl using the large scale production were lower than the commercial molecular sieve type 4A, the maximum adsorption capacity of these samples were higher than the commercial molecular sieve type 3A.
14. A rough cost estimate of the synthesis was calculated, which demonstrated that the total expense per batch of zeolite synthesized by the large scale synthesis was relatively low when compared with the cost of commercial grade molecular sieve.

6.2 Achievements

A large quantity of CFA has been generated from coal combustion in power generation. The management of CFA therefore becomes both an economic and an environmental issue. Several technological options have been proposed for the disposal of CFA such as its use as a raw material substitute in cement production. This study evaluated the technical feasibility of the conversion of waste CFA to zeolite and scaled up of such zeolite synthesis process to propose and examine its feasibility. This is not only to generate a useful adsorbent but also to increase the value of industrial waste CFA. The results from this work reveal that this process is ready for a further up-scale investigation to actual industrial size system. However, a large scale process will encounter many more variables (e.g. the time required to reach the operating conditions etc.) that can affect zeolite properties (e.g. zeolite type and water adsorption performance). If the synthesis of the zeolite at large scale can be better controlled where adjustments can be made such that the desired type of zeolite is generated, a large scale production could become possible and feasible.

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APPENDIX

Table A1 XRF data of zeolite samples synthesized from CFA under various pretreatment and synthesis conditions

Conditions				Chemical composition											
Acid type	Raw CFA	L/S (mL/g)	Si/Al (molar ratio)	%Na_2O (%wt)	%Si_2O (%wt)	%Al_2O_3 (%wt)	%Fe_2O_3 (%wt)	%TiO_2 (%wt)	%MgO (%wt)	%Cao (%wt)	%K_2O (%wt)	%SO_3 (%wt)	%NiO (%wt)	%SrO (%wt)	%ZrO_2 (%wt)
Non-treated	CFA8	25	1.73	11.62	31.48	16.26	17.56	1.85	2.69	18.23	3.93	2.06	0.30	0.06	1.62
H_2SO_4	CFA8	25	1.73	22.46	37.04	15.00	17.24	4.18	-	2.81	0.33	-	0.67	-	0.29
HNO_3	CFA8	25	1.73	24.19	30.02	15.12	19.09	6.47	-	1.86	0.71	-	0.70	-	0.46
HCl	CFA8	25	1.73	21.91	41.37	23.85	4.85	4.69	-	1.47	0.24	-	0.17	-	0.25
HCl	CFA8	5	1.73	21.26	41.32	22.01	5.33	6.08	-	3.24	0.53	-	-	-	-
HCl	CFA8	10	1.73	24.50	40.85	21.10	5.78	4.30	-	2.73	0.50	-	-	-	-
HCl	CFA8	15	1.73	22.10	41.94	20.53	6.48	2.82	-	2.69	0.91	-	-	-	-
HCl	CFA8	20	1.73	22.57	40.29	21.96	6.43	4.64	-	3.00	0.85	-	-	-	-
HCl	CFA8	25	1.73	18.99	38.41	23.93	7.94	5.80	-	3.90	0.43	-	-	0.03	0.03
HCl(Reuse1)	CFA8	20	1.73	19.93	39.17	21.92	8.29	5.69	-	4.67	-	-	-	0.15	0.19
HCl(Reuse2)	CFA8	20	1.73	18.84	38.06	23.69	7.87	4.43	-	4.38	0.39	-	-	0.14	0.14
HCl(Reuse3)	CFA8	20	1.73	17.55	37.94	21.92	9.45	6.78	-	5.60	0.46	-	-	0.20	0.32
HCl(Reuse4)	CFA8	20	1.73	18.75	39.11	22.45	8.34	6.04	-	4.87	-	-	-	-	0.23
HCl	CFA1	20	1.54	21.91	41.37	23.85	4.85	4.69	0.85	1.47	0.24	-	-	0.04	0.05
HCl	CFA2	20	1.81	18.99	38.41	23.95	7.94	5.8	-	3.90	0.43	-	-	0.25	0.34
HCl	CFA3	20	1.84	16.92	39.03	22.48	8.34	7.04	-	4.71	0.68	-	-	0.36	0.43
HCl	CFA4	20	1.82	16.75	40.18	17.81	8.47	9.12	2.04	5.12	-	-	-	0.18	0.34
HCl	CFA5	20	1.83	19.93	39.17	21.92	8.29	5.69	-	4.67	-	-	-	0.15	0.19
HCl	CFA6	20	1.80	16.43	41.98	20.14	11.10	4.58	-	4.50	1.08	-	-	0.23	0.19
HCl	CFA7	20	1.73	21.18	37.36	25.20	7.65	3.62	1.5	2.78	0.42	-	-	0.14	0.15
HCl	CFA8	20	1.75	20.34	36.22	26.16	11.95	2.91	-	1.61	0.37	-	-	-	0.14
HCl	CFA9	20	1.73	19.35	39.42	24.98	7.85	4.89	-	2.57	0.29	-	-	0.30	0.35
HCl	CFA8	20	0.54	21.10	32.97	42.97	1.06	0.74	-	0.89	0.24	-	-	0.03	0.02
HCl	CFA8	20	0.67	22.24	33.85	40.05	1.21	0.81	-	0.88	0.29	-	-	0.03	0.02
HCl	CFA8	20	0.82	23.76	37.12	35.17	1.25	0.94	-	0.93	0.26	-	-	0.04	0.03
HCl	CFA8	20	1.00	25.61	36.90	35.08	0.74	0.66	-	0.69	0.25	-	-	0.33	0.33
Large scale															
5%wt HCl	CFA8	20	1.00	20.29	38.08	34.00	3.90	1.49	-	1.66	0.34	-	-	0.15	0.11
20%wt HCl	CFA8	20	1.00	19.77	42.05	30.18	3.21	2.20	-	1.80	0.51	-	-	0.12	0.16

A.2 Calculation of percent crystallinity

The X-ray diffraction (XRD) data were used to calculate the percent crystallinity of zeolite type A and X. The XRD diffraction peak of zeolite type A and X standard is given in Figure A1. The high intensity of the distinguishable peaks (at least 5 peaks) from the samples and from the zeolite type A and X standard were chosen, and

$$\%\text{crystallinity} = \frac{\sum \text{XRD diffraction peak intensity of zeolite sample}}{\sum \text{XRD diffraction peak intensity of zeolite standrad}} \times 100$$

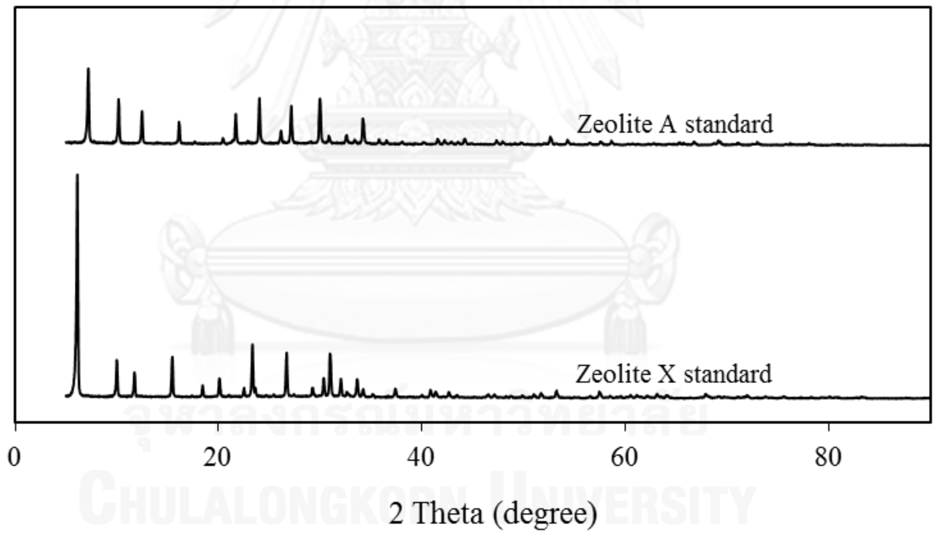

Figure A1. XRD diffraction peak of zeolite type A and X standard

Table A2.1 Summation of XRD diffraction peak intensity of zeolite X standard

Angle (2 Theta)	Intensity (cps)
6.1208	4,747
10.0093	846
15.4529	914
23.3442	1,139
30.9844	996
Sum of intensity	8,642

Table A2.2 Summation of XRD diffraction peak intensity of zeolite A standard

Angle (2 Theta)	Intensity (cps)
7.1956	1,651
10.1896	974
12.4785	723
16.1386	502
21.6988	654
24.0280	997
26.1529	321
27.1632	827
29.9795	1,029
34.2113	593
Sum of intensity	8,642

Table A2.3 Calculation of %crystallinity of zeolite synthesized from CFA without pretreatment and from CFA treated under various acid types

Treatment acid	Angle (2 Theta)	Intensity (cps)
Non-treated	6.1107	615
	10.0053	376
	15.3836	234
	23.3516	273
	30.9517	371
	Sum of intensity	1,869
	%crystallinity (%zeolite X)	21
HCl	6.0873	888
	09.9685	249
	15.4102	410
	23.2722	505
	30.9376	558
	Sum of intensity	2,610
	%crystallinity (%zeolite X)	30
HNO_3	6.1230	415
	10.0250	157
	15.4356	194
	23.3545	177
	31.0029	201
	Sum of intensity	1,144
	%crystallinity (%zeolite X)	13
H_2SO_4	6.1028	877
	9.9971	315
	15.3877	392
	23.3334	420
	31.0272	510
	Sum of intensity	2,514
	%crystallinity (%zeolite X)	29

Table A2.4 Calculation of %crystallinity of zeolite synthesized from CFA treated under various L/S ratios

L/S ratio (mL/g)	Angle (2 Theta)	Intensity (cps)
5	-	-
10	6.1445	501
	9.9664	148
	15.4668	221
	23.3155	299
	31.0020	311
	Sum of intensity	1,480
	%crystallinity (%zeolite X)	0,017
15	6.1962	547
	10.0697	272
	15.4364	271
	23.3650	408
	31.0312	349
	Sum of intensity	1,847
	%crystallinity (%zeolite X)	0,021
20	6.0974	2,850
	9.9835	893
	15.4370	1,064
	23.3331	1,358
	30.9998	1,452
	Sum of intensity	7,617
	%crystallinity (%zeolite X)	0,088

Table A2.4 Calculation of %crystallinity of zeolite synthesized from CFA treated under various L/S ratios (Continued)

L/S ratio (mL/g)	Angle (2 Theta)	Intensity (cps)
25	6.1112	592
	9.9929	187
	15.4028	291
	23.3371	418
	30.9478	412
	Sum of intensity	1,900
	%crystallinity (%zeolite X)	21

Table A2.5 Calculation of %crystallinity of zeolite synthesized from CFA treated with reused acid

Treatment acid	Angle (2 Theta)	Intensity (cps)
Reuse 1	6.0797	609
	9.9723	367
	15.3303	230
	23.2586	278
	30.9047	368
	Sum of intensity	1,852
	%crystallinity (%zeolite X)	21
Reuse 2	6.1182	696
	10.0087	317
	15.3623	303
	23.2962	364
	30.9465	416
	Sum of intensity	2,098
	%crystallinity (%zeolite X)	24
Reuse 3	6.2028	583
	9.9778	246
	15.4217	294
	23.2463	353
	31.0222	402
	Sum of intensity	1,878
	%crystallinity (%zeolite X)	22
Reuse 4	6.1512	873
	10.0067	390
	15.4739	331
	23.3308	406
	30.9527	417
	Sum of intensity	2,417
	%crystallinity (%zeolite X)	28

Table A2.6 Calculation of %crystallinity of zeolite synthesized from various CFAs

CFA	Angle (2 Theta)	Intensity (cps)
CFA1	6.1207	2,751
	10.0051	831
	15.4526	721
	23.3736	1,298
	30.9992	1,158
	Sum of intensity	6,759
	%crystallinity (%zeolite X)	78
CFA2	6.1087	2,567
	09.9947	765
	15.4450	816
	23.3199	975
	30.9709	1,254
	Sum of intensity	6,377
	%crystallinity (%zeolite X)	74
CFA3	6.1407	2,446
	10.0077	834
	15.4252	915
	23.3239	1,013
	30.9895	1,310
	Sum of intensity	6,509
	%crystallinity (%zeolite X)	75
CFA4	6.1207	2,531
	9.9947	821
	15.4429	793
	23.3412	1,201
	30.9521	1,103
	Sum of intensity	6,449
	%crystallinity (%zeolite X)	75

Table A2.6 Calculation of %crystallinity of zeolite synthesized from various CFAs (continued)

CFA	Angle (2 Theta)	Intensity (cps)
CFA5	6.0931	2,318
	10.2939	356
	15.4552	812
	23.3458	1,017
	30.9711	896
	Sum of intensity	5,399
	%crystallinity (%zeolite X)	0,062
CFA6	6.1145	2,519
	10.0072	545
	15.4372	715
	23.4336	1,102
	30.9987	865
	Sum of intensity	5,746
	%crystallinity (%zeolite X)	0,066
CFA7	6.1107	2,831
	10.0095	446
	15.4652	715
	23.3119	1,123
	30.9897	980
	Sum of intensity	6,095
	%crystallinity (%zeolite X)	0,071
CFA8	6.1106	2,712
	9.9949	547
	15.4525	714
	23.3539	978
	30.9845	723
	Sum of intensity	5,674
	%crystallinity (%zeolite X)	0,066

Table A2.6 Calculation of %crystallinity of zeolite synthesized from various CFAs (continued)

CFA	Angle (2 Theta)	Intensity (cps)
CFA9	6.1287	2,548
	10.0047	652
	15.4455	895
	23.3452	1,012
	30.9799	913
	Sum of intensity	6,020
	%crystallinity (%zeolite X)	70

Table A2.7 Calculation of %crystallinity of zeolite synthesized from CFA with the Si/Al ratio adjustment at lab scale experimentation

Si/Al molar ratio	Angle (2 Theta)	Intensity (cps)
0.54	7.2352	1,409
	10.2172	1,143
	12.5018	845
	16.1619	720
	21.7268	975
	24.0468	1,674
	26.1671	431
	27.1794	1,515
	30.0002	1,777
	34.2361	1,060
	Sum of intensity	11,549
	%crystallinity (%zeolite A)	140
0.67	7.2154	1,751
	10.2056	1,454
	12.4901	1,018
	16.1438	770
	21.7072	1,239
	24.0239	1,973
	26.1523	519
	27.1501	1,708
	29.9756	2,237
	34.2179	1,296
	Sum of intensity	13,965
	%crystallinity (%zeolite A)	169

Table A2.7 Calculation of %crystallinity of zeolite synthesized from CFA with the Si/Al ratio adjustment at lab scale experimentation (continued)

Si/Al molar ratio	Angle (2 Theta)	Intensity (cps)
0.82	07.2137	02,292
	10.1949	01,826
	12.4869	01,392
	16.1294	01,097
	21.6945	01,503
	24.0189	02,386
	26.1433	00,665
	27.1447	02,234
	29.9692	02,677
	34.2042	01,615
	Sum of intensity	17,687
	%crystallinity (%zeolite A)	00,214
1.00	7.1869	2,273
	10.1702	1,968
	12.4607	1,278
	16.1031	922
	21.6780	1,545
	23.9952	2,520
	26.1213	626
	27.1282	2,171
	29.9542	2,562
	34.1924	1,621
	Sum of intensity	17,486
	%crystallinity (%zeolite A)	00,211

VITA

Mr. Panu Panitchakarn was born on 9th March, 1983 in Pitsanulok. He finished his secondary course from Pitsanulok Pittayakom School in March, 2001. After that, he studied in the major of Chemical Engineering in Faculty of Engineering at King Mongkut's University of Technology North Bangkok. He continued his further study for Master's degree in Chemical Engineering at Chulalongkorn University. He participated in the Biochemical Engineering Research Group and achieved his Master's degree in April, 2006. He continued studying Doctoral degree of Chemical Engineering, Chulalongkorn University since October 2009 and was grateful for financial support from the Thailand Research Fund (TRF) through grant number IUG5280008. He participated in the Environmental Engineering Research Group and achieved his Ph.D. degree in April, 2014.

His invention patents are as follows:

1. Impurity removal technique for enhancing the properties of coal fly ash. Application No. 1001001732. 11 November 2010.

2. Molecular sieves synthesis process from waste coal fly ash generated in the power plant. Application No. 1201003154. 25 June 2012.

His academic publications are as follows:

1. Synthesis and testing of zeolite from industrial-waste coal fly ash as sorbent for water adsorption from ethanol solution. Panitchakarn, P., Klamrassamee, T., Laosiripojana, N., Viriya-empikul, N., and Pavasant, P. 2014. Engineering Journal.

2. Synthesis of High Purity of NaA and NaX Zeolite from Coal Fly Ash. Panitchakarn, P., Laosiripojana, N., Viriya-empikul, N., and Pavasant, P. 2014. Journal of the Air & Waste Management Association.