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2017

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UNIVERSITY OF CALIFORNIA

Los Angeles

A Single Component Adsorption of Alcohols in Zeolites

A thesis is submitted in partial satisfaction  
of the requirements for the degree of Master of Science  
in Chemical Engineering

By

Abdulaziz Ali Alturki

2017

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## ABSTRACT OF THE THESIS

A Single Component Adsorption of Alcohols in Zeolites

by

Abdulaziz Ali Alturki

Master of Science in Chemical Engineering

University of California, Los Angeles, 2017

Professor Dante A. Simonetti, Chair

Increasing global energy demand serve as the impetus for the development of alternative sources of fuels and chemical intermediates. Toward this goal, many biologically based processes have been recently invented to convert biomass into short chain oxygenated molecules that can be subsequently converted to fuels and chemicals. The primary advantage of these biological processes is their high selectivity and mild operating conditions. However, the major drawback is that the final product is typically produced as a very dilute aqueous solution. The primary purpose of this work is to examine the major factors that affect the performance of solid adsorbent materials for the extraction of small chain alcohols, aldehydes, and ketones from dilute aqueous solutions that contain a wide range of molecules and ions, similar to those derived from fermentation processes. To understand the fundamentals of adsorption using microporous, aluminosilicate materials, and adsorption isotherms were collected for alcohols and aldehydes on proton forms of BEA, MOR, FER, FAU and MFI zeolites. The Langmuir adsorption model was used to develop a quantitative understanding of the relationship between adsorbent structure and performance by determining the effect of solution composition and adsorbent structure on the parameters of each model (equilibria constants, saturation capacities, and interaction parameters). The effects of different zeolite structure on the parameters for the Langmuir model were initially probed using butanol as the adsorbate. Maximum adsorption capacities were similar for all zeolites tested. The adsorption equilibrium coefficient parameter was lower for FAU and MOR compared to BEA and MFI.

The thesis of Abdulaziz Ali Alturki is approved.

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Dante A. Simonetti, Committee Chair

University of California, Los Angeles

2017

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## **Acknowledgements**

I am indebted to everyone who encouraged me in my educational journey towards this degree. For as far back as I can remember, I have always believed in this saying, “your success is reliant on the encouragement and cooperation of others.” As such, I want to take this opportunity to express my gratitude to the people who helped me successfully complete this thesis. I would like to show a great appreciation to Prof. Dante Simonetti, my graduate advisor, for his patience, guidance, support, and motivation, which shaped me into the researcher I am today. I had a unique experience with Professor Simonetti, and I am very thankful for the countless hours he spent it with me.

Besides my advisor, I would like to thank my thesis committee members: Prof. Vasilios I. Manousiouthakis and Prof. Panagiotis Christofides, for their encouragement and insightful comments.

I would also like to thank my friends in the Simonetti Research Group. I have had a delightful time and shared many experiences with them. I would like to thank my colleague Faisal Alshafi from Simonetti group for his support. I will always cherish my memories with them.

Finally, I would like to thank my family for their continued support and encouragement during my time as a graduate student.



## Nomenclature

$C_0$	Initial concentration of solution
$C_e$	Equilibrium concentration of solution
$K_1$	Langmuir adsorption constant related to equilibrium constant
$q_{max}$	maximum adsorption capacity
$r_a$	Adsorption reaction
$r_d$	Desorption reaction
$\emptyset$	Ratio of occupied sites over available sites
$K$	Freundlich isotherm constants capacity parameter
$V$	Volume of solution
$W$	Mass of adsorbent
$n$	Freundlich competitive adsorption coefficient for the system components
$q$	Adsorption capacity

# 1. Chapter 1

## 1.1 Motivation

Population growth and economic development have been the main two drivers for the increase in energy demand worldwide the last two decades. Among the various sources of energy, petroleum is the most significant. The global use of petroleum and other liquid fuels averaged 95 million barrels/day in 2015, with that number projected to increase up to a 100 million barrels/day by 2020 and 121 in 2040. The rising demand is expected to be satisfied by an increase in liquid production by 26 million barrels/day over the 2015-40 period (USEIA, 2016). The projection of future liquid balances includes two categories, petroleum resources and other liquid fuels referred to as natural gas liquid (NGL), biofuels which includes biomass to liquid (BTL), coal to liquids (CTL), kerosen and refinery gain. This increase in demand creates a concern regarding the inevitable depletion of this finite resource.

Alternative resources are essential to provide a portfolio of more diverse feedstocks for future energy supply. Even with the current low prices of oil, prices are expected to return to the range of \$80/b within next decade and for long term sustained increasing in oil prices will encourage consumers to shift from liquid fuels to whatever cost competitive fuel is available (USEIA, 2016). According to (USEIA, 2016), four main factors could provide incentives for a sustained liquid production in the world (1) competition among OPEC for market share, (2) revenue for liquid exporting countries, (3) decrease in service cost, and (4) technology that lowers costs and raises recovery rates. In recent years, biomass conversion technologies have been researched as an attractive alternative resource to offset reliance on petroleum.

Biomass is one of the world's largest single renewable energy resource contributing to 10% of the world's primary energy supply (IEA, 2012). It is expected to be the most potential source among the emerging other liquid fuels. By the gradual shifting toward the more carbohydrate-based economy, 2030, it is anticipated that 20% of transportation fuels and 25% of chemical with 45 billion pounds of bio based chemical and bio products will be produced from biomass (BRD, 2007). Due to their abundance and growing production, they could help alleviate concerns regarding energy security and climate change. Helping climate change is achieved by offsetting fuel mitigation and reducing greenhouse gases as the CO<sub>2</sub> emissions from its combustion is being consumed by plants during the process of photosynthesis producing more biomass. Biomass has the potential of reducing 550 million tons of CO<sub>2</sub> every year (BRD, 2007).

Lignocellulosic biomass is non-edible residues obtained from agriculture, forestry, urban and industrial reuses. They can be converted into solid, liquid and gaseous fuels through different technologies of thermal, thermochemical and biochemical conversion. Figure 1-1 shows a schematic of the different routes available for biomass conversion. Different reactions are involved in these steps includes hydrolysis, dehydration, isomerization, oxidation, dehydrogenation, and hydrogenation which takes place in processes such as, combustion, pyrolysis, gasification, alcoholic fermentation and liquefaction.

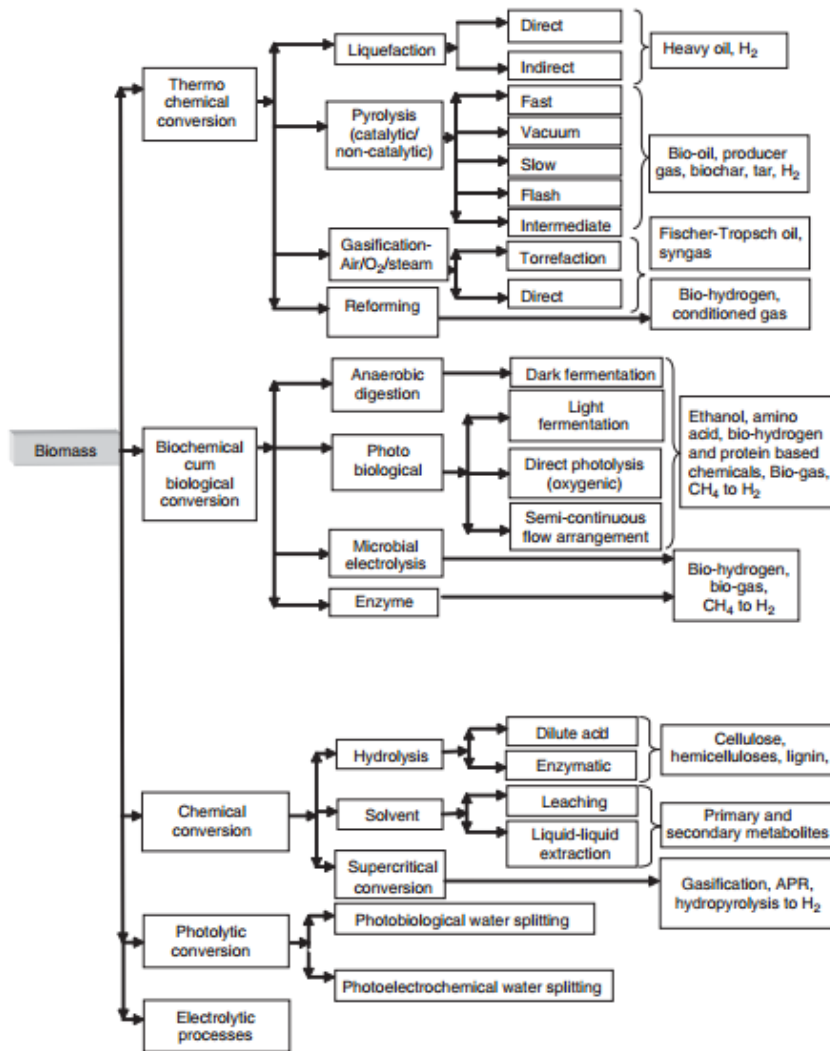


Figure 1-1: Different conversion routes to biofuels (Mohanty, et al. 2014)

Thermochemical conversion and biochemical are two of the widest applications of biogenic waste conversion. Both with the aid of catalysts are having the potential for integrated, developed technologies into the broader infrastructural usage of fuels, power, and chemical. The main difference between these two routes is the primary catalyst system (Foust, et al., 2009). Thermochemical route relies on physical catalysts to convert biomass into an intermediate gas or liquid then convert the intermediate to biofuel. The major drawback of this process is its non-selectivity producing wide range of products. Advancement in this area includes reducing cost and environmental impacts associated with the conversion biomass into useful fuels and products (Huber & Dumesic, 2006)

On the other hand, biochemical conversion route relies on bio catalysis, such as enzymes and microbial cells with the presence of heat and chemicals to convert biomass to an intermediate sugar mixed stream then to fermentation produced biofuel. The primary advantage of this route is the high selectivity and conversion efficiency (Foust, et al., 2009). Advancement in this area needs an improvement to minimize water use, waste water generation and to improve the separation of the final products.

In the biochemical conversion process, Lignocellulosic biomass produce two production routes (ABE) and (IBE). Figure 1-2 shows the metabolic pathways in ABE fermentation. This production route is challenged by low production yield and high energy use for separation (Ezeji, et al., 2004). Therefore, alternative separation techniques to distillation are more attractive and promising for integration. Several online recovery methods were studied including, adsorption, liquid-liquid extraction, pervaporation, and gas stripping. Among them, adsorption is the most promising separation process to separate required molecules from the fermentation broths. (Oudshoorn, et al., 2009). The material and energy balance reported by (Qureshi, et al., 2005), suggested that the energy needed to recover butanol from fermentation broth using zeolites as adsorbent needs 1,948 kcal/kg compared to 5,789 kcal/kg by distillation or gas stripping. The process of adsorption involves adsorbing the required molecules on the surface of adsorbent (zeolite in this study) then desorbing them by increasing the temperature. Different factors affect adsorption such as, adsorption capacity, selectivity, affinity, which are subject to adsorbent type. Therefore, we aim in this project to systematically study these factors to improve the process of separation.

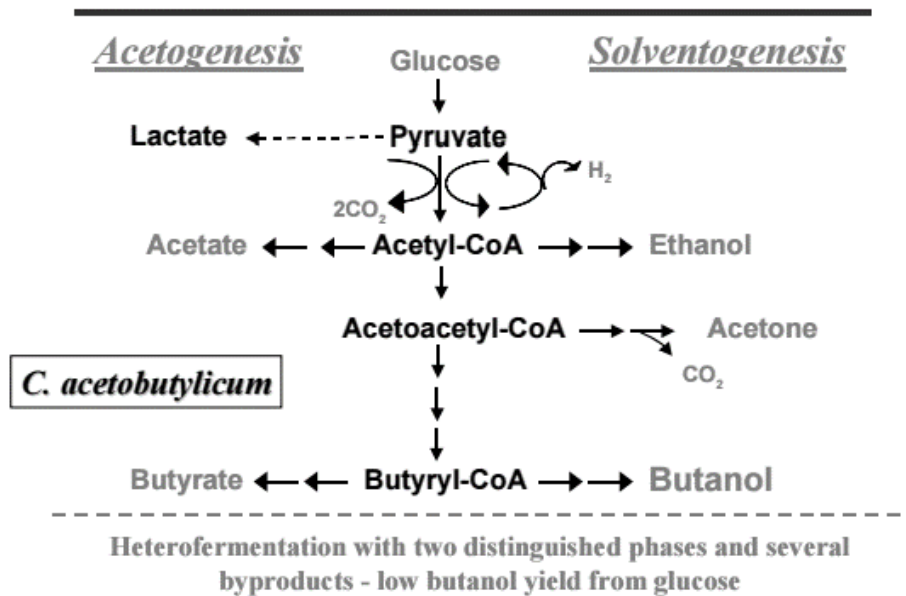


Figure 1-2: ABE Fermentation Pathway (Ramey & Yang, 2004)

## 1.2 Research Objectives

With biomass being the only renewable source of carbon that has the ability to produce energy and chemicals, the field of biological catalysis plays a significant role in the development of biomass-based technologies. However, recent research revealed some challenges to separate fermentation broth molecules in dilute aqueous solutions effectively. These challenges can be summarized as follows:

- Lack of fundamental understanding of oxygenate adsorption behavior in different types of zeolites with various pore structure
- Lack of quantitative understanding of multi-component adsorption on zeolites in dilute aqueous systems
- The need to establish cost effective biorefinery operations for separation and upgrading as well as to meet the current infrastructure of fuel systems.

This thesis addresses some of these challenges by elucidating the fundamental understanding necessary to develop effective adsorption processes to extract and upgrade oxygenates found in fermentation products. The primary objectives of the studies presented herein are to investigate the major factors that affect the performance of solid adsorbent materials for the extraction of small chain alcohols, aldehydes, and ketones from dilute aqueous solutions that contain a broad range of molecules and ions, similar to those derived from fermentation processes. The following paragraphs briefly describe the specific research aims of this thesis.

### 1.2.1 Extension of hydrocarbon-zeolite chemistry to alcohol adsorption

The ability of zeolites to selectively separate alkanes of different length and degree of branching has been widely discussed in literature. Earlier studies have reported that alkane adsorption in zeolites is a function of three major interactions: (i) van der Waals forces between zeolite pore walls and the adsorbate, (ii) electrostatic interactions between the adsorbate and Brønsted acid sites, (iii) and adsorbate-adsorbate interactions within zeolite channels (Mallon, 2012).

Furthermore, it has been shown that confinement quantitatively changes enthalpies and entropies of adsorption. It was revealed by both theoretical and experimental studies that adsorption equilibrium constants ( $K_{ads}$ ) exponentially increase with n- and iso-alkane carbon number in different types of zeolites (Eder, et al., 1997). The increase of  $K_{ads}$  with carbon number is due to the increase in dispersion forces that stabilize adsorbates within zeolite channels and, thus, cause an increase in the magnitude of the enthalpies of adsorption of these molecules (Savitz, et al., 1998). These studies aim to extend the principles of hydrocarbon-zeolite chemistry to oxygenate interactions with the goal of developing analogous relations between confinement and adsorption thermochemistry for oxygenated molecules. Specifically, different types of zeolites were investigated to probe the effects of pore size and channel shape to elucidating the effects of topology on adsorption behavior. These studies are presented in Chapter 3.

### **1.2.2 Multi-component adsorption in the dilute regime**

The primary objective of this analysis is to investigate the major factors that affect the performance of solid adsorbent materials for the extraction of small chain alcohols, aldehydes, and ketones from dilute aqueous solutions that contain a wide range of molecules and ions, similar to those derived from fermentation processes. To understand the fundamentals of adsorption using microporous, aluminosilicate materials, adsorption isotherms were collected for alcohols and aldehydes on proton and Na-exchanged forms of BEA, MOR, FER, FAU and MFI zeolites. Langmuir and Freundlich adsorption models were used to develop a quantitative understanding of the relationship between adsorbent structure and performance by determining the effect of solution composition and adsorbent structure on the parameters of each model (equilibria constants, saturation capacities, and interaction parameters) (Abdehagh, et al., 2016). Earlier studies conducted by (Mallon, et al., 2011), suggested that at low concentration, coverage is linearly proportional to the solution final concentration (i.e., Henry's Law adsorption). In this work, we further probe this observation and its applicability with various molecules and zeolite structures.

## 2. Chapter 2

### 2.1 Fundamentals of Adsorption

Adsorption is defined as the preferential concentration of species on the surface which is the interface between two phases. According to (Thomas & Crittenden, 1998), it is the result of the interactive forces of physical attraction between the surface of porous solids and component molecules being removed from the bulk phase. Figure 2-1 shows a schematic of the adsorption process at the molecular scale. (Bansal & Goyal, 2005) noticed an interaction between the field forces of the solid and gas or liquid when they are contacted. These outstanding forces are satisfied by attracting and retaining the molecules, atoms or ions of the gas or liquid which will result in a greater concentration of these molecules near the vicinity of the stable surface than the bulk. With some changes to the properties of the system, such as concentration, temperature, or pH, adsorbed species can be released back into to the fluid phase (desorption) (Worch, 2012).

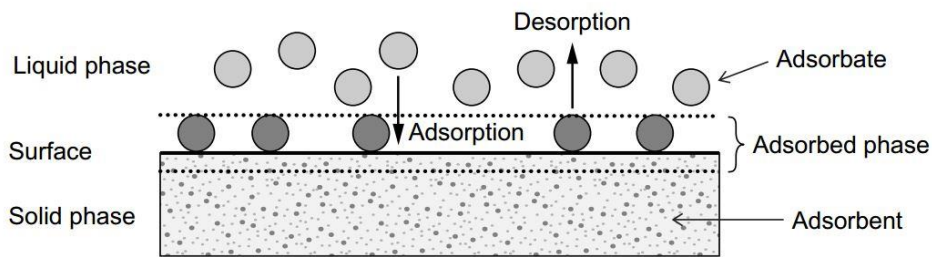


Figure 2-1: Basic Terms of Adsorption (Worch, 2012)

In adsorption, two substances are involved, adsorbent and adsorbate. The process of adsorption can be applied to either gas phase or liquid phase. The most common way to perform adsorption is on high surface area materials because larger surface areas provide more locations for the adsorption to take place, and hence more effective adsorption is achieved. High surface area is commonly obtained via pores. In other words, the more pores, the more surface area per volume. Throughout the pores, molecules are being adsorbed on the surface. Engineered adsorbents are typically highly porous with a range of  $10^2$  to  $10^3$   $\text{m}^2/\text{g}$ .

Adsorption is classified into two types of forces: Physisorption and Chemisorption. Physisorption is due to van der Waal's forces between the adsorbent and adsorbate (i.e., dipole moments, polarization forces, dispersive forces, or short range repulsive interactions). Chemisorption occurs via chemical reaction at the surface of the material involving the redistribution of electrons between adsorbed atoms and solid surface (Bansal & Goyal, 2005). The significant difference between the two types is the magnitude of adsorption enthalpy. Physical adsorption enthalpy range between 10 to 20 kJ per mole, whereas chemisorption is usually higher ranging between 40 to 400 kJ per mol. Another major difference is that chemisorption is specific while physical adsorption is nonspecific and occurs between any adsorbate-adsorbent systems. Physical adsorption surface thickness can be multi-layer while chemisorption is typically limited to monolayer

coverages. Multiple factors determine the types of adsorption including nature of adsorbate and adsorbent, surface reactivity, adsorbate surface area, temperature, and concentration of adsorbate in the fluid phase.

## 2.2 Adsorption Isotherms

Adsorption is usually described using isotherms, which are quantitative functions that describe the fundamentals of adsorption and relate the concentrations of species in the adsorbed and bulk phases. In actual practice, adsorption isotherms are an extensive method to represent the equilibrium states of an adsorption system. They give useful information about adsorbate, adsorbent and adsorption process. Its usefulness may be extended in the determination of adsorbent surface area, pores volume, and size distribution. Furthermore, it will give more information on the magnitude of adsorption enthalpy as well as relative selectivity of molecules to adsorb onto a solid surface at specific conditions. Different isotherm equations have been used to describe experimental adsorption data such as, Langmuir, Freundlich, and Brunauer-Emmett-Teller (BET) equations.

Modeling an isotherm from experimental adsorption data is a useful aid for the prediction of adsorption mechanisms which could lead eventually to an improvement in the science of adsorption (Chen, 2015). Isotherms can follow several forms based on the graph relation between  $q$  (adsorbate concentration on adsorbent) and  $c$  (adsorbate concentration in the bulk fluid) as illustrated in Figure 2-2, typically called I to V. Isotherm type I is limited to a single monolayer completion of adsorbate at an adsorbent surface. This type is usually noticed during chemisorption or physisorption onto solids with the pore of similar size as the adsorbate molecules. That is due to the narrowed sizes which allow a completion of monolayer layers. Type II initially follows type I in which a single monolayer completion is performed near to the first point of inflection before adsorption happens in consecutive layers. This type applied to zeolites with a wide distribution of pore sizes. Similarly, type IV follows the same pattern as II except for the adsorption which ends near to a relative pressure of unity. Types III and V are similar at low concentrations in that they both are continuously convex. However, V at higher concentrations (and after a point of infection) approaches a saturation limit. Among many, three mathematical relationships were recognized to describe the equilibrium distribution of a solute between liquid and solid. These relationships are useful in the interpretation of adsorption data during constant temperature which referred as adsorption isotherms. These are Langmuir, BET, and Freundlich isotherms. The equations for these three isotherms are presented in detail in Section 3.3.



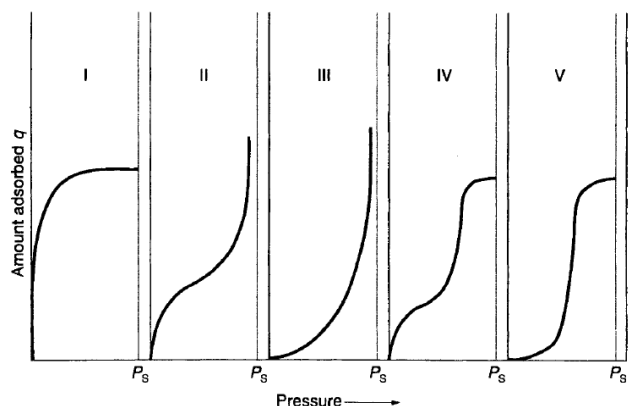


Figure 2-2: Isotherm Adsorption Types (Thomas & Crittenden, 1998)

## 2.3 Previous Studies

In this section, we present previous studies in the area of adsorptive separation for oxygenates in general and in the case of ABE fermentation in more details. This literature review will include studies presented in the single component system for alcohols mainly with the effect of different materials with various pore size and shape.

Finally, we present the potential area of research which includes, details of material composition effects and isotherms in the low concentration regime.

### 2.3.1 Single component adsorption

Recently, significant progress has been made in the field of adsorption, and understanding how zeolite properties could affect adsorption behaviors. Several studies have focused on zeolite pore size and adsorption and shown that adsorption takes place when the volume of adsorbate is equal in size or close to the size of adsorbent which defined as confinement effect. When the size of adsorbate approaches the pore diameter of zeolite, dispersion interactions result between the adsorbate and zeolite causing stronger adsorption. The effect of confinement was mentioned by (Mallon, et al., 2010) on a study of adsorption of alcohols and polyols on zeolites. Liquid phase adsorption isotherms of for  $C_2$ - $C_6$  diols and triols in different pore zeolites have been determined by (Mallon, et al., 2010). The author reported, an increase in Henry constant exponentially with carbon number which is attributed to adsorbate confinement in zeolite to be the driving force. Furthermore, (Elizabeth, et al., 2011) concluded that adsorption enthalpy is linearly proportional to the number of carbon at different zeolite frameworks. This is due to higher dispersion forces between zeolite pore walls and adsorbate with carbon number. Furthermore, (Stückenschneider, et al., 2013) performed both experimental and theoretical studies on alcohol adsorption using BEA and MOR zeolites, BEA shows significantly high adsorption capacity while MOR was only loaded with small amounts of alcohols. This correlates to the pore size effects since BEA is smaller than MOR resulted in more confinement. (Abdehagh, et al., 2013) carried out several equilibrium experiments on different types of adsorbents to probe the highest adsorption of butanol from aqueous solutions. Relatively

high separation factors were determined for Activated carbon (AC) F-400 to be the highest adsorbent for butanol as reported by the author. The same author later (Abdehagh, et al., 2016) investigated selectivity of butanol in the presence of other ABE model solution components. Satisfactory selectivity of butanol/ABE solution was obtained. However, more research was suggested to determine the behavior of each component and their effect on the adsorption process. Recently (Faisal, et al., 2013) investigated the adsorption of butanol and butyric acid from model solutions. These adsorption experiments have shown that both butanol and butyric acid has a high affinity for the hydrophobic MFI zeolite when adsorbed from aqueous model solutions.

For years, there have been extensive studies on the characteristics of zeolite such as microporous structure, acidity and shape selectivity. However, studies on alcohol conversion kinetics and products selectivity are yet limited by the understanding of zeolite topology influence, acidity and alcohol structure. To enumerate, nature and stability of alcohol-zeolite adsorption over the Brønsted acid site is still debatable. Only limited number of experimental works discussed pore structure, zeolite framework, and acidity as important factors in controlling zeolite-alcohol adsorption and reaction. Equilibrium adsorption studies at Henry's region have been successfully used to explain hydrocarbon selectivity for processes such as hydrocracking and dewaxing (Janda et al., 2017). As it approaches zero coverage, Henry region is a critical range to study the intrinsic effects influenced by zeolite topology. (Smit & Theo, 2008) argue that simple thermodynamic analysis adsorbed molecules into zeolite pore structure could help to guide identification of product forms and applicability of zeolite structure for preferred catalytic application.

### 3. Chapter 3:

#### SINGLE COMPONENT ADSORPTION OF C<sub>1</sub>-C<sub>4</sub> ALCOHOLS ON ZEOLITES WITH VARIOUS TOPOLOGIES

##### 3.1 Experimental Methods

###### 3.1.1 Materials

Small, medium and large size pore zeolites with various Si/Al ratios were used to examine the thermodynamic, kinetic, and molecular sieve effects and their consequences on adsorption. The ammonium form of BEA, MOR, FER, and MFI zeolites were purchased from Zeolyst International (see Table 3-1 for formulas and Si/Al ratios) and converted to the proton form via treatment in ambient air at 823 K (rate of 0.2 K s<sup>-1</sup>) for 10 h. H-Y (FAU) zeolite from Zeolyst International was also used.

Methanol (99.8%, Sigma Aldrich), ethanol (95%, Sigma Aldrich), n-propanol (99.7%, Sigma Aldrich), and n-butanol (99.4%, Sigma Aldrich) were purchased from Sigma Aldrich and used as received without additional purification.

Table 3-1: Zeolite framework and properties

Zeolite name	Framework	Si/Al	n
BEA	H <sup>+</sup> <sub>n</sub>   [Al <sub>n</sub> Si <sub>64-n</sub> O <sub>128</sub> ]-*BEA	12.5	4.74
MFI	H <sup>+</sup> <sub>n</sub> (H <sub>2</sub> O) <sub>16</sub>   [Al <sub>n</sub> Si <sub>96-n</sub> O <sub>192</sub> ]-MFI	11.5	7.6
FAU	H <sup>+</sup> <sub>n</sub> (H <sub>2</sub> O) <sub>240</sub>   [Al <sub>58</sub> Si <sub>192-n</sub> O <sub>384</sub> ]-FAU	15	12
FAU	H <sup>+</sup> <sub>n</sub> (H <sub>2</sub> O) <sub>240</sub>   [Al <sub>58</sub> Si <sub>192-n</sub> O <sub>384</sub> ]-FAU	2.6	53.3
MOR	H <sup>+</sup> <sub>n</sub> (H <sub>2</sub> O) <sub>24</sub>   [Al <sub>n</sub> Si <sub>48</sub> O <sub>96</sub> ]-MOR	10	4.36
FER	H <sup>+</sup> (H <sub>2</sub> O) <sub>18</sub>   [Al <sub>n</sub> Si <sub>36-n</sub> O <sub>72</sub> ]-FER	10	3.27

###### 3.1.2 Batch Adsorption Equilibria Tests

Adsorption isotherms were collected using 5 ml of 0.003-0.132 M aqueous solutions of methanol, ethanol, n-propanol, and/or n-butanol. Zeolite samples (0.1-0.5 g) were added to these solutions and shaken periodically until equilibrium was achieved (24-36 hrs). The concentration of alcohol(s) in the liquid were measured daily and equilibrium was determined as being reached when concentrations remained constant for more than 12 hrs. Analysis of the liquid phase occurred via gas chromatography-mass spectrometry (GC—MS; Agilent 5980 GC coupled to 7890 MS; Agilent J&W HP-5 GC Column, 50 m, 0.32 mm, 0.52 μm). The solutions were filtered using a 3 ml mono inject syringe fitted with a 0.2 μm polypropylene filter to remove solids prior to GC-MS analysis.

Initial and final liquid phase concentrations along with solution volumes were used to calculate the amount of molecules adsorbed onto zeolites. Measurements of molecules adsorbed into zeolites were only calculated through liquid phase measurement. Solid phase alcohol concentrations were expressed in terms of moles of adsorbate per mass of adsorbent according to Equation 3.1 (Worch, 2012).

$$q = (C_e - C_0)V/W \text{ --- (3.1)}$$

where,  $C_0$  and  $C_e$  represent the initial and equilibrium concentration of adsorbate, respectively (mol/l), V is the volume of solution and W is the mass of adsorbent.

### 3.2 Modeling

Several mathematical models are used to describe adsorption isotherms. In this study, equilibrium data were modeled using Langmuir isotherm model for single component adsorption.

In this section, isotherm models results will be analyzed.. Non-linear fitting was selected for the analysis because researchers found that linear analysis could lead to a discrepancy between prediction and experimental data even though parameter estimation is easier (Chen, 2015).

#### 3.2.1 Langmuir Isotherm

The Langmuir model was originally developed to explain gas-solid phase adsorption in activated carbon (Langmuir, 1918),

$$q = \frac{q_{max}K_1C_e}{1+K_1C_e} \text{ --- (3.2)}$$

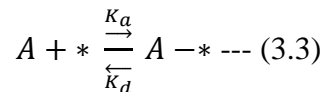
Where,

$q_{max}$  is the maximum adsorption capacity (mol/g)

$K_1$  is constant related to free energy of adsorption (L/g)

$C_e$  is equilibrium concentration.

The following equation illustrates the forward and backward reactions between the adsorbed molecule (A) and the active site (\*) giving the adsorbed species (A\*) according to Equation 3.3



The rate of adsorption is directly proportional to concentration of adsorbate and number of vacant sites of on the surface and the sites are assumed to be single and identical

The rate of the forward reaction will be as follows;

$$r_a = K_a C (1 - \emptyset) \text{ --- (3.4)}$$

Where,

$r_a$  is the rate of the forward reaction normalized by the total number of sites.

$K_a$  is the rate constant for the forward reaction (Adsorption reaction)

$C$  is the concentration of species.

$\emptyset$  is the fraction of surface sites occupied by the adsorbed molecules,

$\emptyset = 1 -$  fraction of vacant sites.

The rate of the reverse reaction will be as follows:

$$r_d = K_d N \emptyset \text{ --- (3.5)}$$

$r_d$  is the rate of the backward reaction, it is normalized by the total number of sites.

$K_d$  is the rate constant for the reverse reaction (Desorption reaction).

$N$  is the number of total sites

$$\emptyset = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}} \text{ --- (3.6)}$$

At equilibrium we have the following,

$$r_a = r_d \text{ --- (3.7)}$$

$$K_a C_e (1 - \emptyset) = K_d N \emptyset \text{ --- (3.8)}$$

Where,

$$K_1 = \frac{K_a}{K_d} \text{ --- (3.9)}$$

Solving Equation 3.8 for  $\emptyset$  leads to the Langmuir Equation

$$\emptyset = \frac{K_1 C_e}{1 + K_1 C_e} \text{ --- (3.10)}$$

At low concentration,  $K_1 C_A \ll 1$  and the concentration of adsorbed species is linearly proportional to the bulk phase concentration.

$$\emptyset = K_1 C_A \text{ --- (3.11)}$$

At High concentration,  $K_1 C_A \gg 1$  and the fraction of total sites occupied by adsorbed species approaches unity.

$$\emptyset = 1 \text{ --- (3.12)}$$

From the above explanation, at low concentration, the Langmuir equation can be reduced to linear equation (3.11) known as Henry's law.

### 3.3 Results and Discussion

#### 3.3.1 Adsorption Equilibrium Data

Adsorption equilibrium data were collected for methanol, ethanol, propanol, and n-butanol at ambient temperature on the zeolites mentioned previously (Figures 3-1 to 3-7). MOR and FAU show linear trends over the studied region (Figures 3-1 to 3-3). On the other hand, BEA, MFI, and FER tend to have a non-linear patterns (Figures 3-4 to 3-6). Figure 3-1 and 3-2 show a similar behavior of adsorption over two different ratios of Si/Al for FAU. In both figures (3-1 and 3-2), butanol adsorption slope was similar giving same maximum adsorption capacity values. However, the slope was relatively higher for smaller alcohols in FAU Si/Al =2.6 compare to FAU Si/Al = 15. In Figure 3-3, MOR shows a similar behavior of non-linear trend. However, the adsorption isotherm slope was less, giving lower values of adsorption capacities for all alcohols compare to FAU. Also, figure 3-3 shows similar observation of the abrupt change between butanol and smaller alcohols. FAU is considered as a large size zeolite. However, MOR is considered medium despite its 12-MR openings because its channels are straight and don't have intersections. They have very different pore structure, but both show linear adsorption.

Figures (3-3 - 3-4) show a non-linear adsorption behavior in a definite pattern with a gradual decrease in adsorption capacity from butanol to methanol. MFI is considered a medium pore with 10-member ring pores and intersecting channels. BEA is large pore with 12 member ring openings, however, BEA has channels similar to MFI. Furthermore, FER has 8-member ring openings and is considered the small pore show similar behavior of non-linear adsorption to MFI and BEA, however, the adsorption was not defined in a well pattern based on molecule size and carbon number. In FER, butanol and ethanol isotherm adsorption slope were similar, as such methanol and propanol with lower isotherm slope.

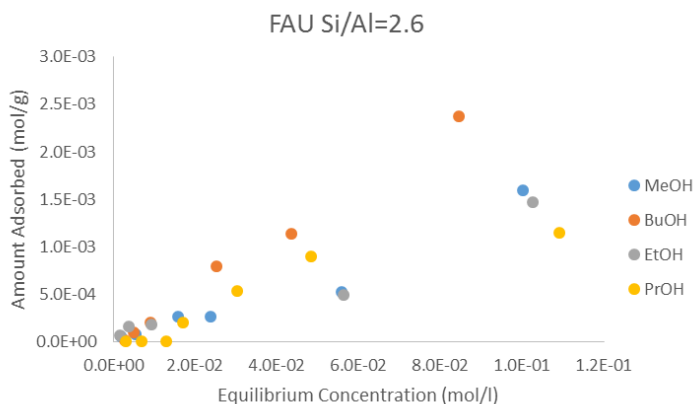


Figure 3-1: Adsorption isotherms for single component alcohols for FAU Si/Al=2.6

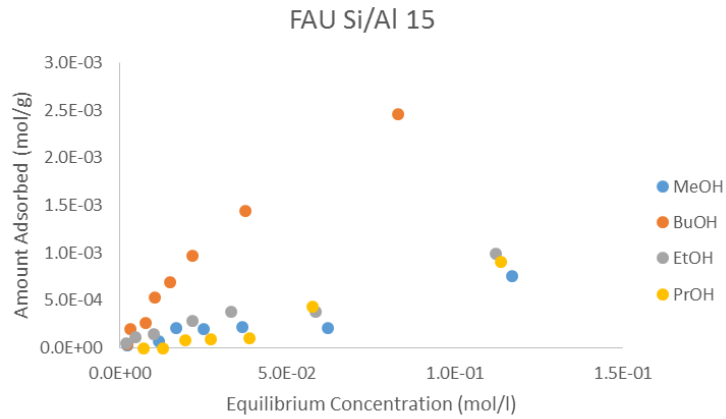


Figure 3-2: Adsorption isotherms for single component alcohols for FAU Si/Al=15

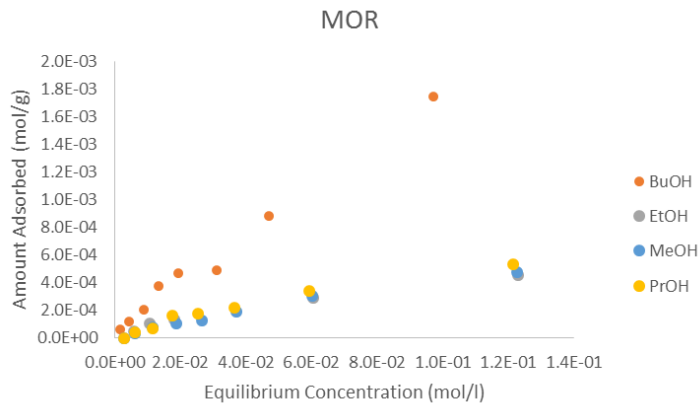


Figure 3-3: Adsorption isotherms for single component alcohols for MOR

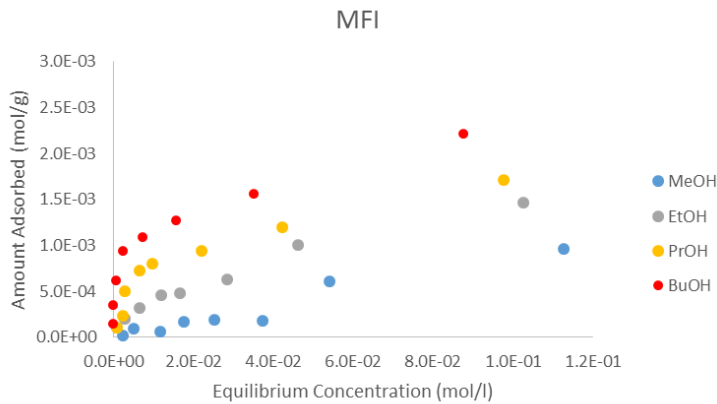


Figure 3-4: Adsorption isotherms for single component alcohols for MFI

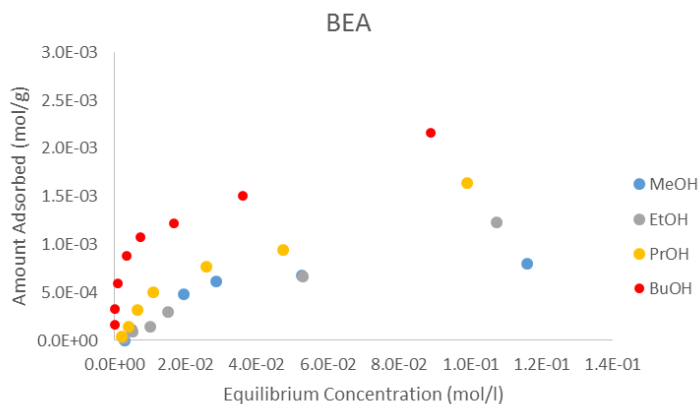


Figure 3-5: Adsorption isotherms for single component alcohols for BEA

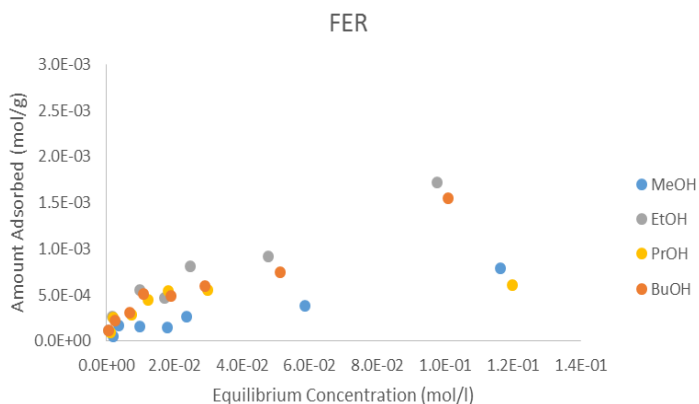


Figure 3-6: adsorption isotherms for single component alcohols for FER

### 3.3.2 Isotherm Modeling Results

Langmuir model assumes monolayer adsorption over adsorbent sites; no further adsorption takes place after a molecule occupies a site. The model assumes homogeneous adsorption, which means that all sites possess equal affinity for the adsorbate. The data in Figures 3-1 through 3-6 were analyzed using the Langmuir model. Model fits are shown in Figure 3-7.



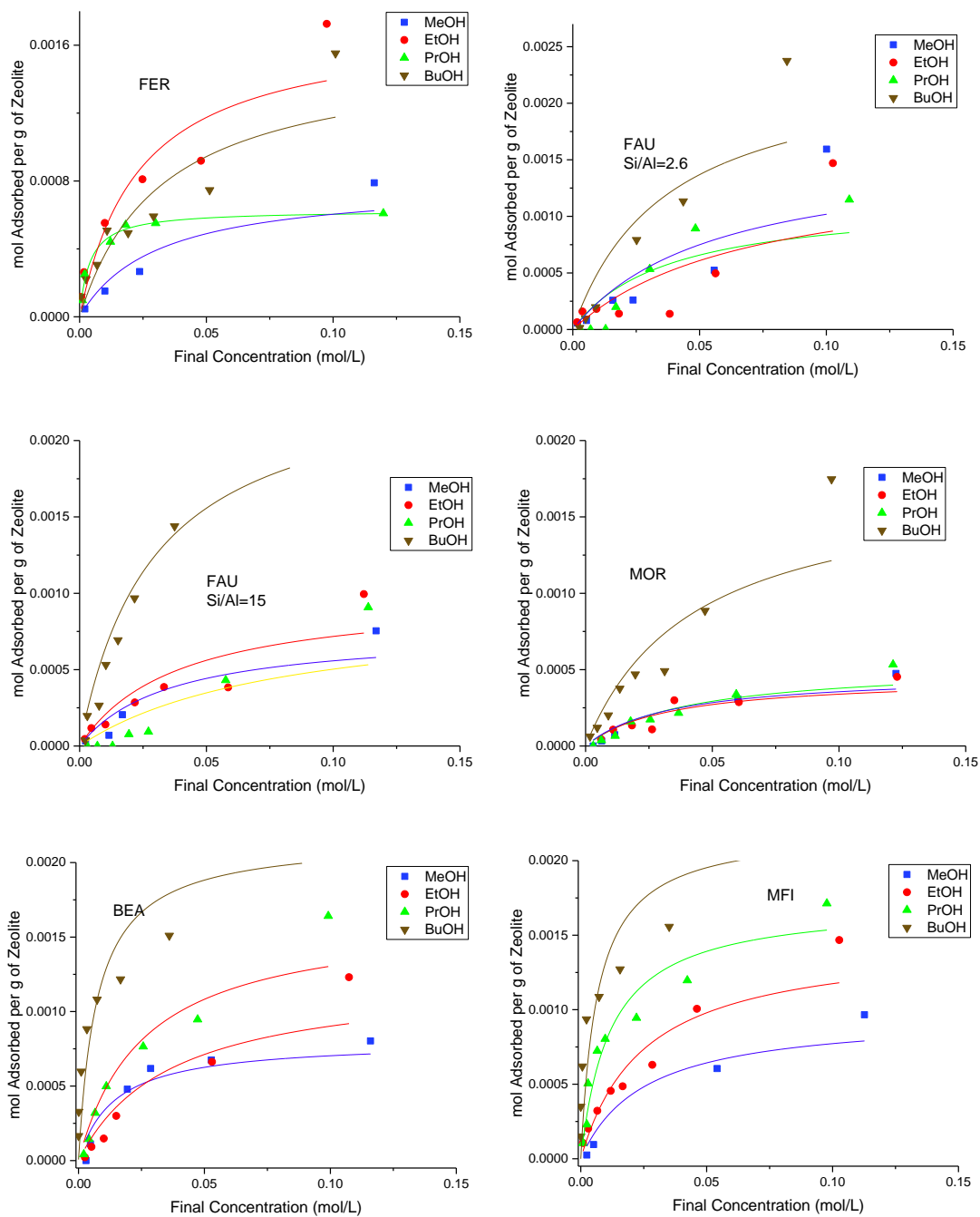


Figure 3-7: Langmuir adsorption isotherms for single component alcohols in aqueous solution for methanol (■ blue line), ethanol (● red line), propanol (▲ light green) and n-butanol (▼ dark green). Symbols are for experimental values and solid lines for model results.

### 3.3.3 Effects of zeolite topology

#### 3.3.3.1 FER

FER consists of straight channels of diameter  $5.4 \times 4.2 \text{ \AA}$  interconnected in a perpendicular direction to cages with 8-ring windows with  $4.8 \times 3.5 \text{ \AA}$  openings. While previous studies observed an increase in adsorption capacity and magnitude of heat of adsorption with increasing alkane size on different types of zeolites (Mallon, 2012), the data for n-alcohol adsorption on FER does not follow an increasing adsorption trend with increasing alcohol size (Figure 3-8). Figure 3-8 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-alcohols on FER. Adsorption equilibrium constants were similar for methanol, ethanol, and butanol, however, this value was 8 times larger for propanol. Because the adsorption was measured at ambient temperature, differences in adsorption entropy are expected to only negligibly affect the adsorption equilibrium constant. Thus, the larger K for propanol must be the result of a larger enthalpy of adsorption (Janda, et al., 2016).

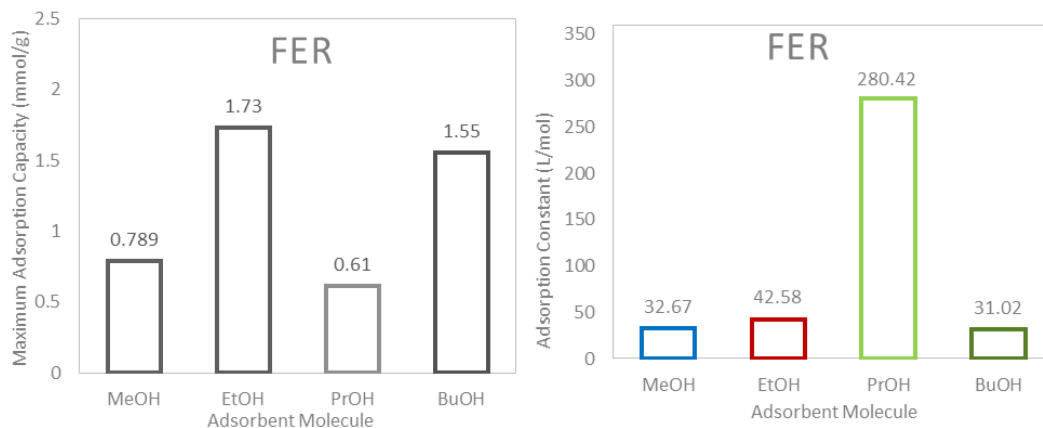


Figure 3-8: Optimal values of Langmuir adsorption model parameters for FER.

#### 3.3.3.2 MOR

MOR consists of a one-dimensional channel, 12-MR of pore diameter  $7.0 \times 6.5 \text{ \AA}$  with 8-MR side pockets  $5.7 \times 2.6 \text{ \AA}$ . The volume of these pockets are smaller than main channels. Figure 3-9 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-alcohols on MOR.

Figure 3-9 shows that maximum adsorption capacity is higher for butanol while,  $C_1$ - $C_3$  adsorption nearly give identical results. Adsorption equilibrium constants were similar for methanol and ethanol, however, this value was smaller for propanol and butanol. The data for n-alcohol adsorption on MOR shows an increase in the adsorption capacity with carbon number, however this effect was abrupt with  $C_4$  and not gradual from  $C_1$  to  $C_4$ . This observation suggests adsorption tend to be limited to the main channels where confinement effect is more pronounced (more dispersion forces) for butanol than smaller alcohol molecules because pore diameter is larger than cross section diameter of  $C_1$ - $C_3$  alcohols. The small adsorption of  $C_1$ - $C_3$  in MOR suggests that side pockets are inaccessible due to its minor axis ( $4.3 \text{ \AA}$ ). Adsorption of butanol in MOR appears to be linear which affects

the values of adsorption equilibrium coefficients not to follow a defined pattern based on molecules sizes. MOR has a high percentage pore volume in the channels and cages 48% and 36% respectively in addition to the large pore size  $\approx 6.75$  Å.

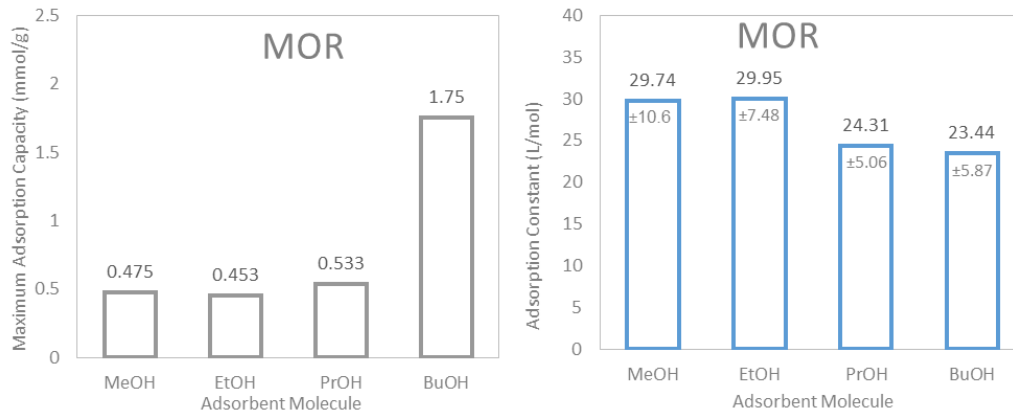


Figure 3-9: Optimal values of Langmuir adsorption model parameters for MOR.

### 3.3.3.3 BEA and MFI

MFI zeolite is an important catalyst for adsorption studies due to its appropriate medium size and pore opening 5.5 Å which is similar to many kinetic diameter molecules (Koningsveld, 1990). Figure 3-10 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-alcohols on MFI. The data for n-alcohol adsorption on MFI observed a gradual increase in adsorption capacity and magnitude of heat of adsorption with increasing alcohol size.

On the other hand, BEA zeolite is considered to be a large size zeolite with two 12 ring size frameworks. (5.6 x 5.6) and (7.7 x 6.6) (Å) in diameters. BEA framework (5.6 x 5.6) (Å) is similar in dimension to the two 10 ring size framework of MFI (5.1 x 5.5) and (5.3 x 5.6). Figure 3-11 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-alcohols on BEA. The data for n-alcohol adsorption on BEA shows a similar observation to MFI zeolite of the gradual increase in adsorption capacity and magnitude of heat of adsorption with increasing alcohol size. On both zeolites BEA and MFI, maximum adsorption capacity increases in well-defined pattern per additional carbon number. BEA and MFI have similar channels and pore diameters (MFI  $\approx 5.4$  Å, BEA  $\approx 6.3$  Å). The higher adsorption capacity is almost certainly associated with channels pore sizes. This is mainly attributed to confinement effect in which molecules are adsorbed into most suited size channels. In other words, the closer the difference between molecule diameter and channel, the higher is the adsorption. MFI medium size zeolite with 10 ring molecules in the range of 4.5–6.0 Å. Similar to the range of alcohol molecules 3.6–5 Å (Table 3-2). Molecules are expected to be adsorbed on the medium size channels while the smaller channels are more suited for water molecules adsorption (Mallon, et al., 2011).

Table 3-2: Kinematic Diameter for adsorbents

Molecule	Kinematic Diameter (Å)
water	3.2
methanol	3.6
ethanol	4.5
n-propanol	4.7
n-butanol	5.0

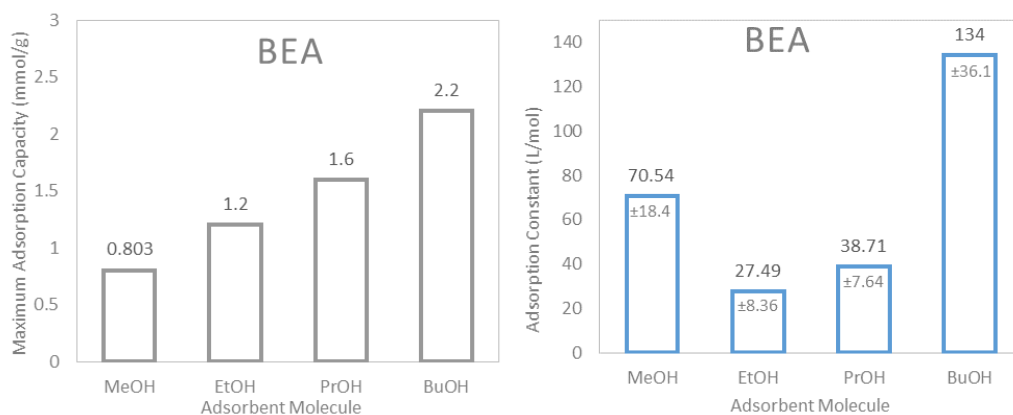


Figure 3-10: Optimal values of Langmuir adsorption model parameters for BEA.

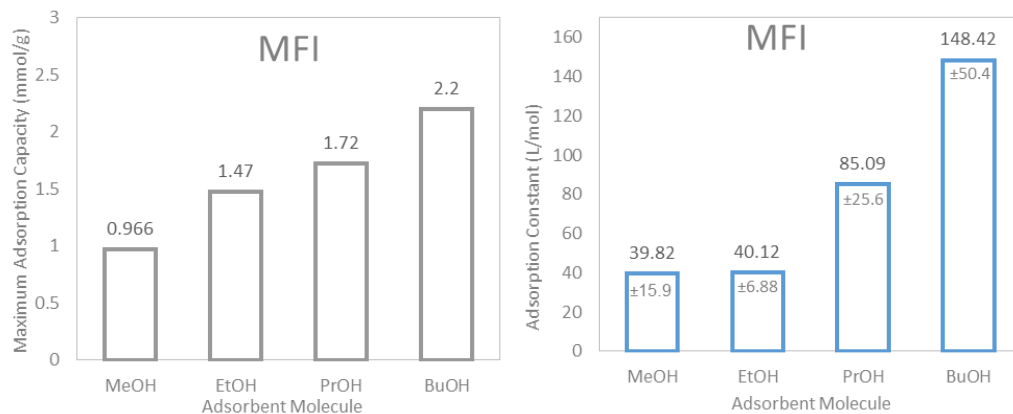


Figure 3-11: Optimal values of Langmuir adsorption model parameters for MFI.

### 3.3.3.4 FAU

FAU is a cubic zeolite characterized by the presence of only one type of large cage 13 Å in diameter and accessed through the 12-ring opening of 7.4 x 7.4 Å, and connected by a straight channel. Figure 3-12 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-alcohols on FAU. The data for n-alcohol adsorption on FAU Si/Al=2.6 observed a gradual increase in the magnitude of heat of adsorption with increasing alcohol size. The same observation was noticed on the FAU Si/Al with the exception of propanol. The maximum adsorption capacity values of butanol for both types FAU Si/Al=15 and Si/Al=2.6 were two times higher for butanol compares to smaller alcohols. The abrupt increase in the maximum adsorption capacity from smaller alcohols to butanol could be attributed to the large size of FAU zeolite associated with large cavity diameter (LCD)  $\approx$  11.9 Å (Table 3.3).

In the zeolite types with no cages, both enthalpy and entropy of adsorption increases as the ratio between minimum to maximum channel diameter decreases. Values of entropy and enthalpy of adsorption become lowest when the ratio becomes 1, corresponding to the circular cross section. Adding cages with large cavity diameter (LCD), higher than pore limited diameter (PLD) increases both, entropy and enthalpy of adsorption. The replacement of channels with cages doesn't change entropy significantly when PLD is similar to molecule length, however enthalpy decrease as a result of the higher surface area of cages relative to surface area (Janda, et al., 2016).

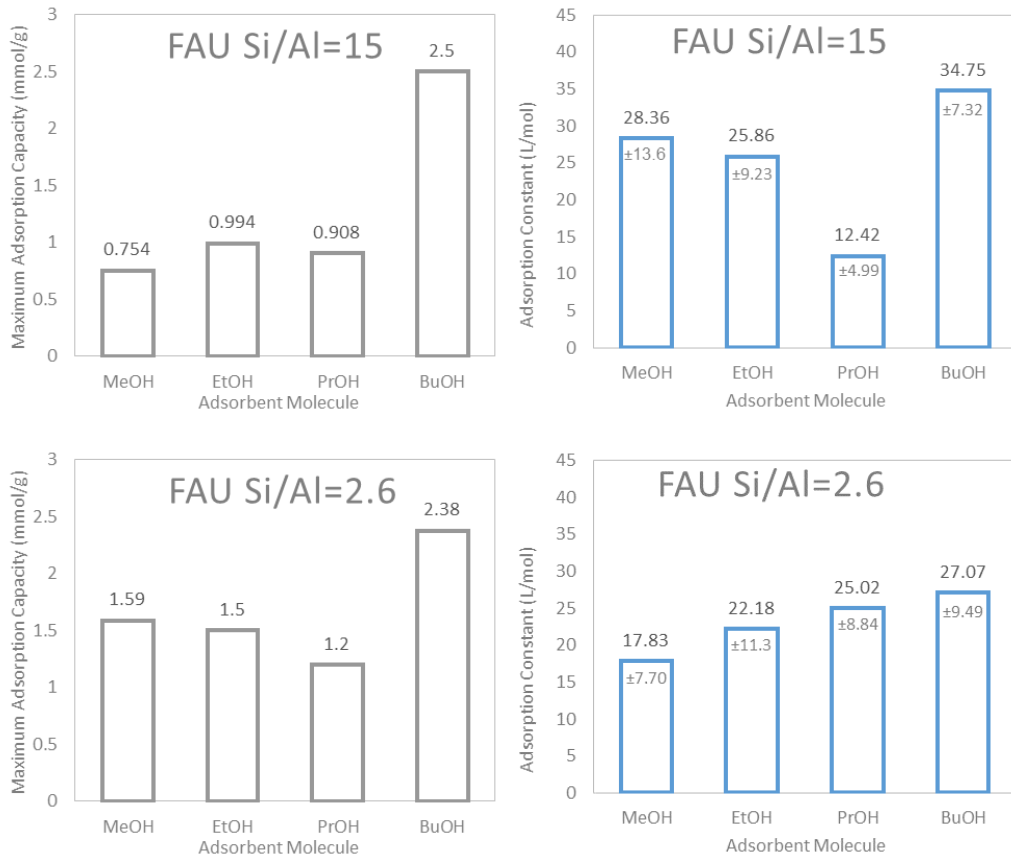


Figure 3-12: Optimal values of Langmuir adsorption model parameters for FAU.

### 3.3.3.5 Effects of Al content

$\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio affects the acidity of zeolite; zeolites become more acidic as the ratio decreases. This is due to the increase of  $\text{AlO}^{-4}$  sites which strengthen electro-static field, thus, availing more acid sites. However, other properties such as electrochemical as well as channels and cages arrangements will play a significant role. Furthermore, increasing the density of  $\text{AlO}^{-4}$  sites might lower the acidity which could be explained by dipolar repulsion of  $\text{AlO}^{-4}$  (Thomas & Crittenden, 1998).

The rate per Brønsted acid site decreases with Si/Al ratio as shown in (Table 3-3), changing Si/Al ratio of FAU from 15 to 2.6 increased number of active sites from 12 to 53.3. (Beaumont & Barthomeuf, 1972) Studied the acidity of FAU acid site and concluded maximum Brønsted acidity approached at Si/Al = 6 with 27 framework aluminum atoms per unit cell. Later (Freude, et al., 1986) reported that acid strength influenced by Si/Al ratio greater than 10 is constant for zeolite types such as H-FAU, H-MOR, and H-ZSM-5. Another study revealed that catalytic activity which is affected by adsorption rate is increased to a maximum of 30 framework aluminum atoms per unit cell then decrease with increasing aluminum framework (Bin, et al., 2007). This study revealed that not all Brønsted acid sites contribute to adsorption especially smaller alcohol molecules, methanol mainly.

Single alcohol molecules were observed in two ranges of Si/Al on FAU zeolite to explain the effect of Al content, 15 and 2.6. It has been shown that high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Butanol adsorption exhibited a negligible effect on maximum adsorption capacity values (Figure 3-18). However, high alumina samples for FAU (Si/Al = 2.6) in smaller molecules showed higher maximum adsorption capacity values than normal FAU (Si/Al = 15). The values increased by double in methanol from 0.754 to 1.60 (mmol/g), and this increment decreased as we moved to larger n-alcohol carbon numbers.

Table 3-3: Theoretical number of active sites for zeolite types studied

Zeolite Type	Si/Al	Zeolite MW [g mol <sup>-1</sup> ]	# Active Site [Al mol. Zeolite g <sup>-1</sup> ]	
BEA	12.5	4224	4.74	892
MFI	11.5	6336	7.68	825
FER	10	2376	3.27	726
MOR	10	3168	4.36	726
FAU	15	12672	12	1056
FAU	2.6	12672	53.3	238

### 3.3.3.6 Comparing different zeolites for butanol

Figure 3-13 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of butanol on different zeolite types. The data for butanol adsorption on these types observed a gradual decrease in the maximum adsorption capacity on the following trend FAU15>FAU2.6>MFI≈BEA>MOR>FER which is similar to the trend of zeolite size with the exception of BEA (BEA has a similar channels to MFI and relatively smaller in pore size than FAU) FAU~BEA>MFI>>MOR>FER. This observation suggests that maximum adsorption capacity is directly proportional to zeolite size within the same molecule studied. On the other hand, adsorption equilibrium coefficients was decreasing in the following trend MFI>BEA>FAU15≈FAU2.6≈MOR≈FER with an abrupt change in coefficient values going from MFI and BEA to the other zeolites. The inverse relationship between adsorption equilibrium coefficient and zeolite pore size is similar to the observation of adsorption enthalpies values and zeolite sizes reported by (Mallon, 2012).

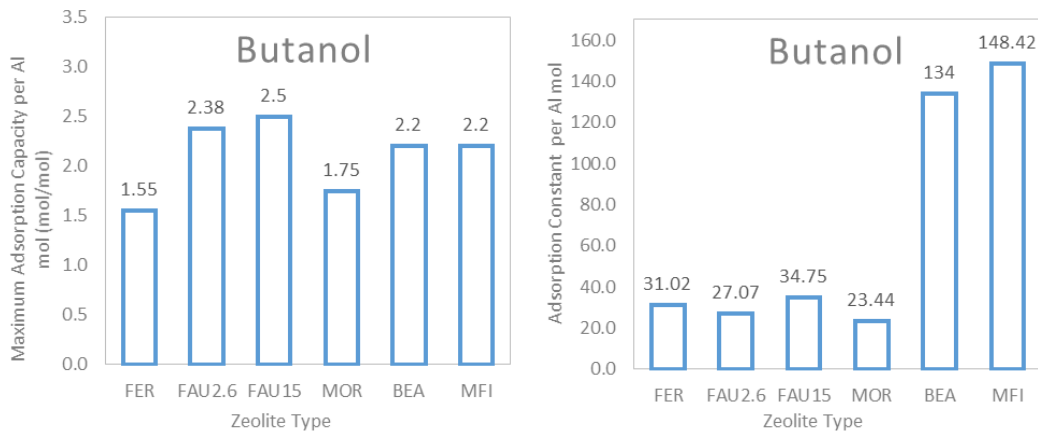


Figure 3-13: Optimal values of Langmuir adsorption model parameters for different Zeolite types.

Table 3-4: Zeolite Topological characteristics for channels and cages (First, et al., 2011).

Framework Type	Channels		Cages		Pore Limiting Diameter
	Ring Size	Channel Pathway	Largest Cavity Diameter	Pore volume in Cages %	
ZSM-5	10	Sinusoidal	7	26	5
	10	Straight			
FER	10	Straight	7	47	5.3
	8	Straight			
MOR	12	Straight	6.5	36	6.5
	8	Straight			
FAU	12	Straight	11.9	77	6.7
BEA	12	Straight	6.9	20	6.7
	12	Straight			

### 3.3.3.7 Alcohol Isomers on BEA Zeolite

Zeolite favors the formation of reaction intermediates with shape proportionate to zeolite pores size. As the conversion of alcohol involves series of consecutive reactions and degree of branching, it is important to arrive at a general explanation for shape-selective conversion understanding (Schenk, et al., 2001). The shape selectivity term argues that zeolite pore shape can change the course of a reaction. Zeolite pore size can inhibit the formation of some branched molecules which are too big to fit inside the pore as well as could result in inverse shape selectivity in which optimum size isomer stabilized and produced preferentially over other species (Smit & Theo, 2008).

(Nguyen, et al., 2011) investigated the adsorption of four butanol isomers (1-BuOH, i-BuOH, 2-BuOH, and t-BuOH) in H-ZSM-5 using periodic [DFT-D] approach. It was concluded that adsorption strength decreases in the following order, 1-BuOH > 2-BuOH > t-BuOH > i-BuOH. In this section, we studied the adsorption behavior of n-butanol and n-propanol isomers 2-butanol and 2-propanol in BEA zeolite. Figure 3-14 shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-butanol, 2-butanol, n-propanol and 2-propanol on BEA. 2-butanol, n-propanol and 2-propanol show similar values of maximum capacity of adsorption, while n-butanol maximum adsorption capacity was higher. Adsorption equilibrium constants were similar for n-propanol and 2-propanol however, this value was different between n-butanol and 2-butanol. This could elucidate that 2-butanol higher kinematic diameter compare to n-butanol might restrict adsorption to occur due to the decrease in enthalpy of adsorption. On the other hand, there was no difference in maximum adsorption capacity and adsorption equilibrium constants between n-propanol and 2-propanol.

Further work is needed to analyze relative adsorption to other isomers based on pore size, adsorption mechanism and thermodynamics effects.

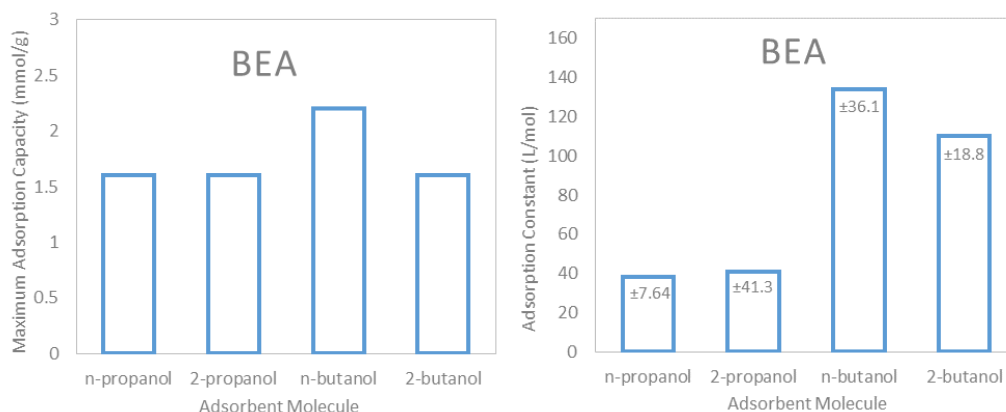


Figure 3-14: Optimal values of Langmuir adsorption model parameters for BEA.



### 3.3.3.8 Comparing n-alcohol, aldehyde and ketone on BEA and MFI

Figures (3-15 and 3-16) shows the maximum capacity and adsorption equilibrium coefficients (for the Langmuir model) for the adsorption of n-alcohols, aldehyde and ketone on BEA and MFI. BEA show n-alcohol < ketone < aldehyde trend for maximum adsorption capacity while MFI trend as follows ketone < n-alcohol < aldehyde. Adsorption equilibrium constants trend for BEA and MFI is similar and as follows ketone < n-alcohol < aldehyde.

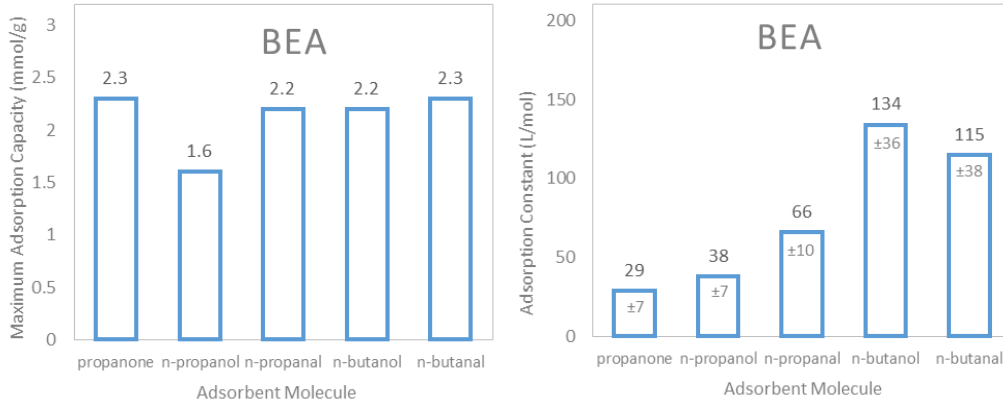


Figure 3-15: Optimal values of Langmuir adsorption model parameters for BEA.

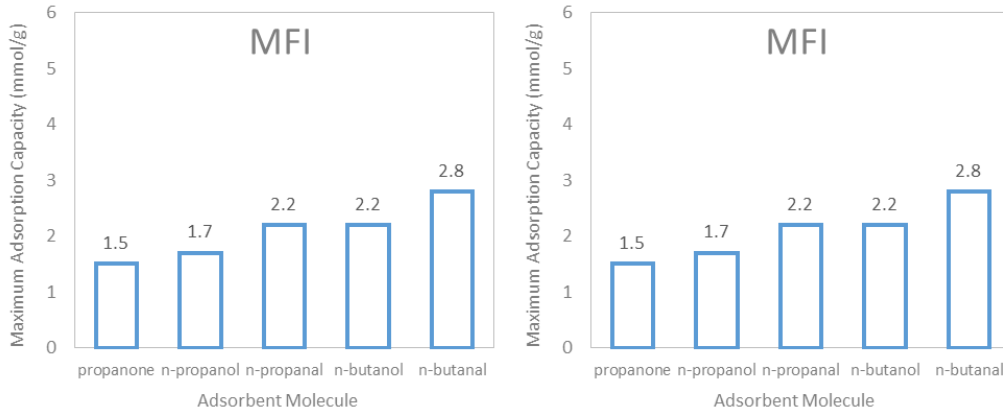


Figure 3-16: Optimal values of Langmuir adsorption model parameters for MFI.

### 3.4 Conclusion

This study revealed that adsorption on zeolites from aqueous solution is a viable and an attractive method for separation. Adsorption is followed by desorption process whereby adsorbed molecules are released from the adsorbed surface. Through the process of thermal desorption, heat is provided through a carrier gas to remove the adsorbed molecules from the system after adsorption is completed. The heat provided through desorption needs energy which will impact the overall energetics of the process. In this work, five types of commercial zeolites were assessed as possible options for butanol recovery. Adsorption isotherms of butanol, propanol, ethanol, and methanol were determined. The Langmuir parameters were found to be within similar ranges to previously published data. By adopting the Langmuir model, basic assumptions can be applied to understand conceptual meanings. A complete theoretical assessment is very complicated; hence reasonable assumptions have been used to simplify explanations of Langmuir model. Obtained results show higher adsorption of butanol compared to other alcohols. For the four alcohols that were tested, alcohols C1-C4, maximum adsorption capacity was directly proportional to molecule size of the same type studied. Furthermore, the data for butanol adsorption on the different types show a gradual decrease in the maximum adsorption capacity as follows: FAU15>FAU2.6>MFI≈BEA>MOR>FER. This is similar to the trend of zeolite size except for BEA (BEA has similar channels to MFI and relatively smaller in pore size than FAU) FAU~BEA>MFI>>MOR>FER. This observation suggests that maximum adsorption capacity is directly proportional to the zeolite size within the same molecule studied. Further explanation and correlation of molecule sizes along with pore size were discussed. In general, MFI had the highest affinity at low concentrations and was found to be more efficient than other types in separating n-butanol from the water. The magnitude of enthalpy of adsorption on zeolite was MFI>BEA>MOR≈FER>FAU, which is in the same order of magnitude reported by (Mallon et al., 2010). In conclusion, the results obtained from these experiments were encouraging and the next step would be to study the effect of multi-component systems.

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