การดูดซับบิวทาไดอีนจากแก๊สผสม C4 บนตัวดูดซับซีโอไลต์ Y ที่แลกเปลี่ยนไอออนด้วยนิกเกิล

นางสาวอัจฉรา บุญมาหล้า

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ADSORPTION OF BUTADIENE FROM C4 GAS MIXTURE ON Y-ZEOLITE ADSORBENT ION-EXCHANGED WITH NICKEL

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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Thesis Title	ADSORPTION OF BUTADIENE FROM C4 GAS MIXTURE ON Y-ZEOLITE ADSORBENT ION-EXCHANGED WITH NICKEL
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อังฉรา บุญมาหล้า : การดูดซับบิวทาไดอีนจากแก๊สผสม C4 บนตัวดูดซับซีโอไลต์ Y ที่แลกเปลี่ยนไอออนด้วยนิกเกิล (ADSORPTION OF BUTADIENE FROM C4 GAS MIXTURE ON Y-ZEOLITE ADSORBENT ION-EXCHANGED WITH NICKEL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.สุพจน์ พัฒนะศรี, 63 หน้า.

งานวิจัยนี้มีจุดมุ่งหมาย เพื่อศึกษาการดูดซับของ 1,3-บิวทาไดอีน จากแก๊สไฮโดรคาร์บอนผสมที่มีคาร์บอน 4 อะตอม โดยตัวดูดซับที่ใช้ในการศึกษา คือ ตัวดูดซับเชิงพาณิชย์ที่มีนิกเกิล และไม่มีนิกเกิล ได้ทำการศึกษาโดยดำเนินการผ่านประสิทธิภาพการดูดซับของตัวดูดซับ ความสามารถในการดูดซับของตัวดูดซับ ศึกษาจำนวนรอบของการดูดซับ และการฟื้นฟูสภาพตัวดูดซับที่ใช้งานแล้วภายใต้บรรยากาศของแก๊สไนโตรเจน และแก๊สเชื้อเพลิงโดยการดูดซับมีสารตั้งต้นที่ประกอบไปด้วยไอโซบิวเทน, นอร์มอล์บิวเทน, ทรานส์-2-บิวเทน, 1-บีวทีน, ไอโซบิวทีน, ซีส-2-บิวทีน, 1,3-บิวทาไดอีน และ C5 จากผลการศึกษาแสดงให้เห็นว่า ตัวดูดซับเชิงพาณิชย์ที่มีนิกเกิลมีประสิทธิภาพในการดูดซับ 1,3-บิวทาไดอีนได้ดีทั้งในการฟื้นฟูสภาพภายใต้บรรยากาศของแก๊สไนโตรเจน และแก๊สเชื้อเพลิง

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

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The removal of 1,3-butadiene from its C_4 mixture was performed via the selective adsorption over the commercial zeolite adsorbent. The adsorption capacity of the adsorbent was studied via the repeated cycles of adsorption and regeneration by desorption until the final adsorption capacity fell short of each initial capacity. The adsorption was tested with the feed consisting of iso-butane, n-butane, trans-2-butene, 1-butene, iso-butene, cis-2-butene, 1,3-butadiene, and C_5. The regeneration by desorption was conducted, upon each saturated adsorption. The effect of different regeneration gases during desorption, i.e. nitrogen and fuel gas, was investigated. It has been found that the commercial adsorbent exhibited the relatively stable adsorption performance of 1,3-butadiene under the desorption atmosphere of nitrogen gas.

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CHAPTER I

INTRODUCTION

In the presently, 1,3-butadiene is produced in very large amounts every year from the petroleum industry. It is recovery of 1,3-butadiene from C_4 hydrocarbon stream generated during ethylene production, or other alkene production.

Dienes, in particular 1,3-butadiene, are common and, at the same time, highly undesirable impurities of many petrochemical streams. Accordingly, diene removal is a critical step in a variety of chemical and petrochemical technologies. As this takes place, adsorption separations with the use of synthetic zeolites, present the most useful commercial approach to solving this problem [1].

The first and most popular zeolite adsorbent for 1,3-butadiene recovery was the standard zeolite [2]. It is an inexpensive, easily accessible product; however, its insufficiently high adsorption capacity at low diene partial pressures cannot satisfy the contemporary requirements for petrochemical stock purity. Such an essential demerit of the commercial product forced immediate research efforts to find more efficient zeolite adsorbents [3].

Several opportunities exist for the application of zeolite adsorbents in the separation of C_4 hydrocarbon streams. The C_4 streams obtained from various hydrocarbon cracking operations contain many important chemicals. The absolute amounts and compositions of the C_4 fraction obtained from cracking are substantially affected by the type of cracking, severity of cracking condition, and the feedstock. The C_4 fraction cannot be separated into its components economically by simple distillation because of the close proximity of their boiling points. Several separation methods have been developed for this application, ranging from the selective reaction of isobutene to extractive distillation of 1,3-butadiene. The remaining C_4 stream consists primary of n-butenes and butanes. This stream can be further separated by selective adsorption of the n-butenes on π -complexation in zeolite adsorbents [4].

The literature reviews focused on: development new adsorbents for adsorption of 1,3-butadiene by ion-exchange method with transition and noble metals such as Ag, Cu over Y-zeolite. However, This is the first attempt to study the characteristic of Ni-Y zeolite adsorbent on the adsorption of 1,3-butadiene which have not been reported yet.

In this research, the deactivation of a commercial adsorbent and its subsequent regeneration has been examined, using the adsorption of 1,3-butadiene. The study is focused on the influence of the conditions and the reaction atmosphere during the deactivation and reactivation periods upon the adsorption capacity.

The present work is arranged as follows:

Chapter II presents the theory and literature reviews of investigation the adsorbents for olefin/paraffin separations and regeneration of adsorbents. The theory of this research, the theoretical consideration on over view of production of 1,3-butadiene and removal of 1,3-butadiene in mixed-C_4 by adsorption.

Following by the description of the experimental systems and the operational procedures in chapter III.

The results and discussions obtained characterization of commercial adsorbents (both fresh and spent adsorbent) used in this study, effect of selective adsorption and regeneration for removal of 1,3-butadiene from C_4 gas mixture is explained in chapter IV.

Chapter V gives overall conclusions emerged from this work and presents recommendations for any future work.

Finally, the properties of 1,3-butadiene, composition of mixed-C_4 hydrocarbon and overview calculations of adsorption capacity are included in appendix at the end of thesis.

1.1 Objectives

1. The removal of 1,3-butadiene from C_4 gas mixture to obtain the proper feed for further metathesis reaction for propylene.
2. To investigate the effect of adsorbent regeneration upon the repeated cycles of adsorption and desorption

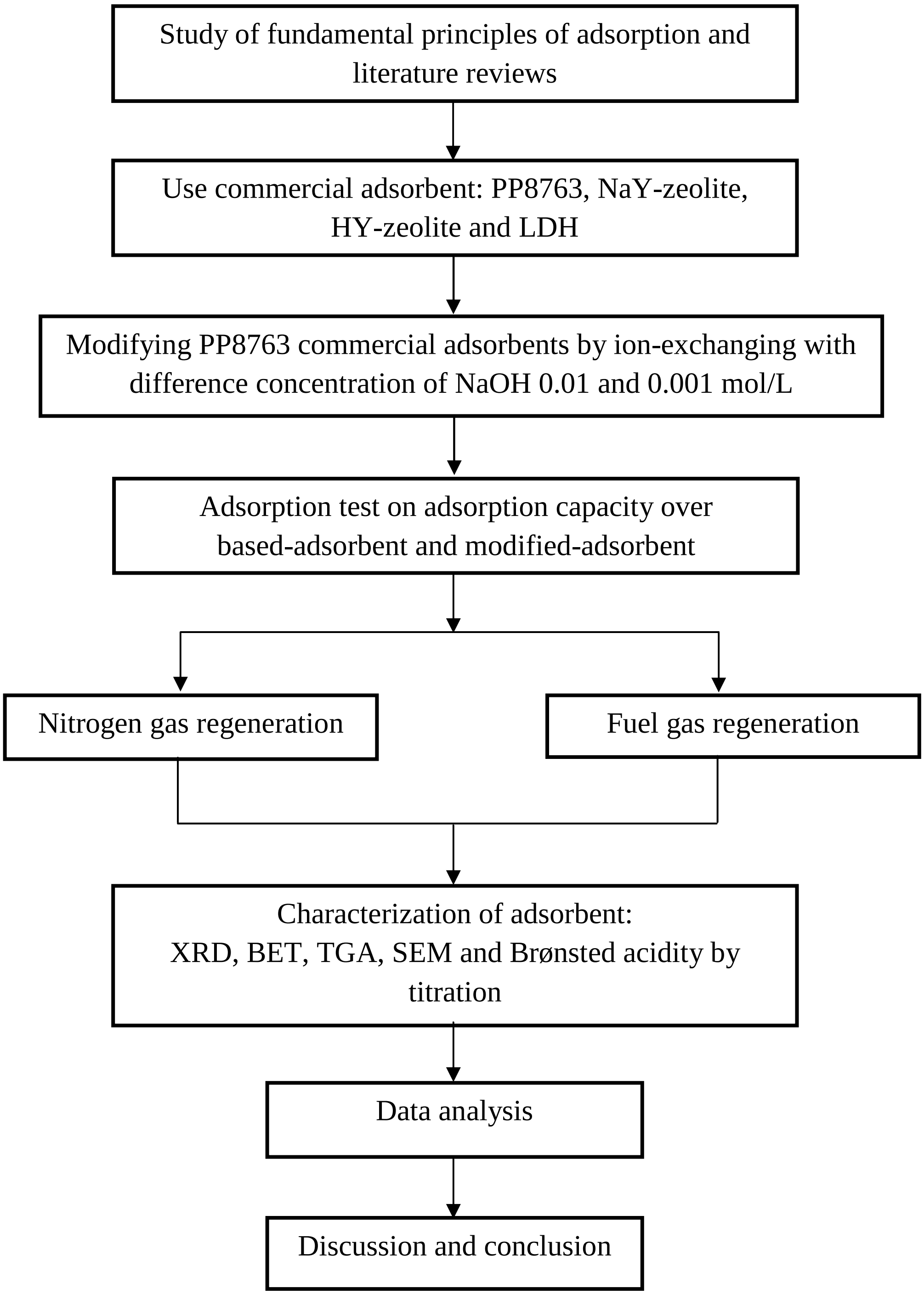
1.2 Research scopes

1. Study fundamental principles of adsorption of 1,3-butadiene and survey previous literatures, related in these topics.
2. Prepare the adsorbent which can be divided into two groups:
   a. Commercial adsorbent: 1. PP8763
      2. NaY-zeolite
      3. HY-zeolite
      4. LDH
   b. Modified PP8763 commercial adsorbents: As obtained adsorbent were ion-exchanged with the desired concentration of NaOH 0.01 and 0.001 mol/dm^3.
3. Use different gases in regeneration procedure :
   a. Nitrogen gas
   b. Fuel gas
4. Characterize the adsorbent by techniques of X-Ray diffraction (XRD), BET surface area assessment, Scanning electron microscopy (SEM), Brønsted acidity by titration, and thermal gravimetric analysis (TGA)
5. Discuss and summarize the results.

1.3 Benefits

To remove 1,3-butadiene from C_4 gas mixture to suppress an adversed effect of 1,3-butadiene in metathesis of ethylene and 2-butene for improved propylene production and understand the characteristic of the adsorbent throughout the repeated cycles of adsorption-desorption processes.

1.4 Research methodology



Scheme 1.1 Flow diagram of research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWD

2.1 Structure, properties and over view of production of 1,3-butadiene

2.1.1 Structure and properties of 1,3-butadiene

1,3-Butadiene is produced in very large amounts every year from the petroleum industry. It is produced as a byproduct of the steam cracking process used to produce ethylene and other olefins [5]. When mixed with steam and briefly heated to very high temperatures (often over 900 °C), aliphatic hydrocarbons give up hydrogen to produce a complex mixture of unsaturated hydrocarbons, including 1,3-butadiene. The quantity of 1,3-butadiene produced depends on the hydrocarbons used as feed. Light feeds, such as ethane, give primarily ethylene when cracked, but heavier feeds favor the formation of heavier olefins, 1,3-butadiene, and aromatic hydrocarbons. The amount of 1,3-butadiene produced during ethylene manufacture is dependent on both the type of hydrocarbon feedstock and the severity of the cracking operation. Typical 1,3-butadiene yields from ethylene production, based on various feedstocks [6].

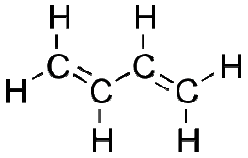


Figure 2.1 Chemical structural of 1,3-butadiene

1,3-Butadiene is a highly versatile raw material that is used commercially in a variety of reactions :

- Diels-Alder reactions with dienophiles to form a six-membered ring compound with a 2,3 double bond,
- conversion to cyclic or open chain dimers and trimers,

- telomerization with active hydrogen compounds,
- addition reactions with electrophilic and free radical compounds,
- oxidation reactions,
- substitution reactions and
- polymerization.

Table 2.1 Physical and Chemical properties of 1,3-butadiene

Properties	Value
Molecular formula	C_4H_6
Synonyms	biethylene, bivinyl, butadiene, erythrene, methylallene, pyrrolylene, vinyl ethylene
Appearance	Colourless gas or refrigerated liquid
Density	0.64 g/cm^3 at -6 °C, liquid
Melting point	-108.9 °C, 164.3 K, -164.0 °F
Boiling point	-4.4 °C, 269 K, 24 °F
Viscosity	0.25 cP at 0 °C

2.1.2 Over view of production and use

1,3-Butadiene production is accomplished through either of two processes: recovery of 1,3-butadiene from a mixed-C_4 hydrocarbon stream generated during ethylene production, or through oxidative dehydrogenation of n-butenes. Almost all, results from recovery of 1,3-butadiene as a byproduct of ethylene generation.

Table 2.2 Physical properties of hydrocarbon in mixed-C_4

Component	MW	NBP (K)	ΔH_f KJ/mol	ΔG_f KJ/mol
N-Butane (n-C_4H_{10})	58.12	272.7	-126.15	-17.15
Iso-Butane (i-C_4H_{10})	58.12	261.4	-134.52	-20.88
Iso-Butene (C_4H_8)	56.11	266.3	-16.90	58.07
1-Butene (1-C_4H_8)	56.11	266.9	-0.13	71.30
Cis-2-Butene (CB-2)	56.11	276.9	-6.99	65.86
Trans-2-Butene (TB-2)	56.11	274.0	-11.17	62.97
1,3-Butadiene (BD)	54.09	268.7	110.16	150.67

2.2 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from *absorption*, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while *desorption* is the reverse process [7].

In commercial processes, the adsorbent is usually in the form of small particles on fixed bed. The fluid that is a solution of several different chemical species is pass through the bed. A species present in the fluid phase is said to be adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid. Adsorption takes place because of the interaction between the species present on the fluid phase and solid surface. The following is a list of qualitative criteria for deciding whether adsorption might be such an alternative [8].

1. Relative volatility between the key components to be separated is in the order of 1.2 to 1.5 or less. An example for this case is the separation of isomers, where the separation factor is practically infinity by using zeolites.

2. Bulk of the feed is a relatively low-value, more volatile component, and the product of interest is on a relatively low concentration. In such situation, large reflux ratios can be required in distillation and can result in high energy requirements.

3. Two groups of component to be separated have overlapping boiling ranges. Several distillation columns are required for such the separation, even though various relative volatilities may be large. This separation may be efficiently dissimilar molecules-that is, with a high separation factor.

4. A low temperature and a high pressure are required for liquefaction.

5. Factors favorable for adsorption separation exist. The major cast for pressure swing adsorption is the compressor costs. If the mixture is available at an elevated pressure, the costs for separation are substantially reduced. The gas throughput and product purities are also important considerations. The costs for adsorption separation are generally lower than distillation for small to medium throughputs, and when high-purity products are not required.

2.3 Adsorbents

This section explains the general characteristics of adsorbents, and why they are important. The following parts deal with classes of adsorbents and several common materials are mentioned, along with a few manufacturers and some typical applications. No attempt has been made to be exhaustive in any lists. Many obvious examples have undoubtedly been omitted. The most important attributes of an adsorbent for any application are: ***capacity, selectivity, regenerability, kinetics, compatibility,*** and ***cost*** [9]. Rarely will a single adsorbent be optimal in all these respects. Frequently it will be possible to narrow the choice to one or two classes of adsorbents, but that still commonly leaves a vast array of possibilities.

To evaluate capacity, selectivity, regenerability, kinetics, compatibility, and cost, a number of different approaches can be taken. First, vendors can be contacted, and if the compound is relatively common, they maybe able to provide information quickly. Otherwise, especially for a relatively large application, they may be willing to do measurements. Second, you might use a database, such as one that was mentioned earlier in this article. Third, you might arrange to conduct the measurements, either yourself or by someone else in your firm. Fourth, you might arrange to have tests conducted by an independent firm, since they could offer an unbiased and cost efficient assessment.

Adsorption ***capacity*** (or “loading”) is the most important characteristic of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid-phase concentration, the temperature, and other conditions (especially the initial condition of the adsorbent). Typically, adsorption capacity data are gathered at a fixed temperature and various adsorbate concentrations (or partial pressures for a vapor or gas), and the data are plotted as an *isotherm* (loading versus concentration at constant temperature). Adsorption capacity is of paramount importance to the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels, and both generally are significant if not dominant.

Speaking of isotherms, there are only a handful of shapes (some are shown in Figure 1), but there are dozens of empirical forms, some of which are discussed later in this article. Beyond those, there exist many other means to express adsorption capacity: isosteres, isobars, and various indices, such as surface area, pore size distribution, Iodine Number and Molasses Number. The latter two are used exclusively to describe activated carbons. Isosteres and isobars, along with isotherms, are discussed morefully later in this article. Surface area is a relative term, usually measured by inferring the monolayer coverage within an adsorbent of a substance with known density and molecular dimensions (e.g., nitrogen near its normal boiling point).Values typically correlate with capacity, and for various adsorbents are in the range of, say, 5 to 3,000 m^2 /g. Related to the weight of a penny (2.5 g), the range is from a 12 ft x12 ft square to nearly two football fields Some specific ranges are listed for common adsorbents in the next section. Surface area alone is not a proper basis for choosing an adsorbent.

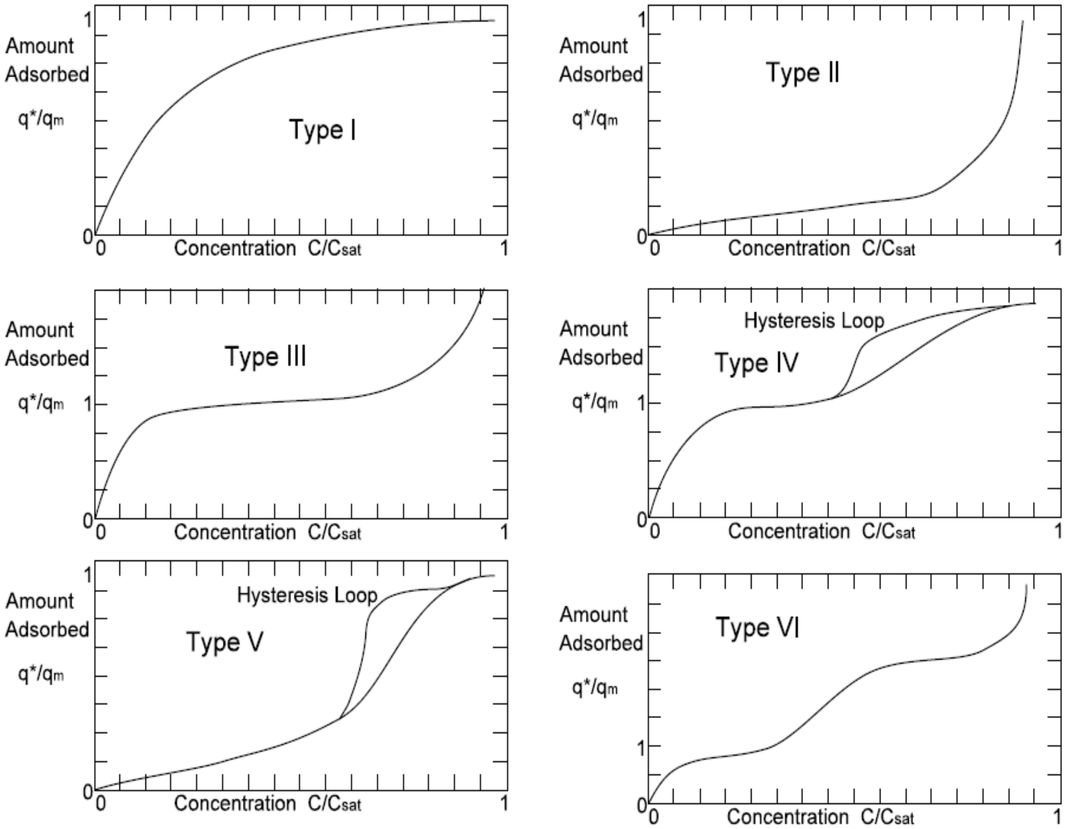


Figure 2.2 Classic Isotherm Types.

Selectivity is related to capacity, but there are several distinct definitions that will be discussed later in this article. The simplest is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration drops towards zero. Of course, the concentrations of interest may not be near zero, so the choice of definitions becomes subtle. The closest analogy is to relative volatility (e.g., in distillation) in that the smaller the value, the larger the required equipment. An ideal situation occurs when the major component is not adsorbed much (so it can be thought of as an inert “carrier”), which leads to a very large selectivity. Some people prefer a bounded selectivity (i.e., 0 to 1), and they employ the inverse of the ratio mentioned above. Thus, it is a good idea to clarify the definition first, or to speak of “good” or “bad” instead of “large” or “small”.

All cyclic adsorption applications rely on ***regenerability***, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component (adsorptive or adsorbate) must be relatively weakly adsorbed (or physisorbed). The heat of adsorption, which is mentioned later, provides a measure of the energy required for regeneration, and in that regard low values are desirable. Regeneration might be accomplished by a thermal swing, pressure swing, chemical (e.g., by displacement, elution, or supercritical extraction), or sometimes by a combination of those. Displacement would involve introducing a species that adsorbs more strongly than the adsorbate of interest, while elution would entail dissolving the adsorbed material by a solvent that is weakly adsorbed if at all. The chemical methods all require a separate separation operation that may be costly, plus a means must be found for purging the bed of the regenerant. In some cases, regeneration takes place by contacting the adsorbent with a fluid in another phase than is used during loading. This requires draining or displacement which might be time-consuming, so it is avoided whenever possible. The regenerability of an adsorbent affects the fraction of the original capacity that is retained (sometimes called the *working capacity*), and the time, energy, etc. required for regeneration. Frequently, a short-term loss of working capacity occurs during the first few cycles, often followed by a gradual decay, perhaps over hundreds of cycles, e.g., due to ageing, poisoning, or other causes unrelated to regeneration, that essentially governs the life of the adsorbent.

Mass transfer ***kinetics*** is a catch-all term related to intraparticle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. Fast kinetics provides a sharp breakthrough curve, while slow kinetics yields a distended breakthrough curve. The effect of a distended breakthrough curve can be overcome by adding adsorbent at the product end, or by increasing the cycle time (which reduces the throughput per unit of adsorbent). Both of these options affect the amount of adsorbent required in that the longer the cycle time, the greater the adsorbent inventory. Despite that, kinetics has even been exploited as the basis of adsorptive separations. Perhaps the most common example is the pressure swing adsorption process that splits nitrogen from air using carbon molecular sieve, which relies on fast diffusion of oxygen compared with very slow diffusion of nitrogen. Normally, however, slow diffusion of any adsorbate is a disadvantage. To compensate for slow diffusion, it is also possible to use small particles, but there is a corresponding sacrifice due to increased pressure drop. The common solution to that dilemma is to use relatively large particles and to employ an extra increment of adsorbent.

Compatibility covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent, such as biological fouling or attrition. For example, the adsorbent, binder, and surface groups (depending on the type of adsorbent), should be inert to the carrier or solvent, and should not irreversibly react with (or chemisorb) the adsorbate(s) or contaminants. Likewise, operating conditions such as velocity, temperature, pressure, and vibration should not cause undue disintegration of the adsorbent particles. This could happen by crushing or abrasion, and there are standard methods for measuring those.

Cost is perhaps the most subtle characteristic to understand because it may vary from week to week, and from sales rep to sales rep, even for the same exact material.

2.2.1 Inorganic Materials

It seems that most minerals and many synthetic inorganic materials have been tried as adsorbents. Some have been successful, despite being poor adsorbents, simply because they were so inexpensive. Other shave turned out to be immensely effective adsorbents. Conversely, some inorganic materials may act more as “absorbents” than adsorbents, but have applications from drying to recovery of PCBs. Among these are metal chlorides ($CaCl_2$), oxides (CaO, MgO, ZnO for life support in the space program), silicates ($MgSiO_3$),sulfates ($CaSO_4$, the familiar “Drierite”), kieselguhr (or diatomaceous earth), and even sodium bicarbonate and limestone (for flue gas treatment). Some are used in an anhydrous state while others are hydrated. Many other inorganic adsorbents have been developed recently, such as pillared clays, aluminophosphates, and mesoporous adsorbents, that have not yet achieved that level of prominence. The inorganic adsorbents covered below are commercial products, and are frequently encountered.

2.2.2 Organic Materials

This section discusses adsorbents that are based on organic material, whether synthetic or naturally occurring. A wide variety of organic materials have been used as for “sorption,” besides activated carbon or charcoal. Some might function as solid “absorbents” rather than adsorbents. Among these are cellulose (the most abundant biopolymer in nature), chitin (the second most abundant biopolymer in nature), collagen, wool, starch-polyacrylamide gels (which absorb many times their own weight of water at ambient temperature, but release most of it by gentle heating), polysaccharrides derived from corn, and miscellaneous forms of biomass (e.g., residue from crop harvests). Some of these may have niches, but none would be considered a general purpose adsorbent. Here we will focus on commercial adsorbents.

2.4 Adsorption Characteristics

This section describes the scientific and quantitative characteristics of adsorbents for specific applications. The properties discussed here are only those relevant as a basis for adsorbent selection. Others, which may be only indirectly relevant, are glossed over. In fact, the material presented here is just an overview, since to understand their impact requires fairly deep understanding of the field of adsorption.

Doing isotherm measurements is painstaking and time-consuming. It is usually even more difficult to set-up the equipment, however, than to do the experiments. Despite that, it is important to know something about how they are done, in order to discuss what they mean. There are three basic types of equipment volumetric, gravimetric, and chromatographic [10]. The equipment and techniques are reviewed briefly here.

The first method, volumetric, generally is a vessel containing adsorbent that is subjected to a measured step change of fluid phase concentration. The ultimate concentration reveals the amount adsorbed via a mass balance. It is easiest if there is a noninvasive way to measure concentration. For gases a pressure transducer will do, since volume and temperature are fixed. For liquids, a variety of instruments exist that can be used *in situ*, but it is also acceptable to extract small samples with a syringe for individual analysis. This method is probably the best in terms of flexibility, decent accuracy, and low cost [11].

Second, the gravimetric approach, mainly applies to gas-phase adsorption. It involves measuring the amount taken up by the adsorbent by weight. These isotherm measurements are quick and accurate, and the interpretation is easy. Some types of equipment are elaborate, with a small adsorbent-bearing pan suspended from a quartz spring. Then, the main problem is cost, plus the fact that the equipment tends to be finicky (each seal is subject to leaks). Other problems that are sometimes overlooked are: adsorption on the walls rather than on the adsorbent, and buoyancy effects (which can amount to more than 10% error). Another version uses a column of adsorbent, through which is passed gas of a known concentration. Periodically the flow is stopped, the column is sealed then weighed. The adsorption capacity can be determined once steady state is reached. This is more tedious, but reliable and relatively inexpensive. Alternatively, the adsorbent can be heated strongly, and the off-gases can be trapped and analyzed to infer the adsorbate composition [12].

Third is chromatographic analysis. This is primarily a screening technique in which adsorbents are crushed and placed in a chromatographic column, then a pulse of the components of interest is injected into a non adsorbing carrier fluid [13]. In principle, the technique applies to both gases and liquids, but the former is much more popular. The Henry’s law coefficient can be determined readily from the retention of each peak [14].

2.5 Removal of 1,3-butadiene in mixed-C_4 by adsorption

When solids are placed in contact with gasses or liquid, forces are exerted between the surface of the solid and compound causing bonds to be formed. This phenomenon is called adsorption. The bonds can vary in strength depending on the nature of compounds in mixtures. From this theory, the adsorption processes have been used in petroleum industry in various applications. Recently, there is growing interest in studying and developing adsorption process for 1,3-butadiene. There are several adsorbents that can be used to adsorb 1,3-butadiene from mixed-C_4 and other petroleum products. In general, typical adsorbents are zeolites, silica gel and activated carbon. Different types of adsorbent show different selectivity and adsorption capacity for 1,3-butadiene. From many research, they found that zeolite was the most attractive adsorbent for adsorption of 1,3-butadiene.

2.5.1 Zeolite

Most zeolites are aluminosilicates which could be thought of as stoichiometric blends of the two previous adsorbents, silica and alumina. Thus, they are generally white, opaque and chalk-like in appearance. One would think that given their make-up, all zeolites would be hydrophilic. Accordingly, most that have significant alumina content are hydrophilic, while those that are predominately silica are hydrophobic. Internally, zeolites are inherently crystalline and exhibit micropores within those crystals that have uniform dimensions, as depicted in the pore size distribution. The micropores are so small and uniform that they commonly can distinguish nearly identically sized molecules. One compound that is not shown is perfluorotributylamine, though it is one of very few that is larger than the micropores (~12Å), so it can be used to ascertain particle properties by immersion. Frequently there is water of hydration within the crystals, and in order to balance the charges, cations are associated with the alumina. The common empirical formula for a zeolite containing a single cation, M, of valence, *n*, is: $M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y].z\,H_2O$, where *x* is the silica-to-alumina ratio (generally >1 to5), and *y* is the molar water of hydration.

Virtually all commercial, zeolitic adsorbents are composites of very fine crystals held together with a corresponding binder. Surprisingly, some types of binder can exhibit substantial adsorption capacity, yet retain strength. To the chagrin of most people who are familiar with adsorption in carbon, the adsorption capacity of zeolites is due to micropores that are so small and curved that it is not useful to express an effective surface area. To promote crystal uniformity, most commercial zeolites are synthesized in autoclaves in which conditions can be controlled tightly. There sulting crystals exist in a meta stable form, and more than one hundred distinct forms have been produced. Only a handful are commercially significant (e.g., A, X, Y, ZSM-5, mordenite and silicalite), although those have different “exchange” forms and are produced in different sizes and shapes. A description of the structures will be given only for the zeolites important in gas separation, Types X and Y [15-16].

The skeletal structures of types X and Y zeolites are the same as that of the naturally occurring faujasite. Three major locations for the cations are indicated in Figure 2.3. The locations are: center of the six-member prism (I) and opposite to I in the sodalite cage (I’); similar to I and I’ but further from the central cavity (II and II’); and at twelve-member aperture (III and III’). The distribution of the cations and is affected by the presence of traces of moisture. The adsorptive properties of X and Y sieves may therefore be greatly modified by ion-exchange and improvement selectivity can sometimes be obtained by using mixed cationic forms [17].

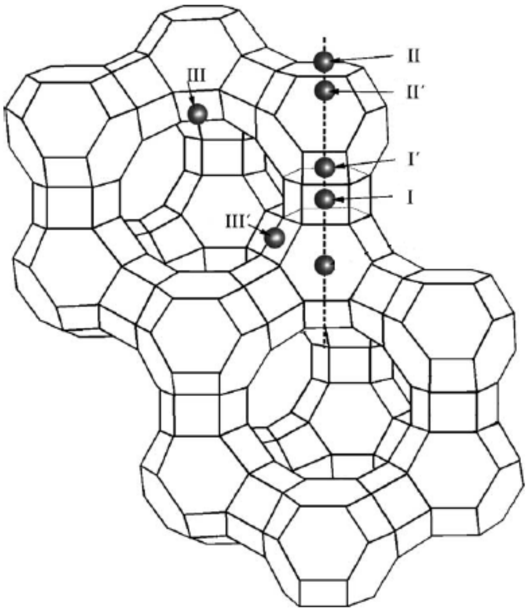


Figure 2.3 Unit cell of types X and Y, or faujasite. Cation positions are indicated by roman numerals.

2.5.2 Adsorbents for olefin/paraffin separations

During the past decade, there have been many research studies on the use adsorption for olefin/paraffin separations.

Takahashi et al. [18] studied various kinds of sorbents by using thiophene/benzene as a model system and vapor-phase experiments. Adsorption isotherms were generated to try to understand the interaction between the sorbate and sorbent. They found that the separation factors of thiophene over benzene (at low concentration of thiophene) exhibited the trend as follows: Ag-Y > Na-ZSM5 > Cu-Y > activated carbon > Na-Y > H-USY > modified activated alumina. The sorbent capacities for thiophene at low pressure followed the order Cu-Y and Ag-Y > Na-ZSM5 > activated carbon > Na-Y > modified activated alumina and H-USY.

Akira et al. [19] studied the purification of normal α-olefins by removal of dienes has been demonstrated previously in our laboratories by π-complexation using Ag^+ ion-exchanged zeolite (Ag-Y) or $AgNO_3/SiO_2$ sorbent. Although Ag-Y could purify 1-butene/1,3-butadiene effectively, the purification performance was degraded by H_2 and/or H_2S poisoning. A new sorbent for 1-butene/1,3-butadiene purification was developed in this study by ion-exchange of Cu^{2+} cations into Y-zeolite followed by reduction of Cu^{2+} to Cu^+. The performance of the Cu^+-zeolite, Cu(I)-Y or Cu-Y, was found to be superior to that of Ag-Y. Cu-Y exhibited higher diene/olefin separation factors than Ag-Y by approximately an order of magnitude. Furthermore, unlike Ag-Y,exposure to H_2S/H_2 at 120 °C had virtually no effect on 1,3-butadiene/1-butene adsorption, indicating the excellent poisoning resistance of Cu-Y.

Arturo J. et al. [20] studied desulfurization by using Cu(I)-Y, Ag-Y, H-Y and Na-Y in a fixed-bed adsorber using thiophene/benzene, thiophene/n-octane as the model systems. From the fixed-bed adsorption, Ag-Y was shown to adsorb almost twice as much as sodium-based one for benzene/thiophene mixture. Cu(I)-Y showed a little higher selectivity toward thiophene as compared to other adsorbents for benzene/thiophene mixture at the same condition. However, for n-octane/thiophene mixture at the same feed conditions, Cu-Y showed the highest selectivity and capacity among the adsorbents studied.

Padin, J. et al. [21] studied new adsorbents for olefin/paraffin separations are synthesized by incipient wetness impregnation and ion exchange of Ag^+ cations on high-surface-area substrates. The separation/purification is achieved by selective adsorption of olefins and/or dienes by π-complexation. It was shown that the monolayer $AgNO_3/SiO_2$ sorbent has a selective adsorption ratio of 8.33 for butene/butane at 70 °C and 1 atm. The isotherm linearity for olefin is ideally suited for cyclic adsorption-desorption processes. Moreover, the performance of the π-complexation sorbent (AgY zeolite) for the purification of butene by removal of trace amounts of butadiene was found to be superior to that of sorbents based on physical adsorption (5A zeolite and NaY).

Curtis L. et al. [22] studied purifying of 1-butene by selective adsorbing trace amounts of 1,3-butadiene. The effect of Ag content in Ag ion-exchanged Y-zeolite (Ag-Y) on 1,3-butadiene/1-butene adsorption was investigated using Ag-Y with different Si/Al ratios and different degrees of Ag^+/Na^+ exchange (AgNa-Y). AgNa-Y with a Ag content of 34 Ag/u.c. exhibited excellent adsorption performance in terms of both separation factor and uptake rate. The influence of H_2S exposure on sorbent performance was also examined. Although both 1,3-butadiene and 1-butene adsorption amounts were decreased by H_2S exposure, the separation factors remained well over 100, which were still good for purification

However, This is the first attempt to study the characteristic of Ni-Y zeolite adsorbent on the adsorption of 1,3-butadiene which have not been reported yet.

2.5.3 Desorption and regeneration of adsorbent

Regeneration is a very important part in the adsorption process which aims to bring the adsorbents for reuse. In general, these are four types of regeneration method: lowing total pressure, striping with an inert gas, increasing temperature, and displacing by desorbent. As a result, several researchs have studied various ways to regenerate used sorbents to their original properties.

Hernandez et al. [23] studied the desulfurization of thiophene in benzene and n-octane by using Cu(I)-Y, Ag-Y, H-Y and Na-Y in fixed-bed adsorber and also investigated the regeneration of these adsorbents. They found that Cu(I)-Y adsorbent under air at 350 °C, followed by reactivation recovered almost all of the original capacity of the adsorbent.

Yang et al. [24] studied the regeneration of the activated carbon/Cu(I)-Y by using layered bed. The air calcinations and solvent elution were chosen for regeneration teats. They found that the activated carbon/Cu(I)-Y bed can only recover 85% of the original adsorption capacity for regeneration with air at 350°C centigrade for at least 6 hours followed by auto-reduction. For solvent elution technique, CCl_4 was capable of recovering a considerable part of the original adsorption capacity.

Additionally, research the regeneration of zeolite types. *Reif et al.* [25] studied the reactivate of zeolite of type 5A, which has been used to separate normal paraffins from a hydrocarbon mixture containing normal paraffins by bringing the hydrocarbon mixture into contact with the zeolite where by the zeolite absorbs the normal paraffins and then desorbing the normal paraffins from the zeolite by contacting the zeolite with water-containing ammonia vapour, is reactivated by first contacting the zeolite with at least one of water, aqueous solutions and water-containing gases at a temperature below 350°C. They found that after regeneration, the adsorption capacity of zeolite increased.

CHAPTER III

EXPERIMENTAL

This chapter describes method of adsorbent preparation, characterization and the experimental procedures in this research. A description preparation of adsorbent method is given in section 3.1. Next, properties of adsorbent and characterization of adsorbent were explained in section 3.2. The last section, details of experimental procedures, including the materials and apparatus are as follow in section 3.3.

3.1 Preparation of adsorbents

3.1.1 Based Adsorbent

Commercial adsorbent used in the adsorption:

1. PP8763
2. NaY-zeolite
3. HY-zeolite
4. LDH

3.1.2 Modified Adsorbents

PP8763 adsorbent was ion-exchanged with the desired concentration of NaOH, in this study the concentration of NaOH was varied 2 values which were 0.01 and 0.001 mol/dm^3. And then it was stirred at room temperature for 2 h. After that, the mixture was separated and was dried in oven at 110 °C for 24 h following by drying calcinations.

3.2 Adsorbent Characterization

3.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to obtain information about the adsorbent structure, composition, and state of polycrystalline materials. Before testing, the sample powder was mounted in a sample holder with appropriate smooth surface. After that, the sample holder was place in x-ray diffractometer. The beam of monochromatic x-radiation was directed at the sample. The reflection or diffraction of the x-ray was observed at various angles with respect to the primary beam. The diffraction pattern of the prepared adsorbent was compared with the standard diffraction pattern for confirmation.

The XRD was performed to determine the bulk phase of adsorbent by SIEMENS D5000. X-ray diffractometer connect with a computer Diffract ZT version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using CuK_{α} (λ = 1.54439 A) radiation with Ni filter in the 2θ range of 20-80 degrees resolution 0.04°. The crystallite size was estimated from line broadening according to the Scherrer equation and α-Al_2O_3 was used as standard.

3.2.2 BET surface area measurement

The specific surface area, the pore volume and the pore diameter of the different adsorbent were measured by N_2 physisorption, with nitrogen as the adsorbate using a Micronmeritics model ASAP 2000 automated system degassing at 200 °C for 4 hours prior to N_2 physisorption. Calculations were performed on the basis of the BET (Stephen Brunauer-Paul Hugh Emmett-Edward Teller) isotherm for specific surface area and pore size distribution was calculated by BJH (Barrett-Joyer-Halenda) desorption branch analysis.

3.2.3 Brønsted Acidity

The number of acid Brønsted sites was also estimated by using a method involving an aqueous ion-exchange step of the catalyst H^+ ions with Na^+ ions, followed by titration of the resulting solution. The 0.2 g of adsorbent was added to 10 ml of a 3.42 M aqueous solution of NaCl under stirring. After 30 hour of ion-exchange at room temperature between the adsorbent H^+ ions and the Na^+ ions in solution, the solid sized was filtered and titrated with a 0.05 M aqueous NaOH solution and calculated the number of acid Brønsted sites in unit μmol H^+/g-adsorbent [26].

3.2.4 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis was performed using TA Instrument SDT Q600 analyzer. The samples of 10-20 mg and a temperature from 30 to 700 °C at 10 °C/min were used in the operation. The carrier gas was air.

3.2.5 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to determine the morphology and elemental distribution of the catalyst sizeds. Model of SEM: JEOL mode JSM-5800LV at the Scienctific and Technological Research Equipment Center, Chulalongkorn University (STREC).

3.3 The Reaction Study in Adsorption

The adsorbent sample was placed at the center of stainless steel tubular reactor with inner diameter (ID) of ¾ inch to which a type K thermocouple was mounted. The adsorbent was pretreated at 300 °C under nitrogen flow for 2 h before allowing the adsorbent cooled down under an inert atmosphere to each reaction room temperature. The adsorption conditions were as follows: room temperature, pressure 5 bar., the feed were use C_4. The sample analysis was performed on a Agilent GC-7820 gas chromatograph.

Product and feeds were analyzed by a gas chromatograph equipped with a flame ionization detector-type, Agilent GC-7820 was used to analyze the quantity of mixed-C_4 hydrocarbon in feed and effluent gases. The operating conditions are summarized in Table 3.1

Table 3.1 Operating conditions for gas chromatograph

Gas chromatography	Agilent GC-7820
Detector	FID
Packed column	RT-QPOT capillary column
Carrier gas	Ultra high purity N_2
Carrier gas flow rate (ml/min)	10
Injector temperature (°C)	120
Detector temperature (°C)	150
Initial column temperature (°C)	80
Initial holding time (min)	5
Programmed rate (°C/min)	3 °C/min to 120 °C
Final column temperature (°C)	120
Final holding time (min)	2
Analyzed gas	1,3-butadiene in mixed-C_4 hydrocarbon

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results and discussions are classified into two major parts. Firstly, characterization of commercial adsorbents (both fresh and spent adsorbent) used in this study is explained in section 4.1. Second, effect of selective adsorption and regeneration for removal of 1,3-butadiene from C_4 gas mixture is explained in section 4.2-4.4.

4.1 Physical characterization

4.1.1 Crystalline structures of adsorbents

Phase identification is carried out on the basis of data from X-ray diffraction analysis. The XRD patterns of fresh and spent commercial adsorbents are shown in Figure 4.1. All the XRD peaks indicate the presence of aluminum silicate were obvious at 10.5°, 12.2°, 15.9°, 23.9°, 27.5°, 31.4°, 32.0°, and 34.8° [27].

XRD peaks for nickel metal or oxides should occur at 37.3°, 43.4°, 62.9° and 75.3° [28] but non of those peaks were observed due probably to the very low amount of the metals present on the adsorbents and/or overlapping with the aluminum silicate peaks. All the XRD peaks of fresh adsorbents are similar to those of spent adsorbents in terms of both position and shape. It is suggested that the conditions used in selective adsorption of 1,3-butadiene does not affect to phase and crystal size of aluminum silicate even the adsorbent is used for long period of time.

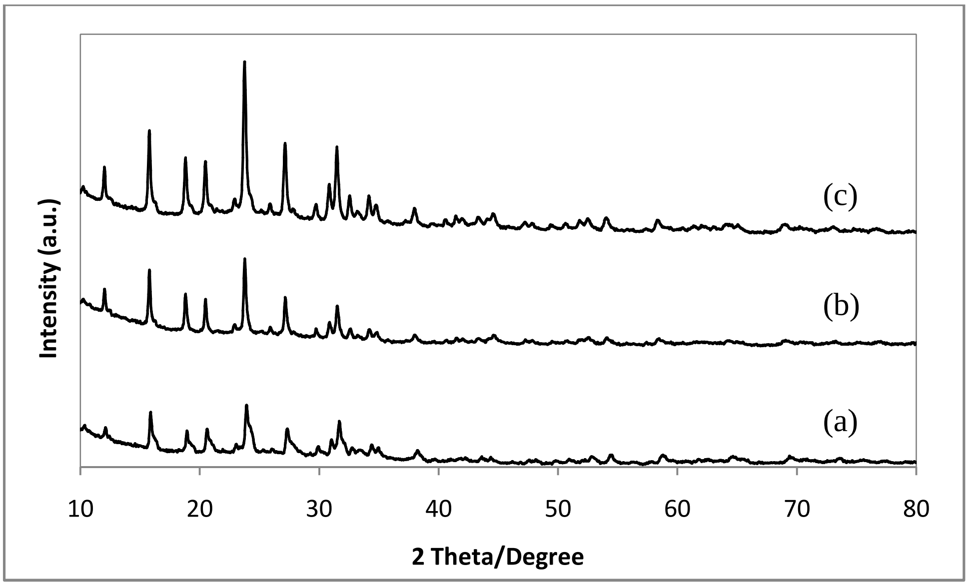


Figure 4.1 The XRD patterns of PP8763 commercial adsorbents: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas by using nitrogen gas, (c) spent adsorbent with regeneration gas by using fuel gas

Figure 4.2 and 4.3 were XRD patterns of modified PP8763 commercial adsorbents with various concentration of NaOH 0.001 and 0.01 mol/dm^3. The result was compared with 4.1. It found that new peak was occurred in adsorbents with silicate hydroxide obvious at 10.7°, 18.9°, 20.9°, 22.8, 23.5°, 29.4°, 30.0°, 31.8°, 32.6°, 33.8°, 34.1° and 41.2° [29].

All the XRD peaks indicate the presence of aluminum silicate were obvious at 10.5°, 12.2°, 15.9°, 23.9°, 27.5°, 31.4°, 32.0°, and 34.8° [27]. XRD peak of nickel or nickel oxide should occur at 37.3°, 43.4°, 62.9° and 75.3° [28] but non of those peaks was observed probably because of small loading amount of nickel.

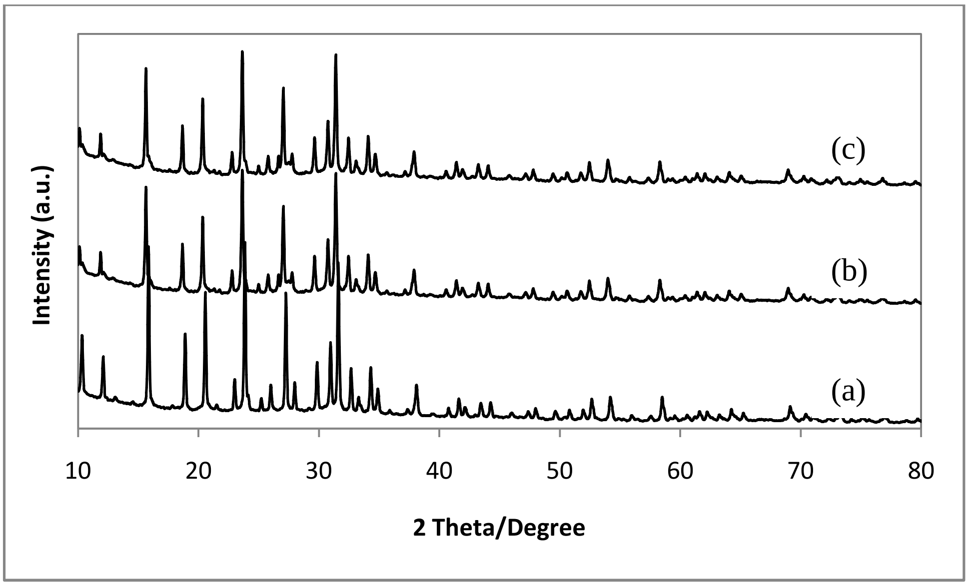


Figure 4.2 The XRD patterns of modified PP8763 commercial adsorbents with NaOH 0.001 mol/dm^3: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas by using nitrogen gas, (c) spent adsorbent with regeneration gas by using fuel gas

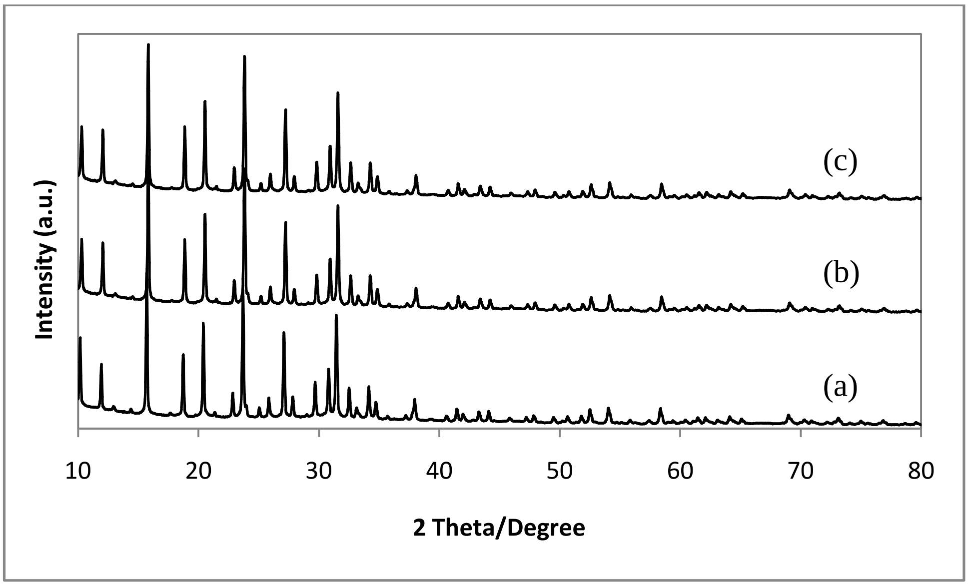


Figure 4.3 The XRD patterns of modified PP8763 commercial adsorbents with NaOH 0.01 mol/dm^3: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas by using nitrogen gas, (c) spent adsorbent with regeneration gas by using fuel gas

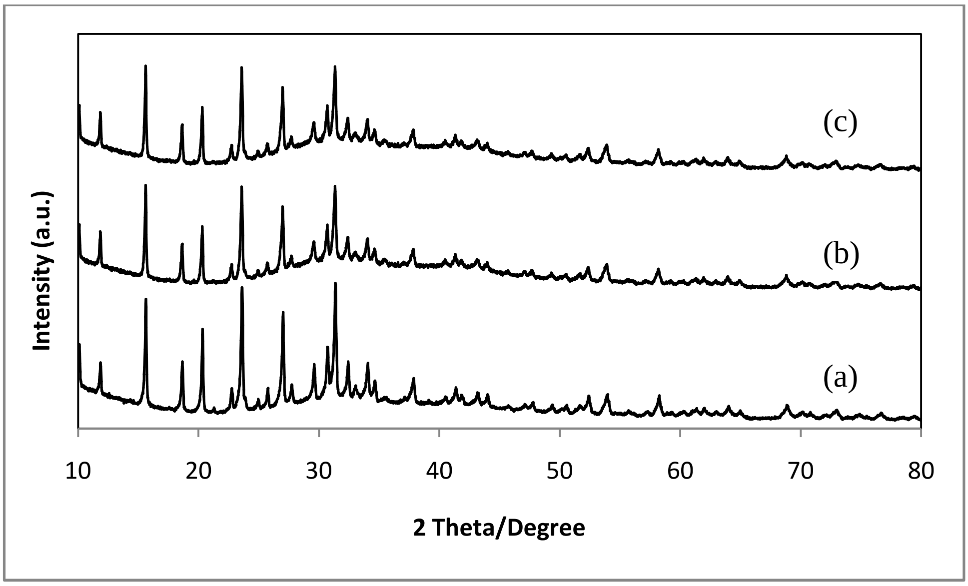


Figure 4.4 The XRD patterns of NaY-zeolite commercial adsorbents: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas by using nitrogen gas, (c) spent adsorbent with regeneration gas by using fuel gas

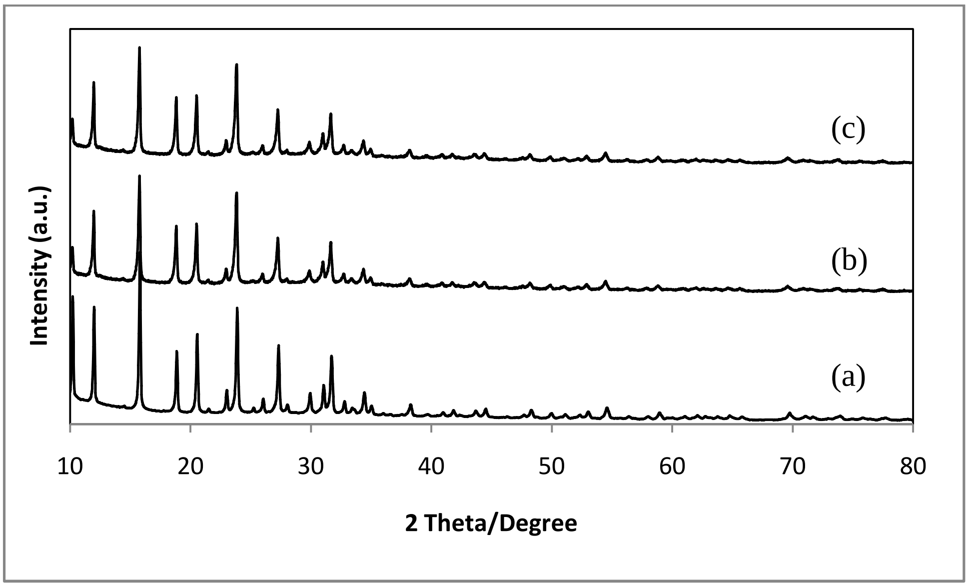


Figure 4.5 The XRD patterns of HY-zeolite commercial adsorbents: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas by using nitrogen gas, (c) spent adsorbent with regeneration gas by using fuel gas

Figure 4.4 illustrates the reference XRD pattern of zeolite Y (NaY) commercial adsorbent that used in this research. This indicates that the structure of NaY-zeolite is similar to that of the fresh adsorbent. Figure 4.5 displays the XRD pattern of HY-zeolite. In the same way this pattern is not difference. It is evident that the H from of zeolite Y does not significantly change the main structure of zeolite.

The X-ray diffraction patterns of LDH commercial adsorbent are shown in Figure 4.6. The XRD patterns were occured at 18.6°, 32.9, 38.1°, 50.9°, 58.7°, and 62.1° as MgO [30].

All the XRD peaks indicate the presence of magnesium oxide (MgO). All the XRD peaks of fresh adsorbents are similar to those of spent adsorbents in terms of both position and shape.

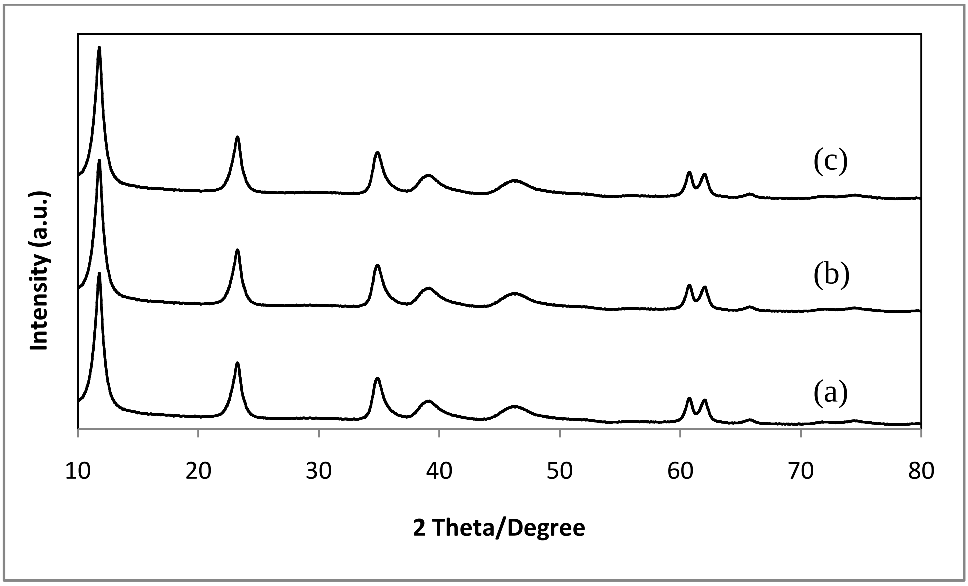


Figure 4.6 The XRD patterns of LDH commercial adsorbents: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas by using nitrogen gas, (c) spent adsorbent with regeneration gas by using fuel gas

4.1.2 Textural properties of adsorbents

Table 4.1, 4.2 and 4.3 shows the BET surface area total pore volume and average pore diameter of fresh and spent commercial adsorbents are determined by BET technique. It performed that the specific surface area decreased. All adsorbents had similar total pore volume and average pore diameter.

The specific surface areas of commercial adsorbent NaY-zeolite (Si/Al ratio = 5.5), and HY-zeolite (Si/Al ratio = 10). It is found that specific surface area of all adsorbents decreased. Total pore volume and average pore diameter of the adsorbents is is not different.

It is found that specific surface area of modified PP8763 adsorbents decreased with the addition of NaOH. Total pore volume and average pore diameter is not different with the addition NaOH though the decrease of pore size was found.

However, for LDH adsorbents is lowest specific surface area when compare with different all adsorbents.

Table 4.1 The Textural properties of fresh adsorbents

Adsorbent	S_{BET}(m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
NaY-zeolite (Si/Al=5.5)	700.00	0.30	10.94
HY-zeolite (Si/Al=10)	650.00	0.42	12.48
PP8763	640.00	0.35	11.20
PP8763NaOH 0.001 mol/L	638.45	0.33	11.17
PP8763NaOH 0.01 mol/L	636.27	0.33	11.15
LDH	120.00	0.12	7.30

Table 4.2 The Textural properties of spent adsorbents by using N_2 gas

Adsorbent	S_{BET}(m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
NaY-zeolite (Si/Al=5.5)	697.28	0.30	10.92
HY-zeolite (Si/Al=10)	646.31	0.41	12.16
PP8763	638.94	0.34	11.12
PP8763NaOH 0.001 mol/L	635.23	0.32	11.03
PP8763NaOH 0.01 mol/L	632.45	0.32	11.01
LDH	119.82	0.12	7.28

Table 4.3 The Textural properties of spent adsorbents by using fuel gas

Adsorbent	S_{BET}(m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
NaY-zeolite (Si/Al=5.5)	694.73	0.30	10.88
HY-zeolite (Si/Al=10)	642.38	0.40	12.09
PP8763	638.06	0.33	11.07
PP8763NaOH 0.001 mol/L	630.41	0.31	10.96
PP8763NaOH 0.01 mol/L	629.15	0.31	10.93
LDH	119.32	0.12	7.26

4.1.3 The Acidity of adsorbents

For the amount of Brønsted acid of fresh adsorbents were calculated and shown in table 4.4. Considering, the amount of Brønsted acid of spent adsorbents were calculated and shown in table 4.5.

Table 4.4 The amount of Brønsted acid of fresh adsorbents by ion-exchanged titration

Adsorbents	Brønsted acid (µmol of H^+/g. of adsorbent)
HY-zeolite (Si/Al=10)	95.000
NaY-zeolite (Si/Al=5.5)	61.576
PP8763	37.987
PP8763NaOH 0.001 mol/dm^3	30.000
PP8763NaOH 0.01 mol/dm^3	24.752
LDH	12.315

Table 4.5 The amount of Brønsted acid of spent adsorbents by ion-exchanged titration

Adsorbents	Brønsted acid (µmol of H^+/g. of adsorbent) by using N_2 gas	Brønsted acid (µmol of H^+/g. of adsorbent) by using fuel gas
HY-zeolite (Si/Al=10)	90.686	89.552
NaY-zeolite (Si/Al=5.5)	59.701	56.650
PP8763	35.483	32.020
PP8763NaOH 0.001 mol/dm^3	29.703	26.961
PP8763NaOH 0.01 mol/dm^3	24.631	22.059
LDH	12.195	12.189

4.1.4 Thermal Gravimetric Analysis (TGA)

Thermogravimetric or TGA analysis can be useful for determining temperature of decomposition of the templating agent and the temperature of burn out of coke for spent adsorbent. Figure 4.7-4.12 are shows thermal gravimetric analysis (TGA) on adsorbent. It has been found that adsorbent with weight loss in the range temperature at 200-500 °C to decomposition of coke on the surface of the adsorbent. The demonstrate burn character for a spent adsorbent where the start of decomposition at about 300°C. However, for hydrocarbon species the analysis can become quite complex to interpret.

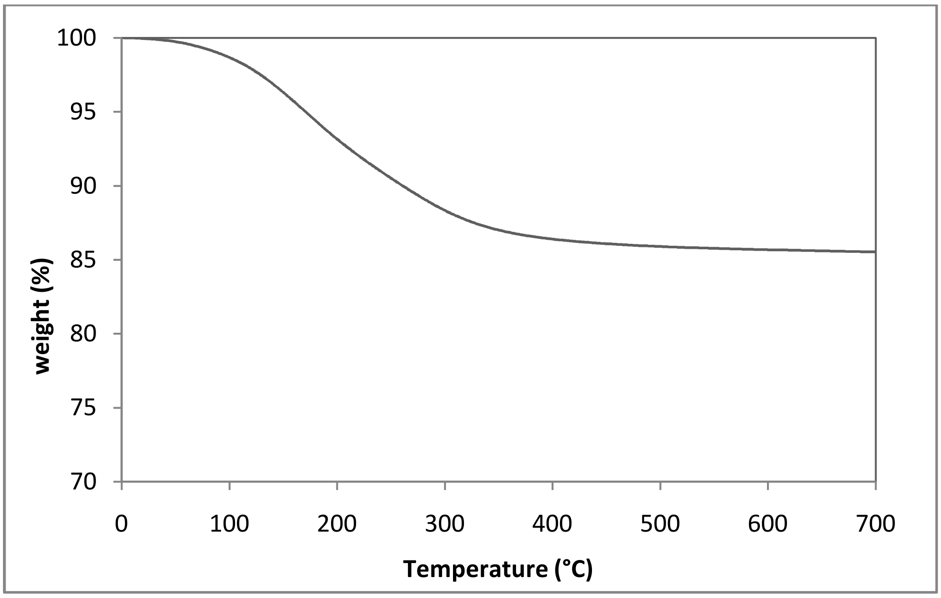


Figure 4.7 Thermal gravimetric analysis (TGA) on PP8763 commercial adsorbent

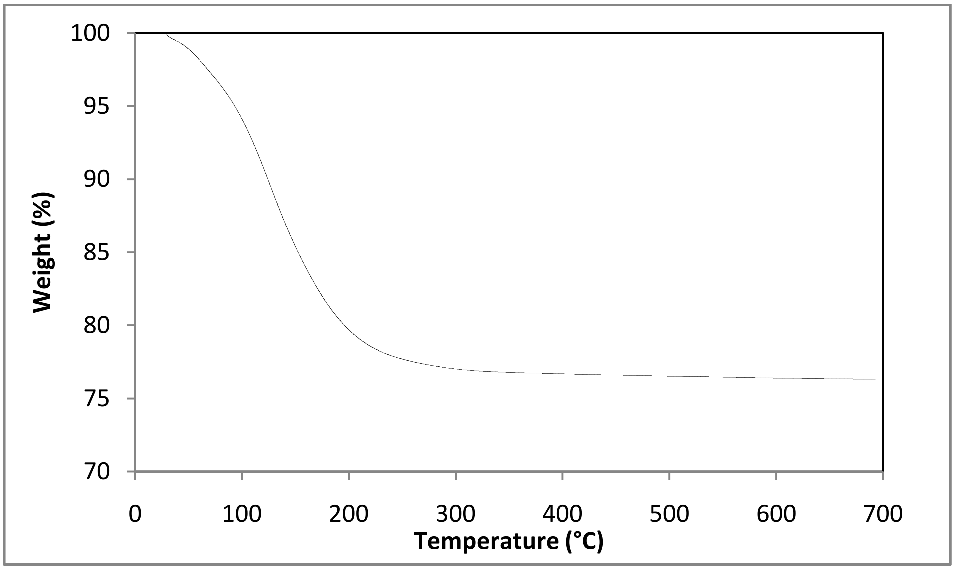


Figure 4.8 Thermal gravimetric analysis (TGA) on PP8763 modified with NaOH 0.001 mol/dm^3 commercial adsorbent

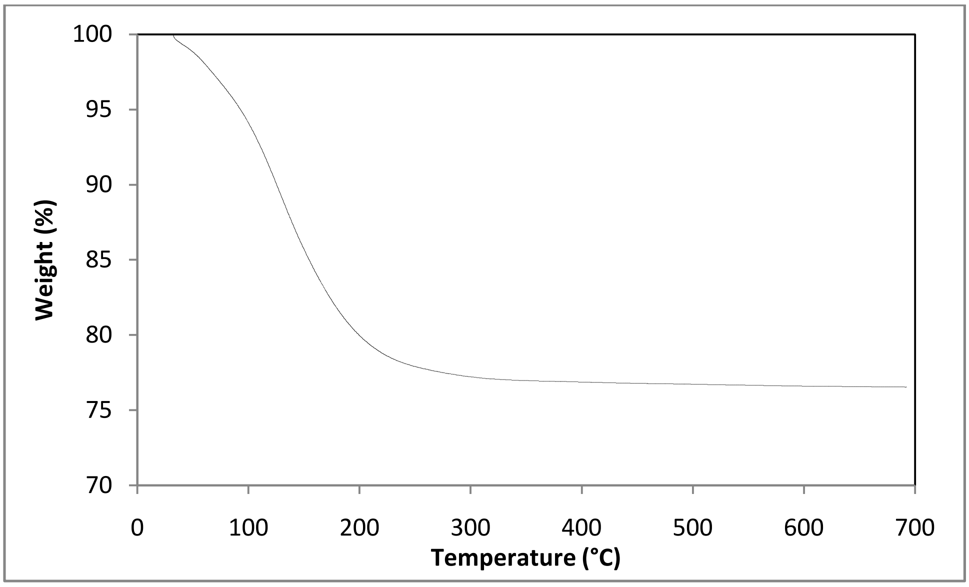


Figure 4.9 Thermal gravimetric analysis (TGA) on PP8763 modified with NaOH 0.01 mol/dm^3 commercial adsorbent

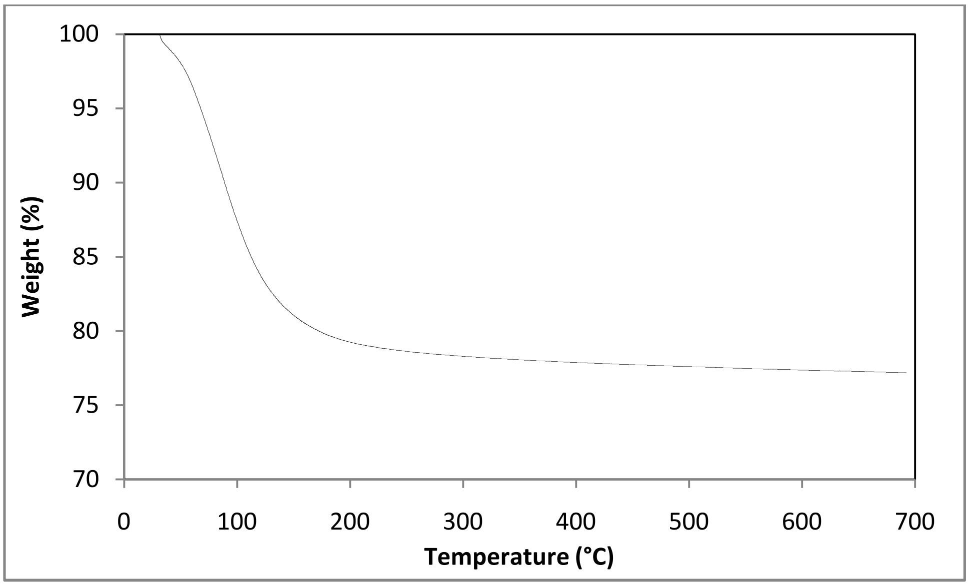


Figure 4.10 Thermal gravimetric analysis (TGA) on HY-zeolite commercial adsorbent

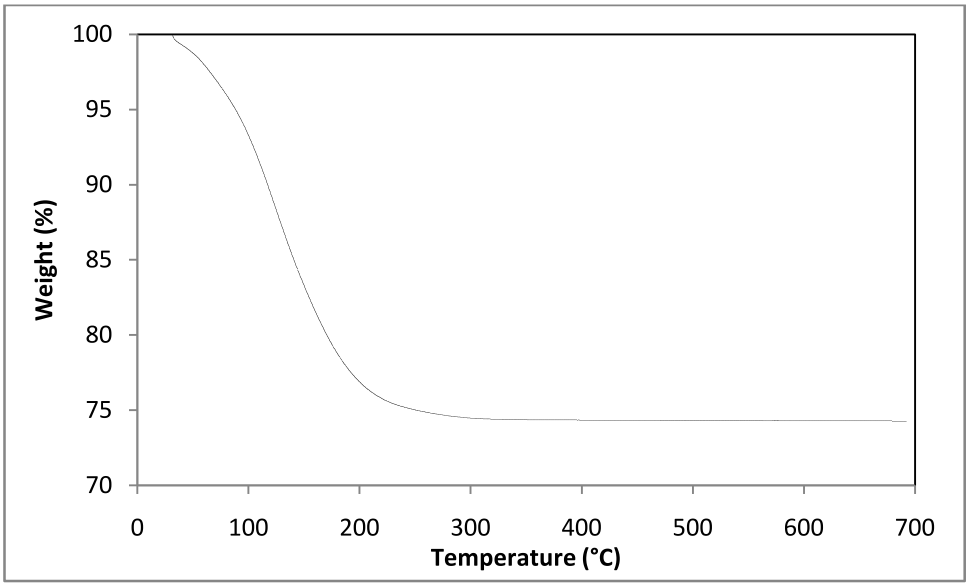


Figure 4.11 Thermal gravimetric analysis (TGA) on NaY-zeolite commercial adsorbent

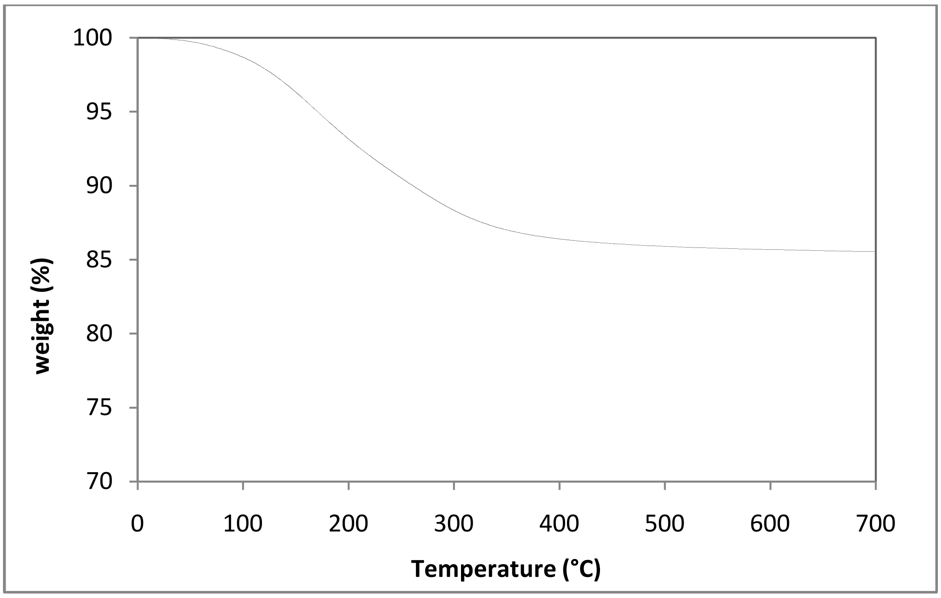


Figure 4.12 Thermal gravimetric analysis (TGA) on LDH commercial adsorbent

4.1.5 Scanning electron microscopy (SEM)

The morphology characterized by Scanning Electron Microscopy (SEM). Figure 4.13-4.18 shows SEM images of fresh and spent adsorbent.

In the image of adsorbent clear crystal faces were observed from each particle. There is no apparent difference in morphology between fresh and spent adsorbent. The surface of each particle looks rough in contrast with the smooth surface. It is likely that the surface roughness was caused by too much carbon deposition on the external surface of the particles. Moreover, filament carbon species was observed on spent adsorbents.

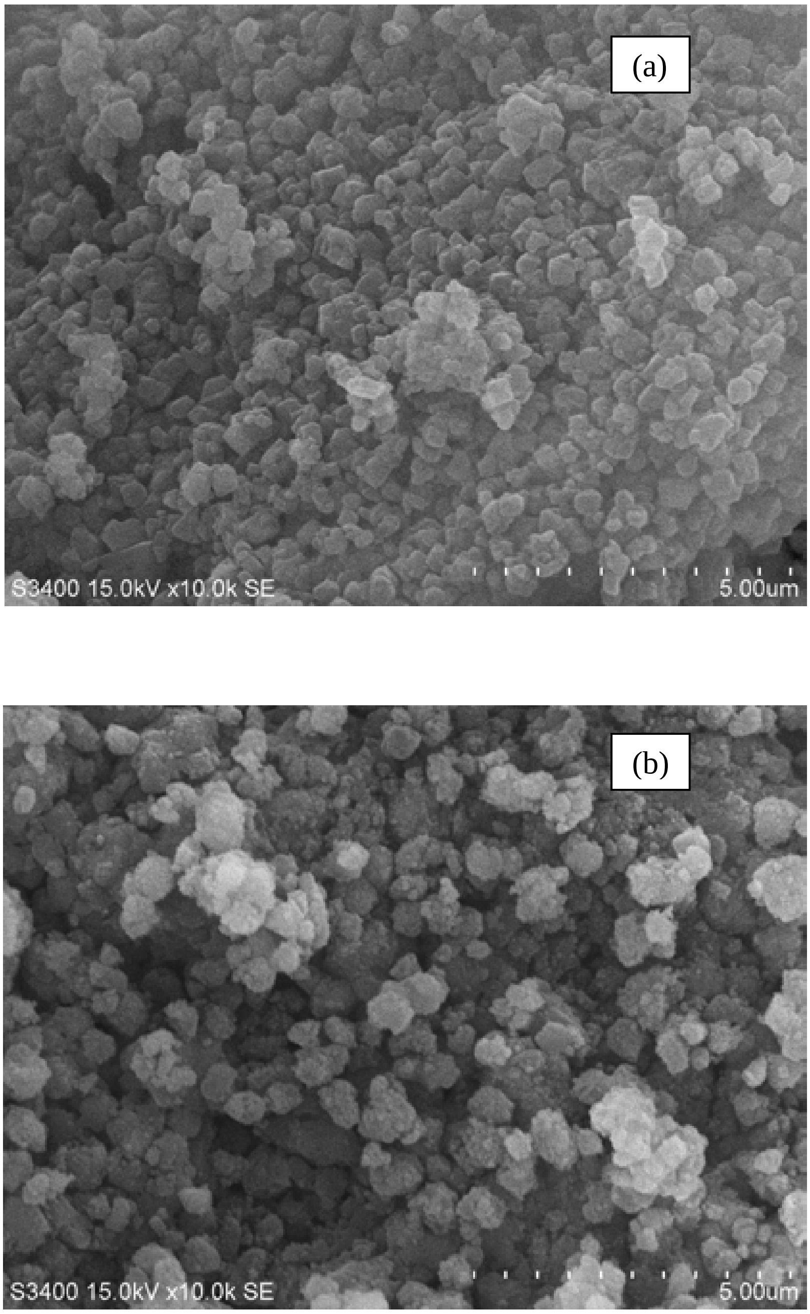
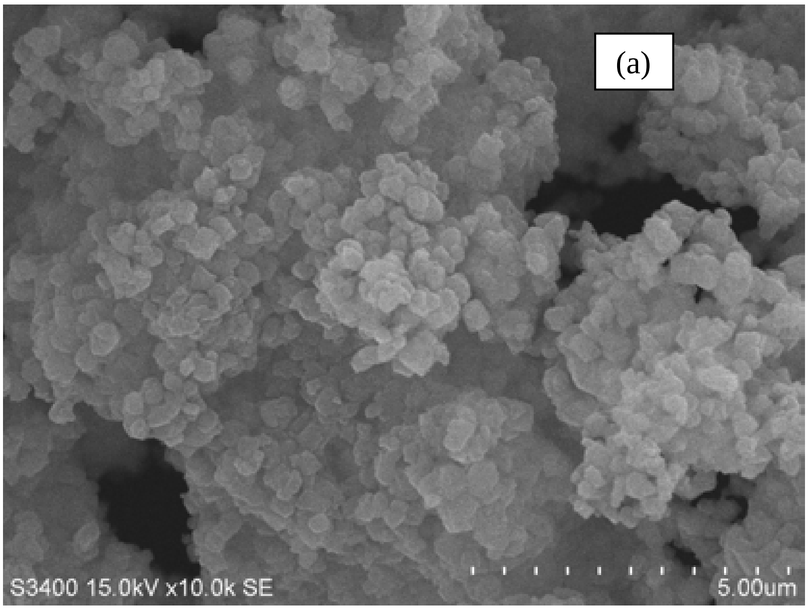


Figure 4.13 SEM images on PP8763 commercial adsorbent: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas



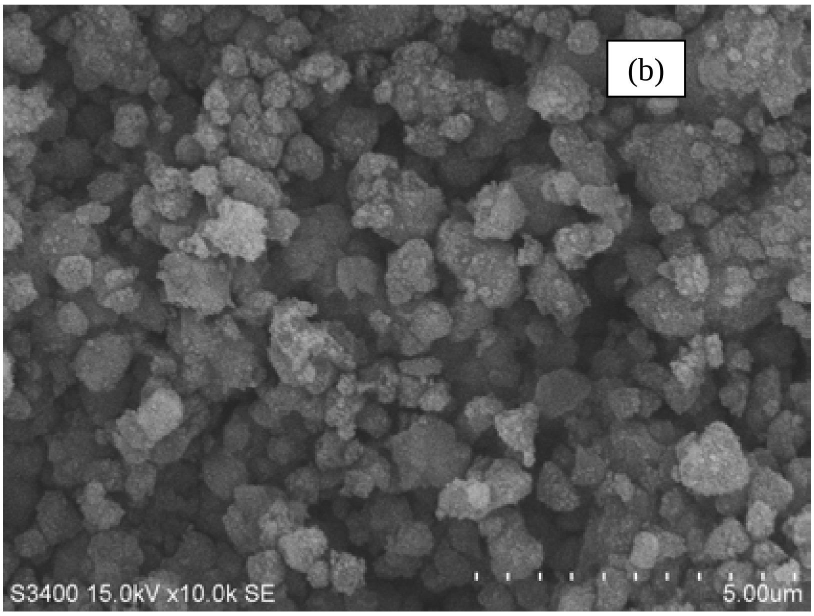


Figure 4.14 SEM images on PP8763 modified with NaOH 0.001 mol/dm^3 commercial adsorbent: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas

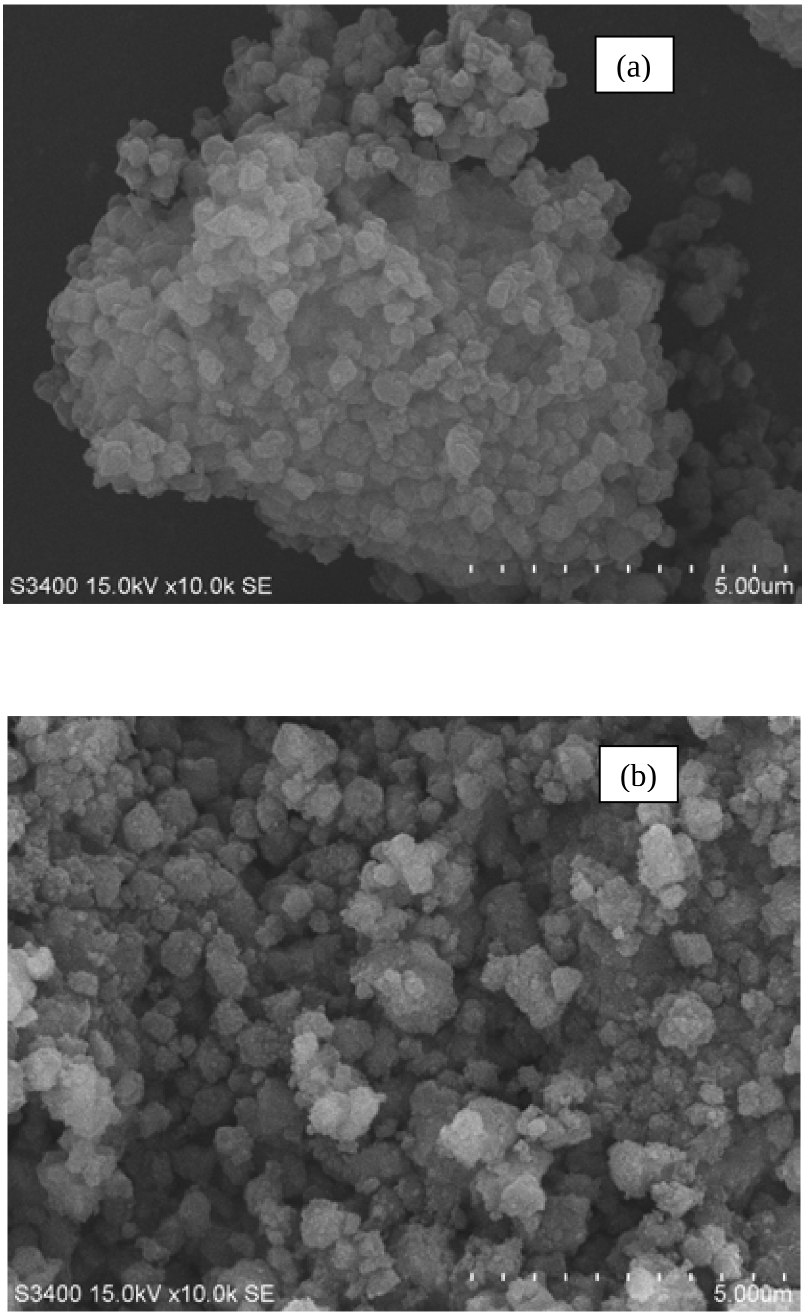


Figure 4.15 SEM images on PP8763 modified with NaOH 0.01 mol/dm^3 commercial adsorbent: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas

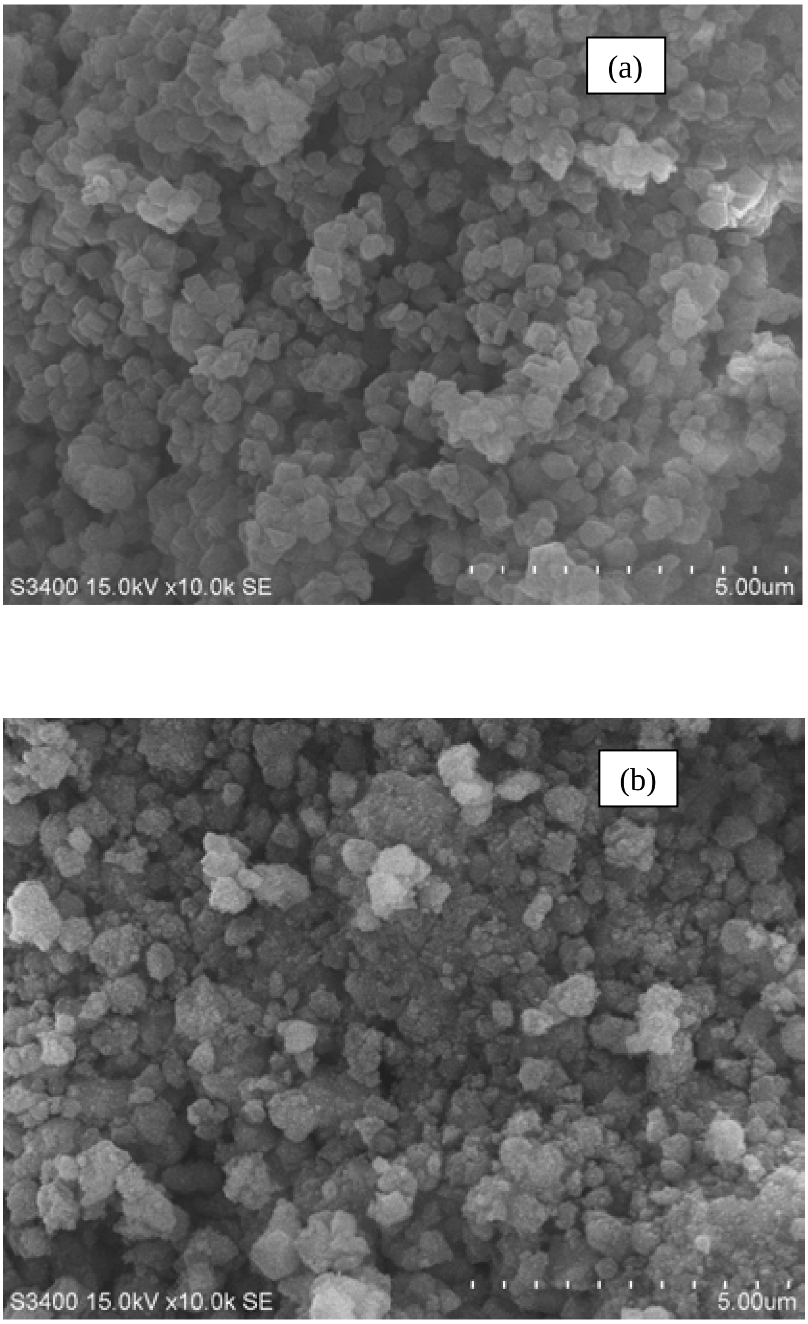


Figure 4.16 SEM images on HY-zeolite commercial adsorbent: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas

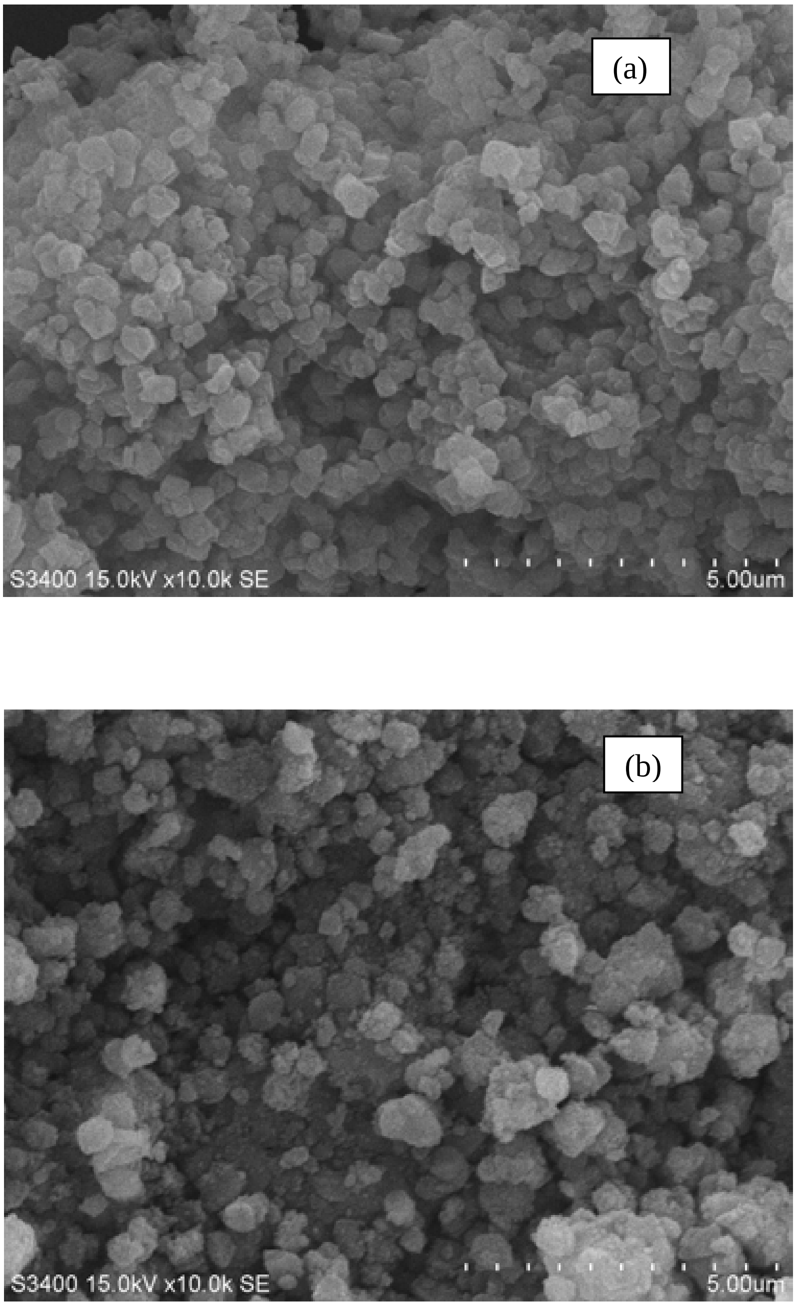


Figure 4.17 SEM images on NaY-zeolite commercial adsorbent: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas

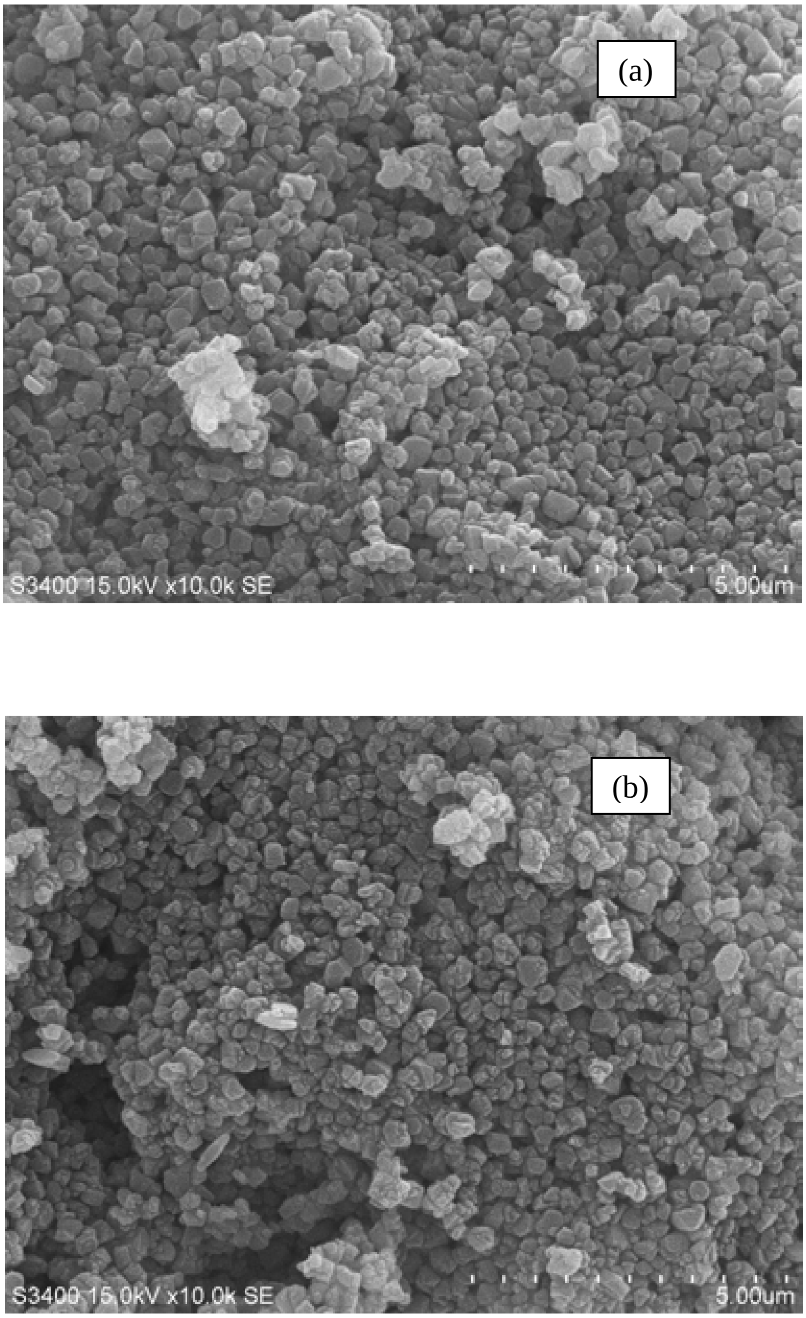


Figure 4.18 SEM images on LDH commercial adsorbent: (a) Fresh adsorbent, (b) spent adsorbent with regeneration gas

4.2 Effect of adsorption capacity and regeneration for removal of 1,3-butadiene from C_4 gas mixture by used nitrogen and fuel gas

The adsorption capacity for 1,3-butadiene was investigated under the periodically repeated cycles of adsorption until no significant adsorbed amount of butadiene was observed in each cycle. Then the saturately adsorbed adsorbent was regenerated under the flow of regeneration gas at 300 °C until almost constant desorbed butadiene was attained.

Subsequently, the regenerated adsorbent was subjected to the further cycle of adsorption similarly to the previous adsorption step. The results of periodically repeated cycles of adsorption on the studied adsorbent using nitrogen and fuel gas, respectively, as the regeneration gas are shown in Fig.4.19-4.23. Interestingly, the different types of regeneration gas greatly affected the adsorption capacity. Almost up to 10 repeated cycles of adsorption could be made on the adsorbent regenerated under N_2 flow, while approximately half-shortened repeated adsorption cycles were observed when regenerated under fuel gas atmosphere.

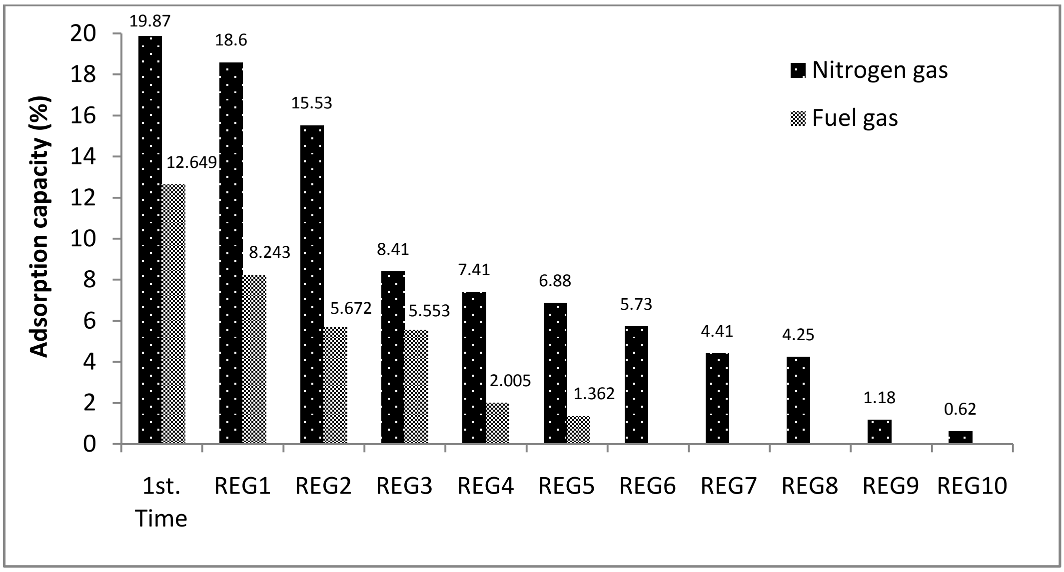


Figure 4.19 Adsorption capacity for 1,3-butadiene on PP8763 commercial adsorbent with different regeneration gas by using nitrogen gas and fuel gas

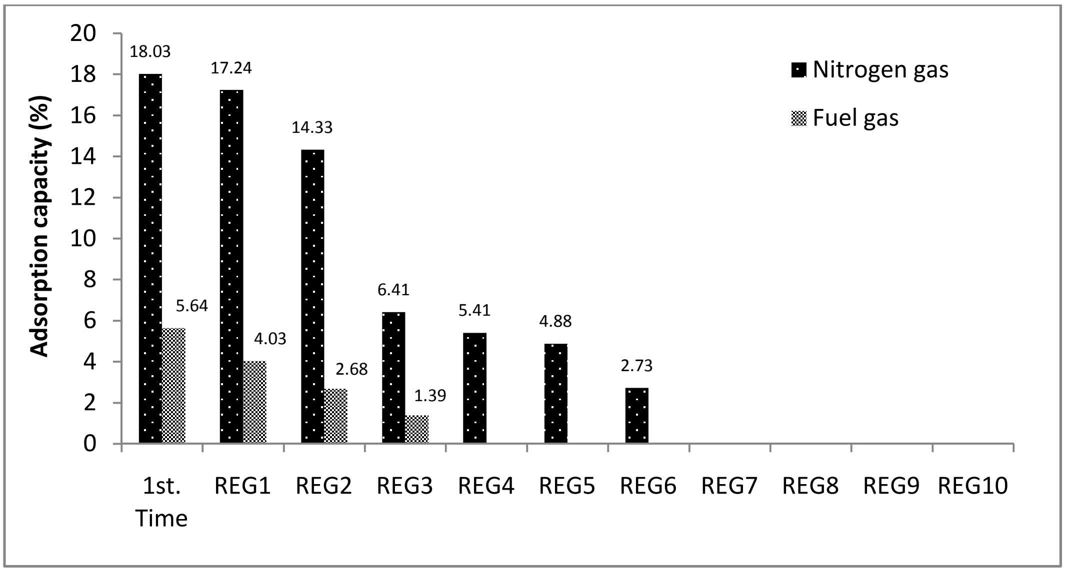


Figure 4.20 Adsorption capacity for 1,3-butadiene on PP8763 modified with NaOH 0.001 mol/dm^3 adsorbent with different regeneration gas by using nitrogen gas and fuel gas

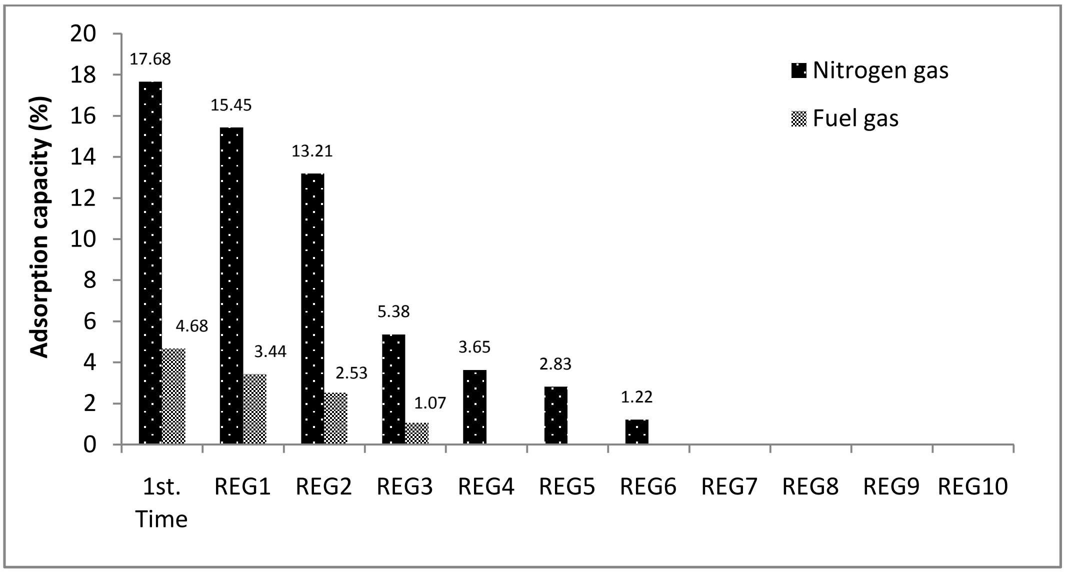


Figure 4.21 Adsorption capacity for 1,3-butadiene on PP8763 modified with NaOH 0.01 mol/dm^3 adsorbent with different regeneration gas by using nitrogen gas and fuel gas

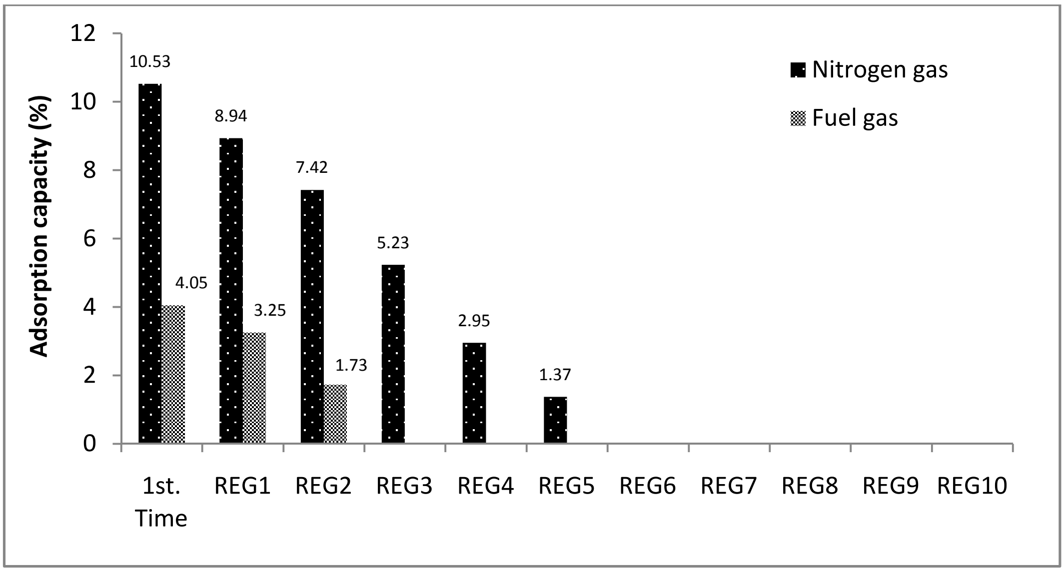


Figure 4.22 Adsorption capacity for 1,3-butadiene on HY-zeolite adsorbent with different regeneration gas by using nitrogen gas and fuel gas

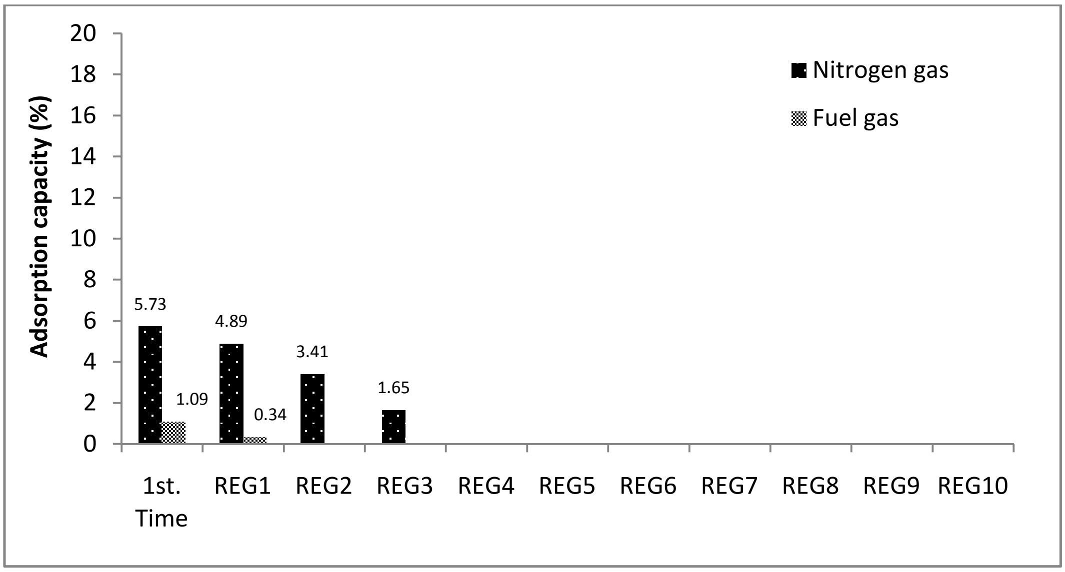


Figure 4.23 Adsorption capacity for 1,3-butadiene on NaY-zeolite adsorbent with different regeneration gas by using nitrogen gas and fuel gas

Figure 4.24 Adsorption capacity for 1,3-butadiene on LDH adsorbent with different regeneration gas by using nitrogen gas and fuel gas

4.3 The cycle of regeneration

The cycle of regeneration in the adsorption of 1,3-butadiene on commercial adsorbents is reported in this section.

Table 4.6-4.7 illustrates that the cycle of regeneration different purging gases during desorption, i.e. nitrogen and fuel gas, was also investigated. It has been found that the PP8763 commercial adsorbent exhibited the relatively stable adsorption performance of 1,3-butadiene under the desorption atmosphere of nitrogen gas. Additionally, both are regeneration by nitrogen gas and fuel gas, PP8763 commercial adsorbent had the highest cycle of regeneration and adsorption capacity.

Moreover, It has been found that the LDH adsorbent does not prefer to adsorb of 1,3-butadiene under the desorption atmosphere of nitrogen gas and fuel gas.

Table 4.6 The cycle of regeneration on commercials adsorbents with regeneration by using nitrogen gas

Adsorbent	Adsorption capacity of 1,3-butadiene (%)	Cycle of regeneration
PP8763	19.87	10
PP8763NaOH 0.001 mol/dm^3	18.03	6
PP8763NaOH 0.01 mol/dm^3	17.68	6
HY-zeolite (Si/Al=10)	10.53	5
NaY-zeolite (Si/Al=5.5)	5.73	3
LDH	0.00	0

Table 4.7 The cycle of regeneration on commercials adsorbents with regeneration by using fuel gas

Adsorbent	Adsorption capacity of 1,3-butadiene (%)	Cycle of regeneration
PP8763	12.64	5
PP8763NaOH 0.001 mol/dm^3	5.64	3
PP8763NaOH 0.01 mol/dm^3	4.68	3
HY-zeolite (Si/Al=10)	4.05	2
NaY-zeolite (Si/Al=5.5)	1.09	1
LDH	0.00	0

4.3 Effect of adsorbents acidity on adsorption capacity and cycle of regeneration for adsorption of 1,3-butadiene

The effects of adsorbents acidity on adsorption capacity with different regeneration gases by using nitrogen and fuel gas are shown in figure 4.25-4.26. It has been shown that the adsorption capacity increased with the increasing adsorbents acidity among each individual group of adsorbent, i.e. Y-zeolites with Ni-ion exchanged and those without Ni-ion exchanged.

Interestingly, regarding the Ni-containing adsorbents, PP8763 with and without NaOH modification, their adsorption capacities despite less acidity were far higher than those of their counterpart without Ni. Therefore, the pronounce effect of π-complexation derived from the presence of nickel was predominant over the acidity. The favourable effect of π-complexation, derived from the presence of some metals, on adsorption capacity of mixed C_4 and other hydrocarbons has been reported somewhere else [4, 18, 20, 21, 23].

The similar trend was also interestingly observed for the correlation between cycle of regeneration and adsorbents capacity as shown in figure 4.27-4.28, respectively.

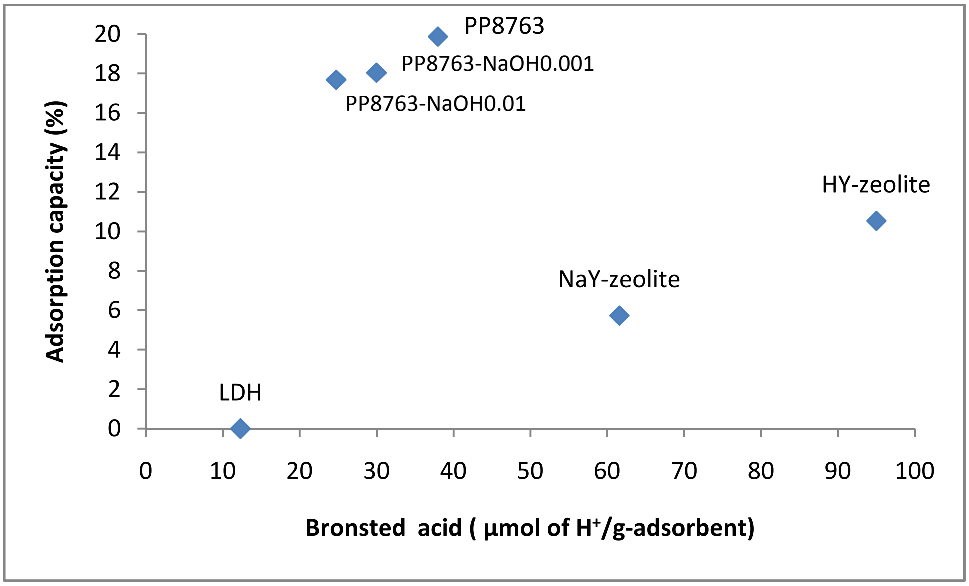


Figure 4.25 Adsorbents acidity on adsorption capacity for adsorption of 1,3-butadiene with regeneration gas by using nitrogen gas

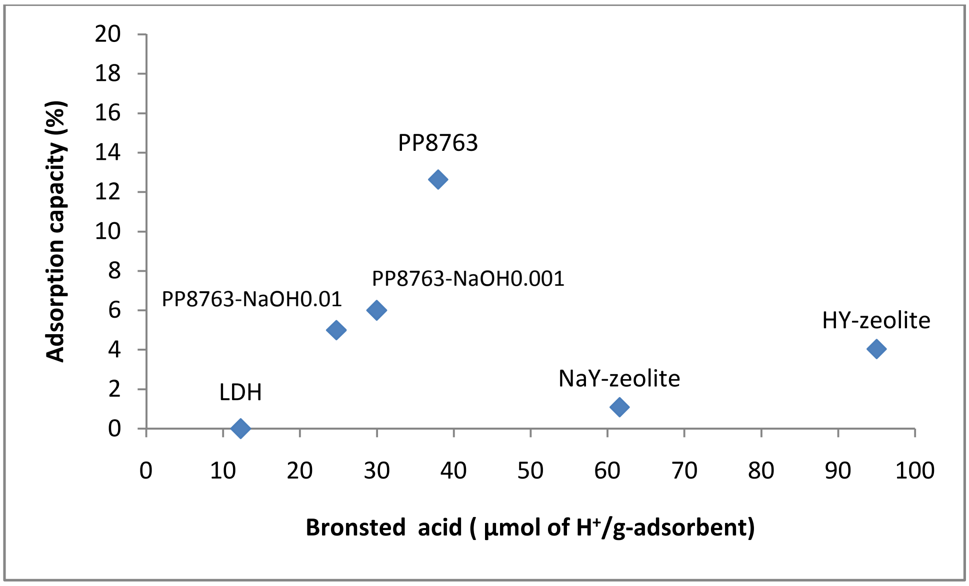


Figure 4.26 Adsorbents acidity on adsorption capacity for adsorption of 1,3-butadiene with regeneration gas by using fuel gas

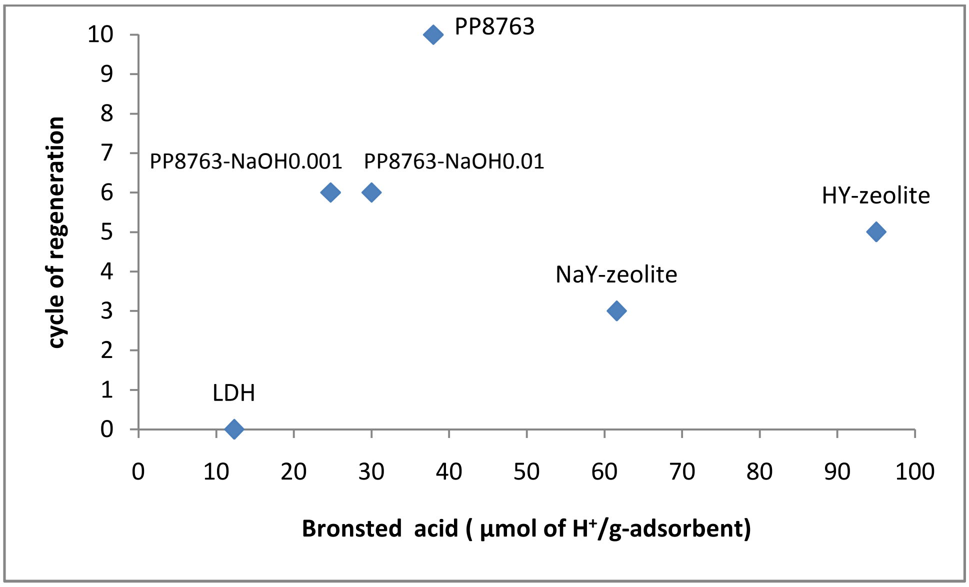


Figure 4.27 Adsorbents acidity on cycle of regeneration for adsorption of 1,3-butadiene with regeneration gas by using nitrogen gas

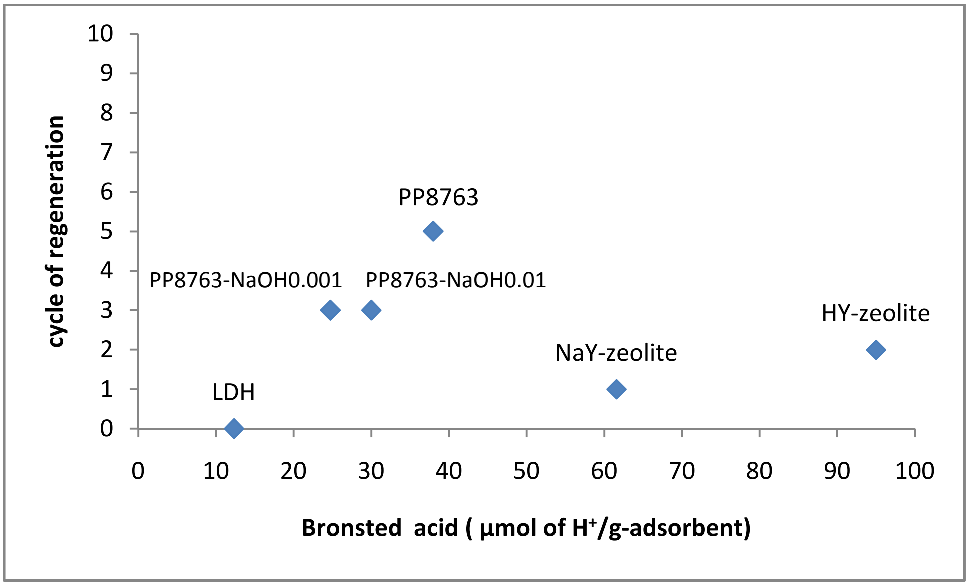


Figure 4.28 Adsorbents acidity on cycle of regeneration for adsorption of 1,3-butadiene with regeneration gas by using fuel gas

CHAPTER V

CONCLUSION AND RECOMMEDATION

5.1 Conclusions

This chapter is focused upon the conclusions of the experimental results of the adsorption of 1,3-butadiene over fresh and regenerate adsorbents, in which effect of regeneration gas with nitrogen and fuel gas was studied. Recommendations for further study are given afterwards

The effects of regeneration with nitrogen and fuel gas can be summarized as follows:

1. Effect of different purging gases during desorption, i.e. nitrogen and fuel gas, was investigated. It has been found that the PP8763 commercial adsorbents exhibited the relatively stable adsorption performance of 1,3-butadiene under the desorption atmosphere of nitrogen gas.

2. High efficiency selective adsorption and regeneration for removal of 1,3-butadiene from C_4 gas mixture can be possibly made by the regeneration of the commercial adsorbents under nitrogen gas.

3. The removal of 1,3-butadiene from C_4 gas mixture to suppress an adverse effect of 1,3-butadiene in metathesis of ethylene and 2-butene for improved propylene production can be possibly made via the adsorption on Y-zeolites ion-exchanged with nickel.

5.2 Recommendations

Upon the completion of this study, the adsorption of 1,3-butadiene in using NaY-zeolite was established. It is interesting to further study towords the modification of NaY-zeolite by loading various metal ions on zeolites. Subsequently, comparison between NaY-zeolite and zeolite loaded with other metal ions for their surface adsorption capacity can be done.

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APPENDICES

APPENDIX A

PROPERTIES OF 1,3-BUTADIENE

Molecular formula	:	C_4H_6
Synonyms	:	biethylene, bivinyl, butadiene, erythrene, methylallene, pyrrolylene, vinyl ethylene
Molecular Weight	:	54.09
Appearance	:	Colourless gas or refrigerated liquid
Density	:	0.64 g/cm^3 at -6 °C, liquid
Melting point	:	-108.9 °C, 164.3 K, -164.0 °F
Boiling point	:	-4.4 °C, 269 K, 24 °F
Flash Point	:	-105 °C
Viscosity	:	0.25 cP at 0 °C

APPENDIX B

COMPOSITIONS OF MIXED-C_4

The adsorption was tested with the feed consisting of mixed C_4:

- iso-butane,
- n-butane,
- trans-2-butene,
- 1-butene,
- iso-butene,
- cis-2-butene,
- 1,3-butadiene,
- and C_5.

APPENDIX C

COMPOSITIONS OF FUEL GAS

The compositions of fuel gas consisting:

- carbon dioxide,
- hydrogen,
- C_2,
- oxygen,
- nitrogen,
- methane,
- water,
- and carbon monoxide.

APPENDIX D

CALCULATION OF BRONSTED ACID

Example: PP8763 commercial adsorbent

$g._{cat}$	$V_{titration}$
0.202	0.14
0.204	0.14
0.200	0.15

N_{NaOH} = 0.05 M

$[H^+]$ = NV

= (0.05 x 0.15 x 2) / (1,000 x 0.202)

= 3.45×10^{-5}

= 34.65 µmol/g-cat

$g._{cat}$	$V_{titration}$	$[H^+]$
0.202	0.14	34.65
0.204	0.14	34.31
0.200	0.15	37.50

$[H^+]_{ave}$ = (34.65 + 34.31 + 37.50) / 3

= 35.48 µmol/g-cat

APPENDIX E

CALCULATION OF ADSORPTION CAPACITY

Calculation of adsorption capacity:

- Calculate, % loss
  %conc. of feed – %Area 1,3-butadiene

- Calculate, Amount of adsorbate
  (Interval volume x (%loss)) /100

- Calculate, Adsorption capacity
  (Total Amount of adsorbate(g)/ amount of adsorbent 3 g)) x 100

APPENDIX F

LIST OF PUBLICATION

1. Atchara Boonmala, Suphot Phatanasi, Kongkiat Suriye and Pruphanya Lekngarm, Role of Regeneration Gas on the Adsorption of 1,3-butadiene over Zeolite Adsorbent. Proceeding of The 3rd International Thai Chemical Engineering and Applied Chemistry Conference 2013, October 17-18 (2013), Khon Kean, Thailand.

VITA

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