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Microwave Assisted Regeneration of Na-ETS-10

by

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Abstract

In adsorptive separation of binary gas mixtures, regeneration techniques require either a long operation time or high energy consumption. Microwave heating offers the advantage of faster heating and lower energy consumption. A comparison of microwave heating and conductive heating for the regeneration of sodium exchanged Engelhard titanosilicate (Na-ETS-10) showed that, for microwave heating, the energy consumption was 0.7 kJ/g Na-ETS-10, and the gas recovery was 94% for C_2H_4/C_2H_6 and 70% for CO_2/CH_4. Conductive heating had an energy consumption of 7.7~7.9 kJ/g Na-ETS-10 and resulted in 71% gas recovery for C_2H_4/C_2H_6 and 57% for CO_2/CH_4.

In another comparison, it was observed that water desorption required more energy than microwave heating in both the constant power and constant temperature modes and, therefore, was not a potential technique for regenerating Na-ETS-10. To achieve 50% gas recovery, constant power microwave heating required 110 seconds and 0.32 kJ/g energy while constant temperature required 460 seconds and 0.6 kJ/g energy. Hence, microwave heating can be used as a more efficient and energy-saving regeneration technique for Na-ETS-10 for adsorptive separation of binary mixtures.

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LIST of ABBREVIATIONS and NOMENCLATURE

ACFC	Activated carbon fiber cloth
BTEX	Benzene, toluene, ethyl benzene and xylene
C_2H_4	Ethylene
C_2H_6	Ethane
CO_2	Carbon dioxide
CO	Carbon monoxide
CH_4	Methane
DAC	Data acquisition and control
DAY	Dealuminated Y
EB+	Envisorb B+
FAU	Faujasite
FTIR	Fourier transform infrared
GC	Gas chromatogram
GAC	Granular activated carbon
GHG	Green house gas
HCl	Hydrochloric acid
HNO_3	Nitric acid
HPA	Hypercrossliked polymeric adsorbent
MEK	Methyle ethyle ketone
Na-ETS-10	Sodium- Engelhard Titanosilicate
NaOH	Sodium Hydroxide
Na-MOR	Sodium Mordenite
Na_2O	Sodium oxide
NO_x	Nitrogen oxides
N_2	Nitrogen gas

PAC	Powder activated carbon
PCP	Pentachlorophenol
PID	Proportional integral derivative
PSR	Pressure swing regeneration
SO_2	Sulphur dioxide
TCD	Thermal conductivity detector
TCE	Trichloroethylene
TSR	Temperature swing regeneration
VOC	Volatile organic compounds

CHAPTER ONE: INTRODUCTION

1. 1 Introduction

1. 1.1 Separation and purification of hydrocarbon

The world's petrochemical industries require 90 million tonnes of ethylene (C_2H_4) every year for producing plastic, rubber and films. Ethylene is usually obtained from ethane (C_2H_6) by applying thermal decomposition or steam cracking (Anson et al., 2008). These processes produce a complex mixture of ethylene, un-cracked ethane and other hydrocarbons. The petrochemical industries require 99.9% pure ethylene for their production, and, therefore, the ethylene must be separated from the produced mixture (Shi et al., 2010). Typically, cryogenic distillation is the dominant technology in use for this separation. Cryogenic distillation is effective and reliable but highly energy-intensive due to the similar volatilities of ethane and ethylene. In a typical ethylene plant, 75% of the total production expense is for heating, dehydration, recovery, and refrigeration systems (Anson et al., 2008). A practical approach to producing highly enriched ethylene feed stock needs to be considered to reduce cost in hydrocarbon separation and purification.

Typically, natural gas contains traces of CO, CO_2 and SO_2, therefore it is considered as one of the cleaner fuels. Currently, one-fourth of the world's energy needs is fulfilled by natural gas. Typically, it contains more than 90% methane with some CO_2 and N_2 as minor impurities. In countries such as Australia and

Germany, natural gas consists of more than 10% CO_2 and hence fails to meet the "pipeline quality" of methane (< 2% CO_2). "Pipeline quality" is a set standard for methane to limit corrosion in pipeline and equipments. Traditionally, the separation of CO_2 is accomplished by chemical absorption with amines. This process is energy-intensive and requires high reagent cost (Rao et al., 2002). Therefore, an alternative separation technique that would reduce the energy need could greatly contribute to the purification of natural gas (Caventi et al., 2004).

1.1.2 Engelhard Titanosilicate (ETS-10)

Adsorptive separation is an effective alternative to cryogenic distillation or chemical absorption as such separation reduces cost and energy consumption (Eldrige et al., 1993). Engelhard titanosilicate (ETS-10) has shown great potential in gas separation (Kuznicki et al., 1992) and ion exchange (Pavel et al., 2002). ETS-10 is a large-pored mixed coordination titanium silicate molecular sieve with interconnecting channels (Kuznicki, 1991). ETS-10 has a pore size with an average kinetic diameter of ~ 8 °A, which is larger than that of C_2H_4, C_2H_6, CO_2 and CH_4 (Sircar and Myers, 2003). Model predictions and experiments have shown that ETS-10 adsorbs all these gas components efficiently and that Na-ETS-10 demonstrates a preference to C_2H_4 over C_2H_6 (Al-baghli and Loughlin, 2006) and to CO_2 over light saturated hydrocarbons during adsorption (Anson et al., 2009). Therefore, ETS-10 can be a potential alternative to cryogenic distillation or chemical absorption for the separation and purification of hydrocarbons.

1.1.3 Microwave Regeneration

Adsorptive separation is typically a cyclic process: adsorption is followed by regeneration. The current two regeneration techniques are pressure swing (PSR) and temperature swing regeneration (TSR). PSR has been found to be effective in the separation of C_2H_4/C_2H_6 (Shi et al., 2011), but requires additional compressors and pumps to maintain low or high pressure and hence is inconvenient (Cherbanski et al., 2011). TSR uses hot gas or steam in the regeneration process and hence requires a larger footprint and longer regeneration time (Cherbanski and Mogla, 2009). Microwave regeneration has been recognized as a faster and more efficient, and, therefore, very promising technique for regenerating porous adsorbents in order to intensify chemical processes.

Microwaves are electromagnetic waves with a frequency range from 300MGz to 30GHz. Although microwave regeneration is a branch of thermal regeneration, the heating mechanism of microwaves differs from that of conventional techniques. Microwave heating, which propagates from inside to the outside of the material, is the opposite of conventional heating. This process is called “volumetric heating” (Das et al., 2009). Unlike steam regeneration microwave regeneration is capable of heating a material without using any heating medium or chemical. Microwave energy dissipates into a material due to ohmic loss, magnetic loss and electric loss (Bathen, 2003).

The application of microwave heating has been found to be promising in the adsorptive control of VOCs (Hashisho et al., 2007). The success of microwave heating in adsorptive separation depends on the interaction between the electromagnetic waves and the adsorbate-adsorbent. Depending on a property called “dielectric heating”, microwaves can selectively heat a material. The heating mechanism is controlled by the dipolar polarization and conduction loss of the adsorbate and adsorbent (Cherbanski and Mogla, 2009).

1.2 Research objective

The goal of this research was to determine whether microwave regeneration can be a faster and less energy consuming technique than other conventional techniques for regenerating ETS-10. This topic will be investigated by using Na-ETS-10 as an adsorbent, and two binary gas mixtures C_2H_4/C_2H_6 and CO_2/CH_4 as adsorbates. This investigation had the following objectives:

1. Develop a low-power microwave system that can regenerate Na-ETS-10.

2. Compare microwave heating with conductive heating as regeneration techniques based on swing capacity, net energy consumption and gas recovery.

3. Investigate the performance of a microwave heating system under the constant power and constant temperature modes based on swing capacity, energy consumption and gas recovery.

4. Compare water desorption followed by microwave drying, with constant power and constant temperature microwave heating as regeneration techniques based on swing capacity and net energy consumption.

This research is significant because it investigates the potential of microwave heating to provide a more effective way of separating hydrocarbons instead of cryogenic distillation. ETS-10 provides a potential alternative to cryogenic distillation. But the regeneration of the adsorbent requires a faster and less energy intensive method than current PSR or TSR. Microwave heating is selective due to the difference in microwave absorption ability of adsorbent and adsorbate. Therefore, this research investigates the potential of microwave heating as an energy efficient regeneration method for ETS-10. From an environmental engineering perspective, capturing hydrocarbons can reduce green house gas (GHG) emission and, therefore, reduce the environmental impact of GHG. The use of ETS-10 can reduce the separation barriers of hydrocarbon industry only if a quicker and less expensive regeneration technique than the current ones can be established.

1.3 Thesis outline

This thesis contains five chapters each of which will contribute to fulfill the overall objective of this research. Chapter 1 describes the background and goals of the present research. General literature review on adsorbent regeneration under microwave heating is presented in Chapter 2. Chapter 3 compares microwave heating with conventional heating as prospective regeneration techniques for Na-ETS-10. Chapter 4 explores the best microwave heating mode for Na-ETS-10. This chapter also provides a feasibility study of water desorption as a Na-ETS-10's regeneration technique and compares its regeneration efficiency with that of constant power and constant temperature microwave heating. Chapter 5 presents the conclusions derived from of the work presented in Chapters 3 and 4, as well as some recommendations for future work.

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CHAPTER TWO: LITERATURE REVIEW ON REGENERATION OF VARIOUS ADSORBENTS BY MICROWAVE HEATING

2.1 Introduction

The separation and purification of gas mixtures by selective adsorption onto a micro or mesoporous solid adsorbent is a major unit operation in most of the chemical, petrochemical, environmental, medical and electronic gas industries (Sircar and Myers, 2003). There are many different paths or combinations of materials or processes that can satisfy the same separation criteria. The infinite variety of material combinations is the driving force for discovering new norms of separation (Pyra and Dutta, 2003). An overview of adsorptive separation can be found in various studies published in this field (Ruthven, 1984; Yang, 1987).

Adsorption is a promising alternative to expensive cryogenic distillation in the field of gas separation. Once the adsorbent becomes saturated, it needs to be regenerated for reuse. The adsorbent's regeneration is a time- and energy-consuming step, so most of the expense of a separation process is for the regeneration operation. Two conventional regeneration methods are now commonly used: pressure swing regeneration (PSR) and temperature swing regeneration (TSR). The principle of PSR is to reduce the partial pressure of the adsorbate (Ko et al., 2003). PSR is widely used in removing CO_2, H_2S from ethylene and propane gas (Dechow, 1989) and in separating the components of air. PSR is nonlinear and therefore is not easy to simulate (Chatsiriwech et al., 1994). PSR is effective in enhancing chemical reactions inside the reactor and also in decreasing deactivation of the catalyst in a catalytic bed reactor. However, pumps, compressors and fans are needed to create such a pressure difference, increasing cost of production. The operation becomes even more complex for moving bed reactors (Cherbanski and Mogla, 2009).

TSR uses a hot gas stream such as steam or inert gas to heat the adsorbent bed and a cold gas stream to cool the bed to the room temperature for another cycle. The main disadvantages of this process are its large footprint, high energy need and long regeneration time. Some optimization of this process has been discussed in the literature, but the method is not yet flawless (Clausse et al., 2004; Youngsunthon and Alpay, 1998).

Microwave heating can be a promising alternative to the aforementioned regeneration methods. Microwave-induced regeneration of adsorbents was first discussed in the 1980s (Roussy and Chenot, 1981; Roussy et al., 1984). Microwaves were first used for the rapid heating of food in ovens. Later, microwaves' heating capability made them popular in industrial drying as well. For example, Dupont applied microwaves to dry nylon (Michael and Mingos, 2006). In a conventional thermal regeneration process, the thermal energy is transferred from the surface to the bulk of the material. In contrast, microwaves propagate through the molecular interaction of the material and the electromagnetic field (Das et al., 2009). The ease of microwave desorption depends on the interaction of the electromagnetic waves with the adsorbent and adsorbate.

The literature also discusses various adsorbents which interact with microwaves at different degrees. Adsorbents are usually various types of porous materials. Roughly, they can be classified into three groups: inorganic materials (silica gel and zeolite), organic polymers, and carbon-based material (activated carbon, charcoal) (Dechow, 1989). Organic polymeric adsorbents are mainly macro-porous resins that have various industrial names depending on the functional group present in the structure (Dechow, 1989). Activated carbon is a micro-porous material which has a wide range of pore distribution (Dettmer and Engewald, 2002). On the other hand, zeolites have a defined pore size. Zeolites are alumina silicates and can be both natural and synthetic (Li et al., 2010; Siriwardane et al., 2005). According to the literature, all of these adsorbents have the potential to remove trace contaminants from air (Kong and Cha, 1996; Lordgooei, et al., 1996; Ozturk and Ylmaz, 2006; Pires et al., 2001; Tao et al., 2004) and water (Sohrabnezhad and Pourahmad, 2010). In the last few decades, a new form of zeolite has become a source of immense interest for researchers. Dr. Steven Kuznicki and his group introduced titanosilicate (large-pored zeolite), which, during synthesis was involved in an unusual event named the molecular gate effect (Tsapatsis, 2002) and was named Engelhard titanosilicate (ETS-10**).** ETS-10 was found to be very effective in the adsorptive separation of hydrocarbons (Anson et al., 2008; 2009).

The aim of this literature review is to summarize the recent developments in the field of microwave regeneration of various adsorbents. This review highlights the microwave desorption of activated carbon, zeolite and polymeric adsorbents used in numerous applications; e.g., the purification of gas and water, and the separation of gas components. The disadvantages of microwave regeneration are also discussed.

2.2 Microwave technology

2.2.1 Historical development

Microwaves are electromagnetic waves with a frequency ranging from 0.3GHz to 30GHz which corresponds to a wavelength ranging from 1mm to 1m. In Europe, 2450MHz microwave generators are generally used, while in the UK and North America, 915MHz generators are used. The larger the frequency of the microwaves, the smaller are their penetration depth and the size of the equipment (Bathen, 2003).

The concept of microwaves was first anticipated by Maxwell's equation in 1864 and was later demonstrated by Heinrich Hertz in 1888. A major development in this field was initiated during World War II. In 1951, microwave ovens became popular as rapid and energy-efficient heating devices. Japanese technologists reengineered microwave ovens, making them cheap, reliable, and consumer-friendly (Michael and Mingos, 2006; Yuen and Hameed, 2009).

2.2.2 Basic principle

2.2.2.1 Dielectric Heating and loss factor

Materials can be classified into three groups depending on their ability to be heated by microwaves: conductors, insulators and absorbers. Figure 2-1 shows microwave absorption characteristics of various materials.

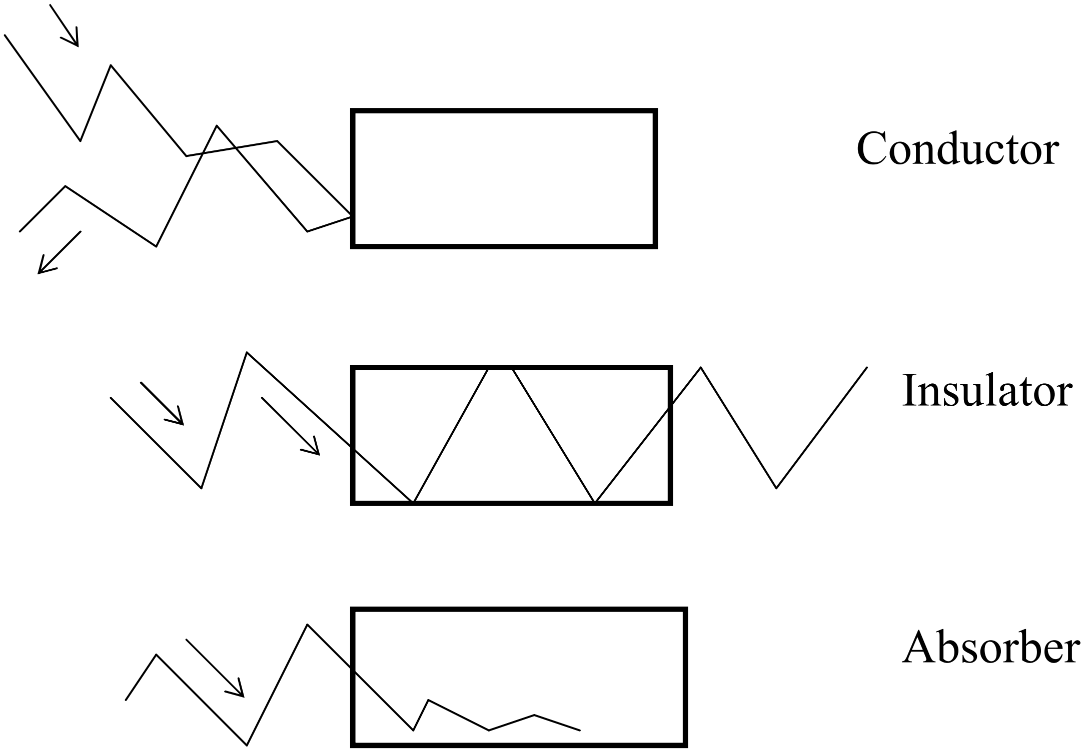

Figure 2-1: Microwave absorption characteristics of various materials (Jones, 2002).

Microwave heating depends on two factors: dielectric polarization and conduction loss. Materials with the ability to absorb microwaves are called dielectrics (Jones, 2002). Typically, two parameters define the dielectric properties of a material and have been extensively reviewed: dielectric constant and the dielectric loss. The dielectric constant defines the ability of a molecule to become polarized under an electric field. The dielectric loss measures the ability to convert electromagnetic energy into heat. At low frequency, most of the energy becomes stored in the material, and, therefore, the dielectric constant becomes maximized. The dielectric loss reaches its maximum at a frequency where the dielectric constant falls. The ratio of the dielectric constant to the dielectric loss is defined as the loss tangent, which describes the ability of a material to convert electromagnetic energy into heat energy at a given temperature and frequency. Two phenomena are important in dielectric heating of material: dielectric polarization and the rubbing action between polarized molecules (Leonardo energy, 2007). An electric field can distort the electron cloud of a polar material and induce dipole moment. Even a non-polar material or molecule can temporarily be polarized.

The ability of a material to convert microwave energy into thermal energy can be expressed by equation 2-1:

$$\epsilon''=\epsilon'\tan\delta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-1)}$$

Here, ϵ'' = the relative permittivity or dielectric constant of a material. The dielectric constant gives a material the ability to be polarized in an electric field. ϵ' = the loss factor, which provides the measure of converting energy to heat, and δ = the loss angle, which depends on the phase orientation of the molecules and change in the electric field.

The power dissipation (absorption) of a dielectric material (for a small volume) can be derived by using equation 2-2:

$$\mathrm{P} = 2\pi.\mathrm{f}.\epsilon_0\epsilon' \tan\delta\,.\,\mathrm{E}^2 \quad \text{(2-2)}$$

Here, P= power dissipated ($\mathrm{W/m^3}$), f = the frequency of electric field (Hz), ϵ_0= the dielectric constant of the vacuum ($8.854\mathrm{x}10^{-12}\frac{\mathrm{F}}{\mathrm{m}}$), $\tan\delta$= the loss factor of material, and E = the electric field strength of the material ($\frac{\mathrm{V}}{\mathrm{m}}$).

The loss factor depends on the temperature, moisture content, frequency as well as the electric field. Notably, at a critical temperature T_c, thermal runway occurs, and the material can even be damaged due to overheating

In conduction loss, the ions follow the direction of the electric field, collide with other molecules, and thus convert kinetic energy into thermal energy (Cherbanski and Mogla, 2009). For highly conductive liquids and solids, the conduction loss can be even larger than the dielectric polarization effects (Michael et al, 1991). Conduction loss can be expressed by equation 2-3.

$$\epsilon_c^{''} = \frac{\sigma}{\epsilon_0} \quad \text{(2-3)}$$

Here, $\epsilon_c^{''}$ is the conduction loss, and σ is the conductivity ($\mathrm{Sm^{-1}}$)

2.2.2.2 Penetration depth

The penetration depth is a characteristic length that describes the gradual absorption of microwave power. This depth can be defined as the thickness at which 63% of the incident power will be dissipated. The penetration depth (D) can be expressed by equation 2-4 (Leonardo energy, 2007):

$$D \sim \frac{1}{f} . (\epsilon')^{\frac{1}{2}} . \tan \delta \text{..} \quad (2\text{-}4)$$

Equation 2-5 presents another expression of the penetration depth (Bathen, 2003; Cherbanski and Mogla, 2009):

$$D_p \sim \frac{\lambda_0}{2\pi} . \frac{(\epsilon')^{\frac{1}{2}}}{\epsilon''} \text{..} \quad (2\text{-}5)$$

where, λ_0= the wavelength of the microwave radiation.

Therefore, the penetration depth can be calculated if $\epsilon'$and ϵ'' are known (Bathen, 2003). The thickness of the absorbing material should be less than the penetration depth. Otherwise, more than 37% of the microwave power will be lost and may contribute to overheating (Cherbanski and Mogla, 2009). The frequency should be optimum to achieve effective microwave heating without thermal runway. Figure 2-2 illustrates the frequency dependence of the penetration depth.

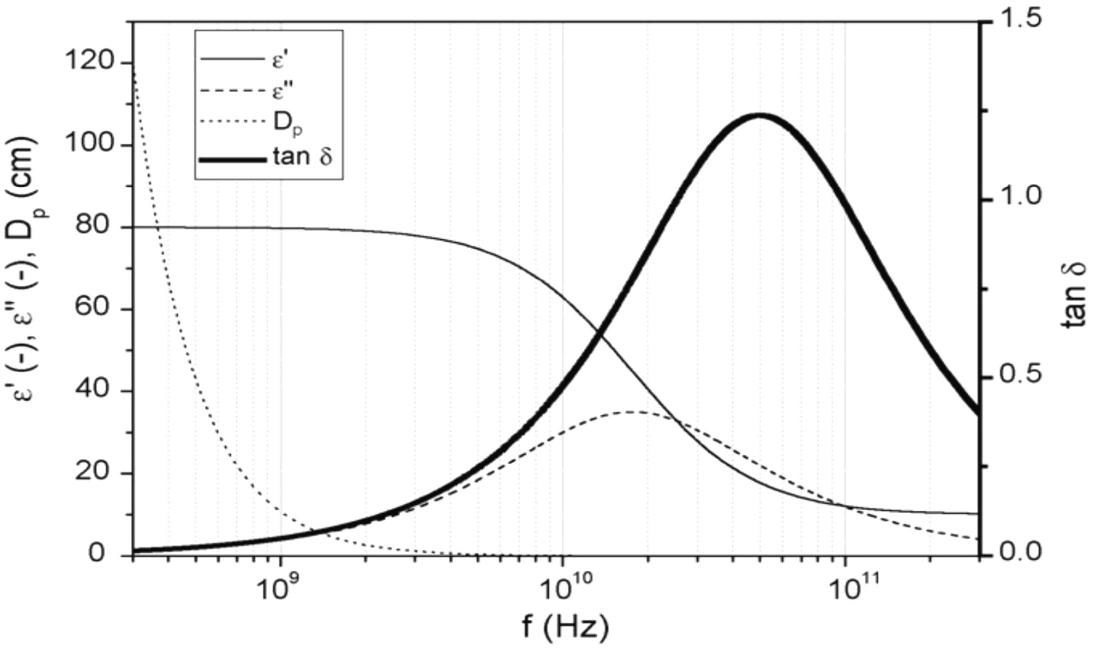

Figure 2-2: Frequency dependence of ϵ´, ϵ´´, D_p and tanδ for water at 20°C (Cherbanski and Mogla, 2009)

2.2.2.3 Hotspot formation

One of the major characteristics of microwave heating is non-uniformity of heating. It occurs due to the nonlinear relationship between the temperature and the electromagnetic and thermal properties of the material. An uncontrolled microwave heating may produce very high temperatures at various locations within the material, which are called hotspots (Reimbert et al, 1996). Hotspot formation can be desirable/ undesirable depending on the purpose of use. Hotspots can lead to the sintering of the adsorbent, which reduces its adsorption capacity. The reflection of the electromagnetic waves from microwave cavity also contributes to hotspot formation. Smyth (1992) developed a model to show the influence of material conductivity and thermal diffusivity on hotspot formation. Zhang et al. (1999) investigated hotspot formation during H_2S decomposition in a metal catalyzed bed. These researchers estimated that hotspots in a metal catalyzed bed have a dimension of 90-1000μm and occur at a temperature 100-200°C higher than that of the bulk. Kriegsmann (1997) developed another model to describe the physical mechanism and mathematical structure of hotspot formation and presented a numerical solution to the problem (Kriegsmann, 1997).

2.3 Regeneration of adsorbents

2.3.1 Drawbacks of conventional thermal regeneration

Thermal regeneration is the most common type of regeneration for any kind of porous adsorbent. Various studies have discussed the thermal regeneration of saturated adsorbents (Moreno-Castilla et al., 1995; Sabio et al., 2004; Suzuki et al., 1975). Thermal regeneration of activated carbon involves several steps: drying, thermal desorption (removal of volatile organic compounds at 100-160°C), pyrolysis, carbonization (removal of non-volatile compounds at 200-260°C) and gasification (at 650-850°C) of residue (Salvador, 1996). All the steps require a high temperature (Peng et al., 2006; Schulz and Wei, 1999; Su et al, 2009) and therefore consume high energy. Dehydration of the adsorbent by heating becomes successful at around 300°C (Belonogov and Tabunshchikova, 1978). For activated carbon, another drawback is the loss of carbon due to attrition, burn-off and washout. Adsorbers can be corroded in a steam-generated regeneration unit (Price and Schmidt, 1998).

Alvarez et al. (2004) were able to regenerate spent granular carbon by using a mixture of CO_2 and nitrogen by removing phenol in a fixed bed column. Regeneration started at 127°C and lasted up to 827°C. A 15% weight loss (due to burn off) of the adsorbent was observed (Alvarez et al., 2004). Baker (2008) developed a thermodynamic model to predict the improvement of the adsorption capacity of an adsorbent under thermal regeneration. The model showed that effective regeneration of zeolite was possible at a temperature greater than 150°C (Baker, 2008). The regeneration of HZSM-5 zeolite by using air (Vitolo et al., 2001) and fluid catalytic cracking (Schulz and Wei, 1999) has also been reported to be highly energy-consuming. Bagreev et al. (2001) found that the regeneration of spent carbon by thermal regeneration was feasible at 300°C in air (oxidizing atmosphere).

2.3.2 Regeneration of activated carbon by microwave heating

Microwaves were used to regenerate activated carbon by keeping its adsorption capacity intact. This approach was perceived as a novel and economic regeneration method that would solve the problem of long regeneration time and the use of a large volume of purge gas (Mezey and Dinovo, 1982). Previous research highlighted the need for an easy and convenient design and procedure to enhance regeneration under microwave irradiation (Woodmansee and Carroll, 1993).

The regeneration of activated carbon has been studied extensively by focusing on different methods of adsorbate removal. The success of regenerating granular activated carbon (GAC) by microwave irradiation has been found to be regulated by the adsorbate concentration, number of stages used, applied power, adsorbent dose, and types of bed used (Liu et al., 2004a; Jou, 1998; Jou and Tai, 1998; Tai and Jou, 1999). As the concentration of the feed adsorbate increases, the regeneration time also increases. For reactors with initial phenol (adsorbate) concentration of 50 mg/L, complete removal occurred after 240 seconds while for reactors with initial concentrations of 5 mg/L it occurred after 120 seconds. Multi-stage reactor systems have been more efficient than single-stage reactors for larger surface areas and volumes (which provide more microwave absorption) (Tai and Jou, 1999; Jou, 1998). Microwave heating sometimes produces high temperature, which is capable of decomposing some of the adsorbates producing non-harmful gases (Liu et al., 2004a; Tai and Jou, 1999). Typically, a higher microwave power application provides enhanced desorption. However, the applied power has to be greater than a certain minimum value to instigate desorption, and smaller than a certain higher value to prevent hotspots and burning.

Repetitive microwave applications preserve the mesopores of activated carbon but reduce micro porosity. Ania et al. (2004, 2005) regenerated phenol saturated activated carbon by using microwave heating and compared their results with those from conventional electric furnace heating. It was found that both heating techniques reduced the micropores, but the reduction provided by conventional heating was more significant. The microwave heating was rapid and provided higher regeneration than electric furnace heating.

Generally, a minimum sample size is also required for effective heating (Tai and Lee, 2007). Sometimes, microwave heating can produce intermediates depending on the adsorbate compounds. A study found that copper-loaded GAC increased the decomposition rate, but the cost became a concern (Liu et al., 2004b). The rate of decomposition is regulated by the contact time of the carrier gas and GAC particles. The use of a fluidized bed instead of a fixed bed can compensate for carbon loss and the formation of any toxic intermediates (Jou, 1998).

Microwaves were also found to be successful in regenerating multi-component odorous compound saturated GAC in a relatively brief time (Robers et al., 2005)**.** GAC requires a particular amount of energy to initiate the desorption process. The rate of desorption is slower at the beginning, but it gradually increases and then again decreases (when desorption is almost complete). Various studies reported the occurrence of arc formation during the heating period. The arcing of GAC begins during the preliminary state of heating and gradually increases as the temperature increases. The arcing spots illuminate at 5000-10,000^{0}C and can give an audible and visible sense of their existence (Jou and Tai, 1998; Tai and Jou, 1999). Identifying the optimum regeneration condition is always difficult, and a trade-off is essential among the abrasion resistance, activity and adsorption capacity (Bradshaw and Van-Wyk, 1998; Clark and Sutton, 1996).

Activated carbon can be in different physical and chemical forms and shapes which are widely applied in the adsorption-regeneration of VOCs, water, NO_x, and many other gasseous compounds. Spent powder-activated carbon (PAC) was successfully regenerated with microwave heating by desorbing ethanol and acetone (Fang and Lai, 1996), but carbon loss was a vital concern in this method. Palletized activated carbon can also be used to remove VOCs and can be regenerated by microwaves, but its regeneration time is much longer than that of GAC (Cha and Carlisle, 2001b, Coss and Cha, 2000).

Activated carbon fiber cloth (ACFC) is another form of activated carbon adsorbent. It can adsorb both polar and non-polar compounds and can be regenerated by microwave irradiation. Microwaves are capable of being selective in heating and therefore can desorb adsorbates, depending on their dielectric properties (Hashisho et al., 2005).

Microwave desorption allows for the sustainability of activated carbon over several cycles. In various studies, the sustainability has been demonstrated for 5 to 25 cycles of adsorption-desorption (Coss and Cha, 2000; Kong and Cha, 1995; Tai and Lee, 2007).

The literature shows that microwave heating enhances NO_x adsorption capacity of coke and char, which perform as better adsorbents than activated carbon. Microwave heating increases the char surface area from 82 to $800 m^2/g$ and converts 90% of the NO_x gas into CO_2 and nitrogen. Toxic and unwanted pollutants such as CO and HNO_3 are produced as secondary pollutants and require a secondary treatment plant (Cha and Kong, 1995; Kong and Cha, 1995, 1996a, 1996b, 1996c).

The microwave desorption of chlorinated compounds provides a high removal rate. Whatever the source of the contaminant is, HCl is always a bi-product of the system. The result is extremely undesirable, so a secondary treatment is needed to to remove the HCl (Jou et al., 2009; Lee et al., 2010). Table 2-1 summarises previous studies on microwave regeneration of activated carbon.

Table 2-1: Summary of research conducted in the field of activated carbon regeneration by microwave heating.

References	Medium	Adsorbent	Adsorbate	Key findings
(Fang and Lai, 1996)	Aqueous solution	Powder activated carbon(PAC)	Acetone, ethanol	PAC was regenerated and reused. High temperature initiated sparks. Carbon loss was a concern.
(Robers et al., 2005)	Air/gas	Activated carbon LUWA R10	Acetic acid and tri-methylamine	Microwave regeneration was feasible and needed 250sec to desorb most odorous compounds
(Tai and Jou, 1999)	Waste water	GAC	Phenol	Satisfactory regeneration was possible within 2minutes, but within this time, temperature became very high (1800^0C or more), and the bed turned red. Thermal decomposition of phenol produced H_2O and CO_2.
(Liu et al., 2004a)	Waste water	GAC	Pentachlorophenol (PCP)	Porosity of GAC increased due to repetitive microwave heating. Weight loss of GAC was also recorded. PCP decomposed into CO_2 and H_2O. GAC dose had to be of a minimum amount to get successful microwave regeneration.
(Liu et al., 2004b)	Waste water	GAC	PCP	Decomposition of PCP was much quicker in a copper-loaded GAC than in same amount of virgin GAC.
(Jou, 1998)	Hazardous/toxic waste from petroleum industry	GAC	Trichloroethylene(TCE)	Decomposition of TCE depended on contact time of GAC particles with carrier gas. Fluidized bed was more efficient in regenerating GAC since the bed did not get heated and therefore no loss occurred.
(Jou and Tai, 1998)	Waste water	GAC	BTEX	Microwave regeneration of GAC took a few minutes while bioregeneration took a few hours
(Ania et al., 2004; 2005)	Hazardous industrial waste in air/water	GAC	Phenol	Porous structure did not change due to microwave heating compared to electrical furnace heating, but in repetitive microwave heating, adsorption capacity was be reduced in both microwave and conventional

References	Medium	Adsorbent	Adsorbate	Key findings
				heating with electric furnace (more in conventional heating) due to loss of micropores.
(Bradshaw and Va-Wyk, 1998)	N_2+Steam	GAC	Water	Microwave heating did not change carbon characteristics but changed adsorption capacity and abrasion resistance factor. Temperature within the bed depended on differential drying. Adsorption capacity became higher than that of virgin carbon and was reusable.
(Coss and Cha, 2000)	N_2	GAC	MEK	Adsorption capacity of GAC was preserved, and results were much better than those from conventional steam regeneration. Some MEK was decomposed on GAC, and therefore 100% regeneration of MEK was not possible.
(Cha and Carlisle, 2001b)	N_2	GAC	MEK, 2-butanol, methyl-n-propyle ketone (MPK) and butyl acetate/ VOC	Microwave regeneration was found to be practical and economical in fixed beds at both the laboratory scale and pilot scale. Pelletized carbon showed better adsorption ability then GAC but its regeneration required a longer time.
(Kong and Cha, 1995)	Flue gas	Char, activated carbon and coke	NO_x	FMC calcinated char withstood microwaves better than activated carbon and preserved adsorption capacity over repetitive treatment cycles. NO_x actually was adsorbed as HNO_3 and was desorbed as gas at a low temperature (47°C). At a higher temperature, hotspot formation and CO evolution occurred.
(Kong and Cha, 1996a, 1996b)	Flue gas	Char	NO_x	Formation of CO was confirmed by GC analysis and occurred due to the reaction between HNO_3 and carbon bed at a temperature higher than $350^{\circ}C$. Char-21

References	Medium	Adsorbent	Adsorbate	Key findings
				showed the best performance in reducing NO_x while char-5 had the worst performance.
(Kong and Cha, 1996c)	Flue gas	Char	NO_x	Microwave regeneration reduced surface complex formation of NO_x. Complex formation was reduced while input power was increased. Activation energy of microwave desorption was reported to be much lower than that of conventional desorption process for NO_x.
(Ko et al., 2003)	Air	GAC	TCE, toluene	Microwave plasma completely destroyed the adsorbates. Excess O_2 was needed to prevent any chlorinated intermediate formation. This is a cost-effective compared to conventional plasma processes. Carrier gas was air, which is relatively inexpensive compared to N_2. No NO_x formation was observed.
(Hashosho et al., 2005)	Air	ACFC	MEK, Tetrachloroethylene, water vapor	Microwave was successful in removing polar and non-polar adsorbents from ACFC. Regeneration process was analyzed by dividing it into three stages: sensible energy consumption, latent heat consumption and temperature rise.
(Hashisho et al., 2007)	Air	ACFC	MEK	Desorption of MEK was linearly dependent on temperature and corresponding power.
(Hashisho et al., 2008)	Air	ACFC	MEK	A steady state condition was obtained in terms of concentration while temperature linearly increased.
(Zhang et al., 2009)	-	GAC	-	Microwave irradiation successfully preserved adsorption capacity.

2.3.3 Regeneration of zeolite by microwave heating

Zeolite has a high potential to remove low concentration VOCs. Hydrophobic zeolite in particular is capable of removing non-polar VOCs. This capability is important in environmental engineering, but the large energy needed for the regeneration of the saturated zeolite makes its use uneconomical. In 2009, Charbenski and Molga (2009) summarized some of the studies published so far regarding the regeneration of zeolite.

Roussy et al. used microwaves to dehydrate and regenerate zeolite 13X (Roussy and Chenot, 1981; Roussy et al., 1984). The microwave desorption of water in zeolite occurs in two stages. In the first stage, the unbound water molecules leave the adsorbent, and in the second stage, diffusion carries out the rest of the water molecules. The diffusion of water requires a longer heating time. Water molecules can be found both on the surface and circulating inside the material. When the circulating molecules come to the surface, they no longer contribute to the heating. The whole regeneration process works over a wide range of temperatures although desorption occurs immediately during heating. Therefore, the desorption rate is at its maximum at the beginning of the regeneration process. The mass reduction of adsorbent is much higher at the first stage compared to the second stage. At low power, regeneration is controlled by the power rather than by the temperature. In contrast, at a high power exposure, a chemical reaction occurs. This result limits the regeneration of zeolite 13X. Hence, at a certain temperature and pressure condition, desorption depends on the power level. Typically, for 50g of zeolite 13X, at a power lower than 500W, the rate of desorption and decomposition increases linearly (Benchanna, 1989).

Zeolite A can be dehydrated by microwaves with and without preheating. The degree of dehydration depends on the moisture content. A minimum level of moisture has to be present in the material. The heating rate of various zeolite A samples varies in the order of 4A>3A>5A. Thus, with microwaves, zeolite with a 4-ring oxygen structure is more compatible than the 8-ring structure (Ohgushi et al, 2001). Even a mixture of zeolites can absorb microwaves and release adsorbed water. It was found that a meticulous combination of Na-X and Ca-X exhibited more than 80% dehydration under microwave heating, compared to only 60-70% in a conventional heating process. Under microwave heating, the zeolite combination can be used over several adsorption-desorption cycles. The adsorptive performance of such a mixture is much better than that of commercial desiccants in terms of the durability and time requirement (Ohgushi and Nagae, 2003, 2005). Microwaves can be selective in heating a mixture of various adsorbates captured by zeolite. Polar compounds absorb microwaves and can be desorbed with ease, while because of their weak interacting ability, non-polar compounds need intense heating and higher temperatures to be regenerated. A mixture of ethanol/toluene was separated efficiently, while a mixture of ethanol/acetone was desorbed but not separated (Reuβ et al., 2002). Transparent zeolite does not absorb microwaves, while the coloured (black) or high silica zeolites do. Therefore, a higher temperature and longer regeneration time are needed to regenerate coloured and high silica containing zeolites. Microwaves even change the selectivity of zeolite. Transparent DAY was found to be more susceptible to microwaves than silicate (high silica zeolite) or envisorb B+(EB+) (silica gel with incorporated activated carbon) (Reuβ et al., 2002; Turner et al, 2000). Mordinate has unique control over its hydrophobic and hydrophilic nature (Okzaki, 1978; Olson, 1980) and therefore is being used as a good adsorbent for polar and non-polar adsorbents like p-xylene, 1-butanol (Takeuchi et al., 1995) and SO_2 (Tantet et al., 1995). It was stressed that the presence of water enhances the heating of mordinite Na-MOR (Kim et al., 2005). The affinity of hydrophilic Na-MOR, to water is so strong that water can be desorbed only at a temperature (277°C) close to the chemisorbed water desorption temperature (Kim et al., 2005). However, due to the dielectric properties of Na-MOR, 277°C cannot be achieved, and, therefore, the complete dehydration of Na-MOR is not possible.

In a microwave heating process, the temperature distribution inside the adsorbent bed is not uniform. Heat transfer occurs due to the microwaves and the convection of carrier gas (if present). As the heating is volumetric, the highest temperature occurs at the center of the bed. A variation in the temperature profile occurs only in the radial direction (Meier, 2009). The temperature rise in the adsorbent bed is faster than that in any conventional heating process (Kim et al., 2007). The key controlling parameter of microwave desorption of VOCs and water is dielectric permittivity. The regeneration performance of zeolite varies in many ways over the period of desorption of various VOCs and water due to dielectric permittivity. The dielectric permittivity of the gas phase is extremely low and hence cannot convert the electromagnetic energy into heat. Therefore, the dielectric permittivity of zeolite plays an important role in the VOC desorption process and is more important than the porosity and molecular structure of the solid (Polaert et al, 2007, 2010; Roussy et al., 1984).

Modified ETS-10 and non-modified ETS-10 have been tested for their applicability in separating various hydrocarbons. ETS-10, is a large-pored, mixed co-ordination material with a three-dimensional network of interconnecting channels (Kuznicki, 1991). Extensive studies including experimental and model prediction have reported the potential of ETS-10 for ion-exchange (Pavel et al., 2002) and hydrocarbon gas separation (Anson et al., 2008). The regeneration of ETS-10 can be accomplished by both microwaves and steam desorption. It was found that microwaves and steam regeneration exhibited a similar gas desorption ability over several cycles, but the microwaves required a lower temperature and shorter time (Shi et al., 2010).

Many studies have reported that all kinds of zeolites can be regenerated and reused over several cycles. Consequent heating reduces the micro-porosity of zeolite, and, therefore, the adsorption capacity degrades over time. Fortunately, the degradation is not significant (Han et al., 2010). Table 2-2 presents a summary of the previous work done to regenerate zeolite using microwaves.

Table 2-2: Summary of the researches conducted in the field of zeolite regeneration using microwave heating.

Reference	Medium	Adsorbent	Adsorbate	Key findings
(Roussy and Chenot, 1981)	Contaminated Gas/liquid	13X	Water	Dehydration occurred at two stages: First stage removed unbound water, and second stage removed water by diffusion.
(Roussy et al., 1984; Thiebaut et al., 1988)	Contaminated Gas/liquid	13X	Water	Whenever circulating water molecules came to the surface of zeolite, they did not contribute to heating anymore.
(Benchanaa, 1989)	Solar energy cells	13X	Water	At controlled temperature and pressure, desorption rate depended on the applied power. At higher power, chemical reaction occurred. Desorption rate was linear up to 500W.
(Ohgushi et al, 2001; Ohgushi and Nagae, 2003, 2005)	Moist air/gas	A	Water	Heating rate varied in the order of 4A>3A>5A. An appropriate mixture of zeolites provided 10 times better performance than commercial desiccants. The life-time was also superior to that of commercial $CaCl_2$.
(Reuβ et al., 2002)	Air/gas	DAY and EB+	Ethanol, toluene, acetone, Water	Transparent zeolite was regenerated at a lower temperature than colored zeolites. A mixture of polar and non-polar compound was separated by microwave desorption.
(Turner et al., 2000)	Air/gas	DAY and silicate	Methanol and cyclohexane	Interaction of microwave with high silica zeolite depended on density and hydroxyl content of each adsorbent. Microwaves changed selectivity of zeolite.
(Meier, 2009)	Air/gas	Silicalite	Methanol	Temperature distribution in the radial direction varied. The maximum temperature was achieved at the center. Chemical reaction occurred during heating.

Reference	Medium	Adsorbent	Adsorbate	Key findings
(Kim et al., 2005)	Exhaust gas/air	Mordinite	Water and ethylene	Hydrophilic NaMOR had high affinity to water and needed higher temperature for regeneration compared to HMOR.
(Kim et al., 2007)	Waste gas, organic solvent and paint	FAU, MS-13X	Toluene and MEK	Microwaves irradiated into one non-polar compound at a time. Temperature rise was faster than that of conventional heating. Amount of desorption depended on the dielectric properties of the adsorbents.
(Polaert et al., 2007)	Wet natural gas	Na-X	Water	A unique microwave set-up measured the energy required for desorption process. It facilitated a cost-effective microwave dehydration technique. A thermal model was developed which simulated the maximum bed temperature.
(Polaert et al., 2010)	Polluted emission	Silica, activated alumina, NaX, NaY	Water, toluene, methylecyclohexane, n-heptane	Microwave desorption of water was different in different adsorbents due to adsorbent structure and dielectric permittivity. In some adsorbents, effective desorption occurred at a reasonably low temperature. Success of microwave desorption depended on the choice of adsorbent-adsorbate couple and also reactor size and shape.
(Han et al., 2010)	Dye loaded wastewater from textile	Natural zeolite	Malachite green	Microwave desorption depended on irradiation time and applied power. Smaller particles provided higher degree of regeneration. Adsorption capacity slightly degraded over the cycle.
(Shi et al., 2010)	Natural gas	ETS-10	Ethane/ethylene	Microwave regeneration was quicker than steam desorption. ETS-10 was regenerated over several cycles without any degradation.
(Di and Chang, 1996)	Gas stream	DAY zeolite	Isopropanol (VOC)	Heating energy was independent of mass of the gas passing through the bed. Gas expansion occurred inside the reactor during heating.

Reference	Medium	Adsorbent	Adsorbate	Key findings
(Price and Schmidt, 1998)	Gas stream from printing and coating	High silica zeolite	MEK	Microwave regeneration was cost-effective compared to other conventional methods.

2.3.4 Regeneration of polymeric adsorbents by microwave heating

Han et al. (2006) compared the regeneration of hypercrosslinked polymeric adsorbent (HPA) desorbing nitrophenol using microwaves and a thermostatic water bath. Hypercrosslinked polymeric adsorbent NDA-150 was the adsorbent used, and the two saturating adsorbates were o-nitrophenol and p-nitrophenol. With intermittent microwave heating, the regeneration efficiency of both o-nitrophenol and p-nitrophenol was higher in microwave-assisted regeneration compared to that in conventional thermal regeneration. The difference was more significant for o-nitrophenol. In thermal regeneration, a chelating ring of benzene forms in the nitrophenol, preventing the dissolution of nitrophenol in water and therefore delaying desorption. In contrast, microwaves provide the induced polarization of o-nitrophenol within the microwave field. This process destroys the chelated ring. This inductive effect cannot be seen in p-nitrophenol, and so the difference is not distinctive. FTIR spectra showed that the structure of the adsorbent remained unchanged before and after irradiation. The adsorption capacity was also the same, even after six regeneration cycles. The rate of the temperature rise is also a factor for regeneration. The rate of temperature rise decreases with the increase of the initial temperature. If an adsorbent is heated for more than 30sec at a time, hotspots can occur and degrade the adsorption capacity. The bed temperature needs to be 67°C, and the initial temperature has to be below 53°C to avoid hotspot formation.

Opperman and Brown (1999) proposed and described a new reactor system for desorbing VOCs and regenerating polymeric adsorbents using microwaves. The reactor was designed so that it could be used both as a fixed bed and a fluidized bed reactor. Low temperature microwave regeneration was possible with this reactor, and desorbed VOCs were collected as a liquid.

2.4 Future developments and existing challenges

Microwave technology has been widely accepted as a non-conventional energy source for various applications (Agazzi and Pirola, 2000). Microwaves offer the unique feature of reduced heating time, lower energy consumption, low cost, volumetric heating, selective and enhanced desorption, and separation (Yuen and Hameed, 2009). Most microwave applications are in food industries for food processing, sterilization, pasteurization, drying, etc. Microwaves have also been useful for soil remediation, pyrolysis of biomass and organic waste, and heterogeneous catalytic reaction (Menendez et al., 2010).

Because of microwaves' adsorbent regeneration capability and also according to Bathen's work, microwaves are applied in three main industrial sectors in pilot scale: gold-ore washing in Canada's Ontario Hydro Technologies by using a fluidized bed of activated carbon, air drying by Arrow Pneumatics, and the VOC recovery unit of Plinke GmbH and Co (Cherbanski and Mogla, 2009). In 2000, the U.S air force built a pilot plant at the McClellan air base as a part of the air force's environmental clean-up. The plant was operated for three months and showed that microwaves were beneficial in destroying chlorinated and nonchlorinated chemicals adsorbed from the soil vapor and in keeping the adsorbent's capacity unchanged (Cha and Carlisle, 2001a). Microwave propagation by using various liquids has been analyzed by using numerical models (Zhu et al., 2007). Microwave heating is rapid and effective compared to other heating techniques (Hashisho et al., 2008). Conventional pressure swing regeneration is not compatible with fluidized beds and with low-pressure application. Steam desorption requires steam-generation facilities and an additional drying unit. In contrast, microwave systems are simpler (Di and Chang, 1996).

A distinct drawback of microwave technology is its short penetration depth. Therefore, fluidized beds are much more practical for industrial use. For a fixed bed application, annular bed geometry may be a solution for overcoming the penetration problem (Bonjour and Clausse, 2006). Non-uniform heating is another disadvantage of microwave heating. The various adsorption abilities of the adsorbent, and reflection and electromagnetic wave scattering are responsible for the non-uniformity, which can result in thermal runway (Ohgushi et al., 2001). The lack of knowledge about the dielectric properties of the materials is another problem. The initial investment cost is also enormous (Yuen and Hameed, 2009).

Mathematical modeling can solve some of the existing problems. Simplified mathematical models can make the hotspot formation and non-uniformity of heating more predictable (Hill and Jennings, 1993; Moitsheki and Makinde, 2007). A combination of microwave heating and hot air heating was found to be more productive than the use of only microwaves or hot air heating. It was also suggested that a combination can be less energy-intensive as well (Kubota et al., 2011).

2.5 Conclusion

Recent studies have looked into the applicability of microwave heating in adsorption-regeneration operations. It has been found that the rapid heating capability of microwaves accelerates the regeneration process and also enhances the adsorbent performance. Microwave technology has overcome the challenges faced by the conventional temperature swing regeneration and pressure swing regeneration techniques. Microwave technology offers reduced energy consumption along with shorter regeneration time. Microwaves not only regenerate adsorbents but also reactivate them without causing significant damage to their adsorption properties. However, more research needs to be conducted in order to understand the nature and distribution of microwaves, heat transfer during microwave heating and material- microwave interaction.

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CHAPTER THREE: REGENERATION OF Na-ETS-10 USING MICROWAVE AND CONDUCTIVE HEATING[*]

3.1 Introduction

High purity ethylene (C_2H_4) is required for the production of polymers, rubber, fibre and various organic chemicals (Kniel et al., 1980). Generally, C_2H_4 is prepared through steam cracking or thermal decomposition of ethane (C_2H_6). The gas product of cracking contains un-cracked C_2H_6. Separation of un-cracked C_2H_6 from C_2H_4 is crucial in the polymer manufacturing production chain (Eldrige et al., 1993). Cryogenic distillation is the most reliable and commonly used technique for C_2H_4/C_2H_6 separation but it is extremely energy intensive (Shi et al., 2011).

Currently, natural gas provides one-fourth of the world's energy needs for homes, vehicles and industries (Cavenati et al., 2004). Typically natural gas contains 80-95% methane; the rest is made of C_2^+ hydrocarbons, nitrogen, and carbon-dioxide impurities. High concentration of carbon dioxide in methane can lead to pipeline and equipment corrosion and therefore, reducing it to trace levels is necessary to achieve the pipeline quality methane (no more than 2% CO_2) (Cavenati et al., 2006). Typically the separation of CO_2 is accomplished by chemical absorption

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with amines which is energy intensive and requires high reagent costs (Rao et al., 2002).

Adsorptive separation is an effective alternative to cryogenic distillation or chemical absorption as it requires less energy and capital cost (Eldrige et al., 1993). Preliminary studies and model predictions suggest that Engelhard Titanosilicate-10 (Na-ETS-10) has great potential as an adsorbent in the separation of C_2H_4/C_2H_6 and CO_2/CH_4 mixtures (Anson et al., 2008, 2009). It has been reported that the adsorption separation of the binary mixture of C_2H_4/C_2H_6 using Na-ETS-10 can achieve a bed selectivity of 5 at ambient pressure and up to 11 at 2580 kPa (Shi et al., 2010, 2011).

ETS-10 is a large pored, mixed octahedral/tetrahedral titanium silicate molecular sieve possessing an inherent three dimensional network of interconnecting channels (Kuznicki, 1991; Anderson et al., 1994). The average pore size of ETS-10 has a kinetic diameter of ~8 Å. Hence C_2H_4, C_2H_6, CO_2 and CH_4 can enter the crystalline lattice as the pore size is larger than the molecular diameter of all four species stated (Shi et al., 2010). Therefore, separation selectivity of C_2H_4 over C_2H_6 or CO_2 over CH_4 would be based on the equilibrium competitive adsorption. Na-ETS-10 could preferentially adsorb ethylene in the binary mixture of C_2H_4 and C_2H_6 (Shi et al., 2010) and preferentially adsorb CO_2 in the binary mixture of CH_4 and CO_2 (Anson et al., 2009).

Despite Na-ETS-10's great potential in adsorptive separation of C_2H_4, C_2H_6, CO_2 and CH_4, its regeneration cost presents a challenge because of the high heats of adsorption of the gases to be separated (Shi et al., 2010; Al-Baghli et al., 2005). In this context, microwave heating can be a promising alternative to the conventional pressure swing and temperature swing regeneration methods that are currently used in separation industry (Roussy et al., 1981, 1984). Although microwave heating was initially used for rapid heating of food, its unique selectivity and fast heating rate proved to be useful in other applications such as industrial drying (Tierney et al., 2005). In a conventional thermal regeneration process, the thermal energy is transferred from the surface to the bulk of the material. By contrast in microwave heating the energy is transferred from the inside to the outside of the material as microwaves propagate through molecular interactions between the material and the electromagnetic field (Das et al., 2009).

Microwave heating has been reported for the regeneration of zeolite 13X (Roussy et al., 1981), DAY (Reuβ et al., 2002; Turner et al., 2000), zeolite 3A, 4A, 5A, (Ohgushi et al., 2001), and Na-X and Ca-X (Ohgushi et al., 2003, 2005). A preliminary study of microwave regeneration of Na-ETS-10 was recently completed using a kitchen microwave and showed that microwave heating is capable of regenerating Na-ETS-10 over several adsorption/desorption cycles (Shi et al., 2010).

Conventional thermal regeneration, known as temperature swing regeneration, is another widely used method for adsorbent regeneration in separation and purification industries. During temperature swing regeneration a hot gas stream or steam is used for bed heating and a cold gas stream is used for bed cooling (Clausse et al., 2004). There have been several reports of using temperature swing to regenerate zeolite 13X (Merel et al., 2006), 4A and 5A (Siriwardane et al., 2005) as well as an extensive review on temperature swing regeneration which can be found elsewhere (Ruthven et, 1984; Suzuki, 1990; Cherbanski et al., 2011).

The objective of this study is to investigate the performance of both conductive heating and microwave heating for the regeneration of Na-ETS-10. Two gas mixtures, ethylene/ethane (C_2H_4/C_2H_6) and carbon dioxide/methane (CO_2/CH_4), commonly used in industry, were separated on Na-ETS-10 in packed bed columns which were later regenerated by microwave heating and conductive heating. The Na-ETS-10 swing capacity, regeneration efficiency and energy consumption were determined and compared between microwave heating and conductive heating. The recovery and purity of the desorbed gases were also determined.

3.2 Experimental

3.2.1 Sample preparation

Na-ETS-10 was synthesized using the hydrothermal technique as described elsewhere (Kuznicki, 1991). A typical sample was prepared by thorough mixing of 50 g of sodium silicate (28.8% SiO_2, 9.14% Na_2O), 3.2 g of sodium hydroxide (97+% NaOH), 3.8 g of anhydrous KF, 4 g of HCl (1M), and 16.3 g of $TiCl_3$ solution. The mixture was stirred in a blender (Waring) for 1h. Then it was transferred to a 125 mL sealed autoclave (PARR instruments) and heated at 215 ºC for 64 h. The resultant material was carefully washed with de-ionized water and then dried in an oven at 100 ºC. The material was reduced to fine powder (< 150 μm) and pelletized by mixing 6 g of the material (equilibrated at 100 ºC) with 2 g of Ludox HS-40 colloidal silica (Aldrich). Morter and pastle were used to homogenize the mixture. Then the mixture was compressed using a pellet press at 10,000 psi for 3 min. The resulting cake was crushed and sieved to acquire 16-20 mesh particles. The prepared pellets were used in the adsorption-desorption experiments.

3.2.2 Adsorption-desorption experiments

Adsorption-desorption experiments were performed by saturating 10 g of pelletized Na-ETS-10 (16-20 mesh) in a double-ended cylindrical quartz column. The adsorbent bed height was 3.75cm and its diameter was 2.9 cm. The sample was activated at 200 ºC in a laboratory oven for 16 h under 120 mL/min helium gas flow. During adsorption, feed gas flow was maintained at 22 °C and 101.325 kPa. Feed gas consisted of either 59% C_2H_4/ 41% C_2H_6 mixture or 10% CO_2/ 90% CH_4. The feed gas mixtures were introduced to the fixed bed adsorbent column at a flow rate of 180 mL/min (C_2H_4/C_2H_6) and 300 mL/min (CO_2/CH_4). The feed gases (Praxair) were surrogate mixtures for the process gas streams of ethylene cracking and natural gas purification units. Outlet gas was sampled using 5 mL syringe at 5 minute intervals. Outlet gas composition was analysed using a 5890A Agilent Gas Chromatograph (GC) equipped with thermal conductivity detector (TCD) and a Supelco matrix Haysep Q column (well suited for hydrocarbon analysis). 0.5 mL samples were pulse injected and analysed with the GC-TCD. A continuous flow of feed gas was maintained until the outlet composition became the same as the inlet composition which occurred after approximately 16 minutes for C_2H_4/ C_2H_6 mixture and 90 minutes for CO_2/CH_4 mixture.

The microwave generation and propagation system consisted of a 2 kW switch-mode power supply (SM745G.1, Alter), a 2 kW microwave source (MH2.0W-S, National Electronics) equipped with a 2.45 GHz magnetron, an isolator (National Electronics), a three-stub tuner (National Electronics) and a waveguide applicator connected to a sliding short (IBF Electronic GmbH & Co. KG). The tuner and the sliding short were manually adjusted at the beginning of the experiment to improve the energy transfer to the adsorbent. The isolator was used to protect the microwave head by conducting reflected power into a water load. The power was monitored with a dual directional coupler with 60 db attenuation (Mega Industries), two power sensors (8481A, Agilent) and a dual channel microwave power meter (E4419B, Agilent). The temperature of the material was monitored using a fiber optic temperature sensor and a signal conditioner (Reflex signal conditioner, Neoptix). The temperature sensor, power meter and power supply were connected to a data acquisition and control (DAC) system (Compact DAC, National Instruments) equipped with a Labview program (National Instruments) to record the data and control power application. Labview program was used to monitor and control heating during desorption. After saturation, the microwave generation system was turned on and the heating was initiated using Labview program. The temperature sensor was not able to withstand more than 200°C. Therefore, the adsorbent bed temperature was maintained at 190°C during desorption. The desorbed gas flowed to a downstream flask and was collected by water displacement. The volume of the displaced water was equal to the volume of the gas that was collected at the outlet. The desorption experiment was continued until no gas evolution was observed. After desorption, the adsorbent was cooled to room temperature by purging with nitrogen at 120 mL/min. Once the bed reached ambient temperature, further adsorption/microwave desorption cycles were initiated.

In conductive heating technique, a double ended cylindrical steel column with an inner diameter of 1 cm and bed height of 7 cm was used as a reactor. Following saturation of the adsorbent bed, the column was wrapped with a heating tape (Omegalux^{TM}) followed by an additional insulation tape. The heating tape was connected to a 120 V AC power source through a solid state relay interfaced to a DAC system. A Labview program was used to initiate and control the heating. The bed temperature was maintained at 190 ºC. A shielded type K thermocouple (Omega) was used to measure the bed temperature. Data were recorded using a DAC and a Labview program as described in the microwave desorption experiments. Desorbed gas collection system and post desorption adsorbent cooling system were analogous to those used in the microwave desorption experiments. Heating was continued until no gas evolution was observed. A block diagram for adsorption and regeneration by microwave heating and conductive heating process is illustrated in Figure 3-1.

Swing capacity is generally defined as the adsorption capacity or working capacity of an adsorbent between two extreme states of the swing force (Anson et al., 2009). In this work, swing capacity of Na-ETS-10 is defined as the amount of gas desorbed during heating from 22 °C to 190 °C. The maximum swing capacity was achieved by water desorption (Shi et al., 2011). Gas recovery was calculated based on the Equation 3-1.

$$\text{Gas recovery (\%)} = \frac{V_{M/C}}{V_W} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3-1)}$$

Where, $V_{M/C}$ is volume of gas desorbed by microwave (M) or conductive (C) heating and V_W is the volume of gas desorbed by water desorption which is equal to the adsorption capacity of the adsorbent.

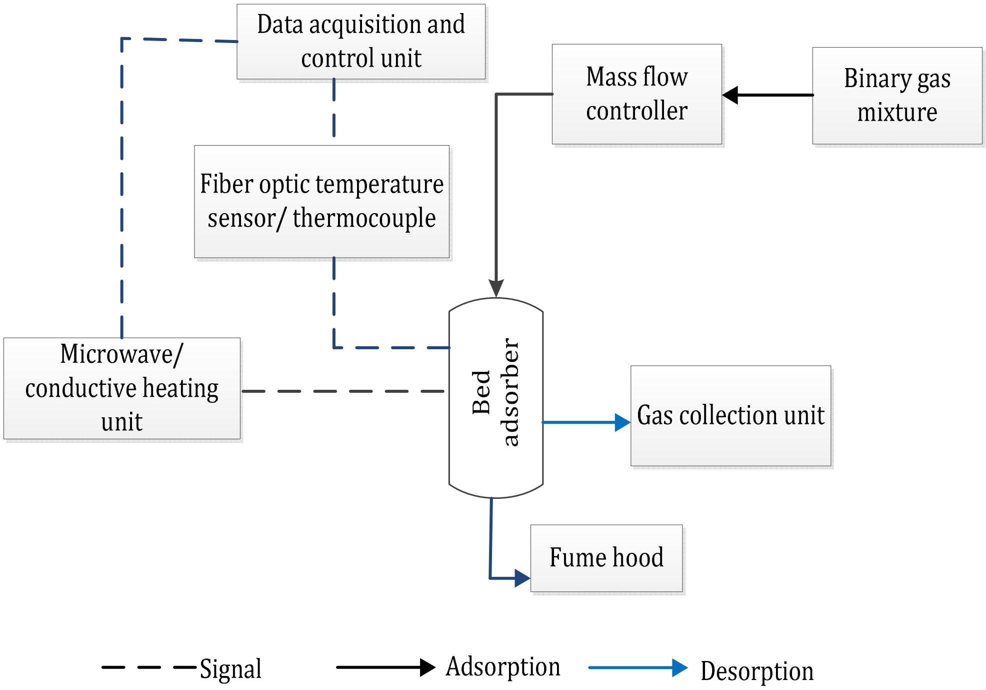

Figure 3-1: Block diagram showing adsorption and regeneration of Na-ETS-10 using microwave and conductive heating.

3.3 Results and discussion

3.3.1 Ethylene/Ethane (C_2H_4/C_2H_6) desorption from Na-ETS-10

Desorption achieved by water desorption is considered as complete (100%) through the mass action displacement mechanism (Shi et al., 2010). Therefore, the saturated Na-ETS-10 was flushed with water and the desorbed gas was collected in a gas collection container. Desorption started immediately after water injection and lasted for 7-8 minutes. A total of 320 mL gas was collected from approximately 10 g of Na-ETS-10 through water desorption; therefore the maximum adsorption capacity is 30 mL/g Na-ETS-10 or 1.24 mmol/g Na-ETS-10. Based on GC-TCD analysis, the desorbed gas consisted of 88% C_2H_4 and 12% C_2H_6 which is equal to the reported data elsewhere (Shi et al., 2010).

A comparison of the temperature profiles for microwave heating and conductive heating is provided in Figure 3-2(a). The temperature profile of microwave heating shows a steep heating rate of 64 ºC/min compared to only 13 ºC/min for conductive heating. The difference in heating duration is because heating was stopped when gas evolution stopped.

The two heating techniques were also compared by power consumption as function of temperature in Figure 3-2(b). During microwave heating, power consumption fluctuates between 0-25 W before it stabilizes around 12 W, while temperature becomes stable around 190 ºC. During conductive heating, power consumption fluctuates between 0 and 112 W and finally stabilizes around 50 W, which is four times higher than that of microwave heating.

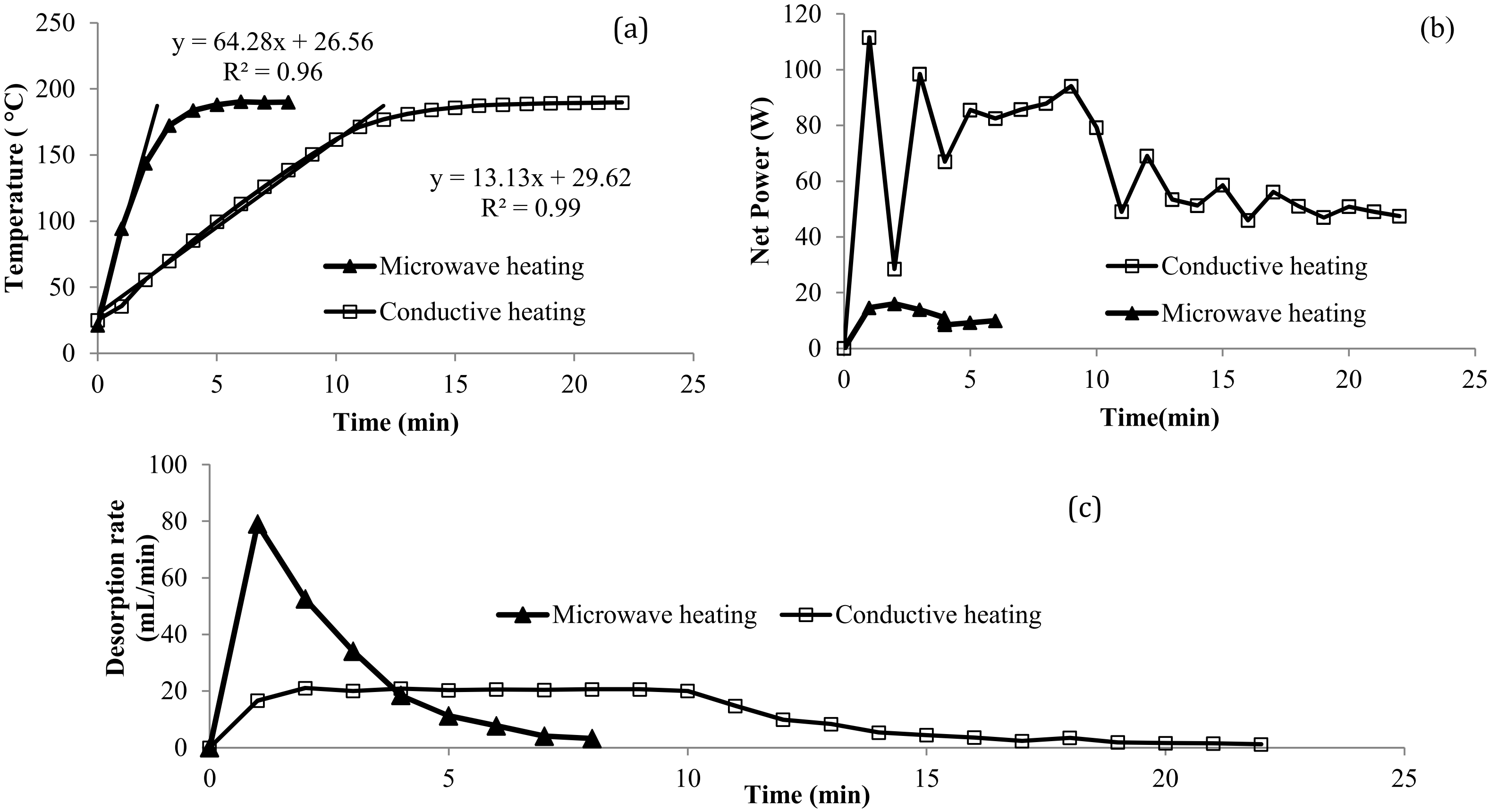

Figure 3-2: Desorption of C_2H_4/C_2H_6 saturated Na-ETS-10 with microwave heating and conductive heating: a) temperature; b) net power consumption; and c) desorption rate.

The comparison of desorption rates of adsorbed C_2H_4/C_2H_6 during microwave heating and conductive heating is shown in Figure 3-2(c). Although net power requirement is higher for conductive heating, the desorption rate is higher for microwave heating. During microwave regeneration, desorption starts immediately and reaches a maximum rate of 79 ml/min (3.25 mmol/min) within one minute. The rate decreases to 3 mL/min as the temperature stabilizes at 190 ºC. In conductive heating on the other hand, desorption starts within the first minute and reaches a maximum rate of 20 mL/min (0.82 mmol/min) during the second minute of heating and maintains it up to the tenth minute. Then the rate decreases as the power decreases until the temperature stabilizes at 190 ºC at which point the rate remains at 1 mL/min. Figure 3-2 illustrates that microwave heating performs better and quicker than conductive heating in terms of heating rate, net energy consumption and gas desorption rate for adsorptive separation of C_2H_4/C_2H_6.

The microwave desorption took 8 minutes and 28 mL gas was recovered from 1 gram of Na-ETS-10 (1.16 mmol/g). Based on GC-TCD analysis, the desorbed gas contained 87% C_2H_4 and 13% C_2H_6, which is consistent with adsorbed phase composition data reported elsewhere (Shi et al., 2010). When conductive heating was applied to regenerate the Na-ETS-10 saturated with the C_2H_4/C_2H_6 mixture, it took 22 minutes to evolve 21mL/g Na-ETS-10 of gas (0.87 mmol/g).

A total of five adsorption/desorption cycles for the C_2H_4/C_2H_6 mixture were completed on Na-ETS-10 for both microwave and conductive heating. No mass loss of the adsorbent was observed after each adsorption-desorption cycles, and the refreshed adsorbent bed has the same weight as the starting adsorbent. A comparison of microwave heating and conductive heating techniques over these five cycles is presented in Figure 3-3 and Table 3-1. The swing capacity of Na-ETS-10 during microwave heating and conductive heating was stable; 1.16 mmol/g Na-ETS-10 and 0.87 mmol/g Na-ETS-10 respectively over five cycles of adsorption/desorption (Figure 3-3). The results indicate that swing capacity of microwave heating is 1.33 times larger than that of conductive heating. The swing capacity also indicates that the adsorption capacity of Na-ETS-10 is not influenced by successive microwave/conductive heating cycles.

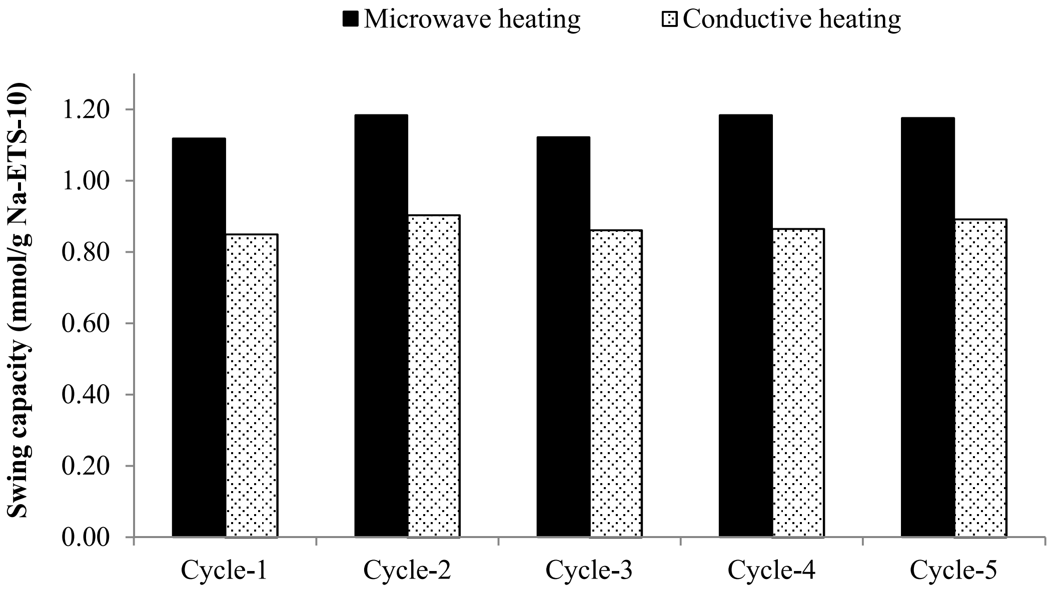

Figure 3-3: Swing capacity of Na-ETS-10 over 5 cycles remains unchanged under microwave heating and conductive heating of C_2H_4/C_2H_6 at 190°C.

Table 3-1 shows that on average 94% of the adsorbed gas was recovered with microwave desorption while only 71% was recovered with conductive heating. However, with both techniques, the adsorption capacity remained steady over repeated adsorption-regeneration cycles. In microwave desorption, an average net energy of 0.73 kJ/g was consumed to achieve such desorption, however, approximately 7.9 kJ/g was consumed in the case of conductive heating.

Table 3-1: Comparison of microwave and conductive heating techniques for desorbing C_2H_4/C_2H_6 from Na-ETS-10.

	Desorption temperature (ºC)	**Heating time (min)**	**Cooling time (min)**	**Gas recovered (%)**					**Applied energy(kJ/g Na-ETS-10)**				
				Cycles					Cycles				
				1	2	3	4	5	1	2	3	4	5
Microwave heating	190	8	20	90	96	91	96	95	0.7	0.7	0.7	0.7	0.7
Conductive heating	190	22	60	69	74	70	71	73	7.6	7.7	8.1	8.1	8.2

On average, 25 J microwave energy and 370 J conductive energy was needed to desorb 1mL of the adsorbed gas (mixture of ethylene/ethane) in each of the five cycles performed (Figure 3-4). While both systems display steady energy consumption during the five cycles of adsorption and desorption, the conductive heating requires 14.8 times more energy than microwave heating to desorb the same volume of gas. In the conductive heating experiments, the reactor was heated first and then the energy was transferred to the adsorbent through conductive heating. However, in microwave heating, the energy is transferred from the inside to the outside of the material as microwaves propagate through molecular interactions between the material and the electromagnetic field (Das et al., 2009). Hence, more energy loss occurred during the conductive heating, which explains why microwave heating is faster and consumes less energy.

Desorbed gas composition of each cycle was analyzed by GC-TCD which was presented in Table 3-2. It shows that 87~87.5% C_2H_4 and 12.5~13% C_2H_6 could be obtained during the microwave desorption and 85~85.5% C_2H_4 and 14.5~15% C_2H_6 could be obtained during the conductive heating. Both methods gave the similar desorbed gas composition as adsorbed phase gas.

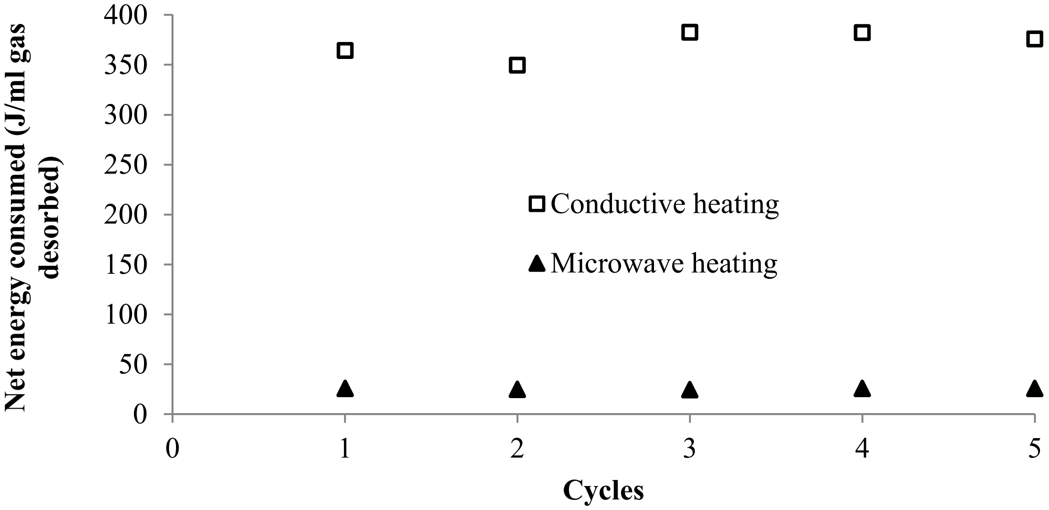

Figure 3-4: Variation in net energy consumption over 5 cycles was insignificant during microwave heating and conductive heating of C_2H_4/C_2H_6 on Na-ETS-10 at 190ºC.

Table 3-2: Summary of the desorbed gas purity measured for microwave heating and conductive heating for C_2H_4/C_2H_6.

		Purity of the gas recovered (%)				
		Cycles				
		1	2	3	4	5
Microwave heating	C_2H_4	87.1	87	87.5	87	87.4
	C_2H_6	12.9	13	12.5	13	12.6
Conductive heating	C_2H_4	85.5	85.1	85	85	85.5
	C_2H_6	14.5	14.9	15	15	14.5

3.3.2 Carbon dioxide/methane (CO_2/CH_4) desorption from Na-ETS-10

Complete (100%) desorption of CO_2/CH_4 from Na-ETS-10 was obtained by water desorption, generating a total of 407 mL of gas from 10 g of Na-ETS-10, indicating a maximum desorption capacity of 39 mL/g. Based on the GC-TCD analysis, the desorbed gas contained 89% CO_2 and 11% CH_4.

Comparisons of temperature profile, power consumption profile and desorption rate of adsorbed CO_2/CH_4 for both methods are shown in Figure 3-5. For microwave heating, power consumption fluctuated between 0-20 W and stabilized around 12 W while temperature stabilized at 190 ºC. For conductive heating power consumption fluctuated between 0-101 W and stabilized around 44 W. Desorption rate for conductive heating is slower than for microwave heating and also net power requirement is higher. Desorption rate during microwave heating reached a maximum of 100 mL/min in the first minute then decreased reaching close to zero at the eighth minute. During conductive heating, the desorption rate reached a maximum of 26 mL/min in the seventh minute, remained constant up to the tenth minute and then decreased and stabilized at 1 mL/min at twenty second minute of heating time. Figure 3-5 illustrates that microwave heating is more efficient and faster than conductive heating in terms of heating rate, net energy consumption and gas desorption rate for adsorptive separation of CO_2/CH_4.

Microwave heating was successful in desorbing CO_2/CH_4 mixture from Na-ETS-10. 27 mL of desorbed gas per gram of Na-ETS-10 was recovered after 8 minutes of microwave heating. The desorbed gas consisted of 82% CO_2 and 18% CH_4 as determined by GC-TCD analysis. After heating, the bed was cooled under N_2 flow at 120 mL/min. Regeneration of CO_2/CH_4 saturated Na-ETS-10 with conductive heating took 22 minutes to evolve 22 mL/g of gas.

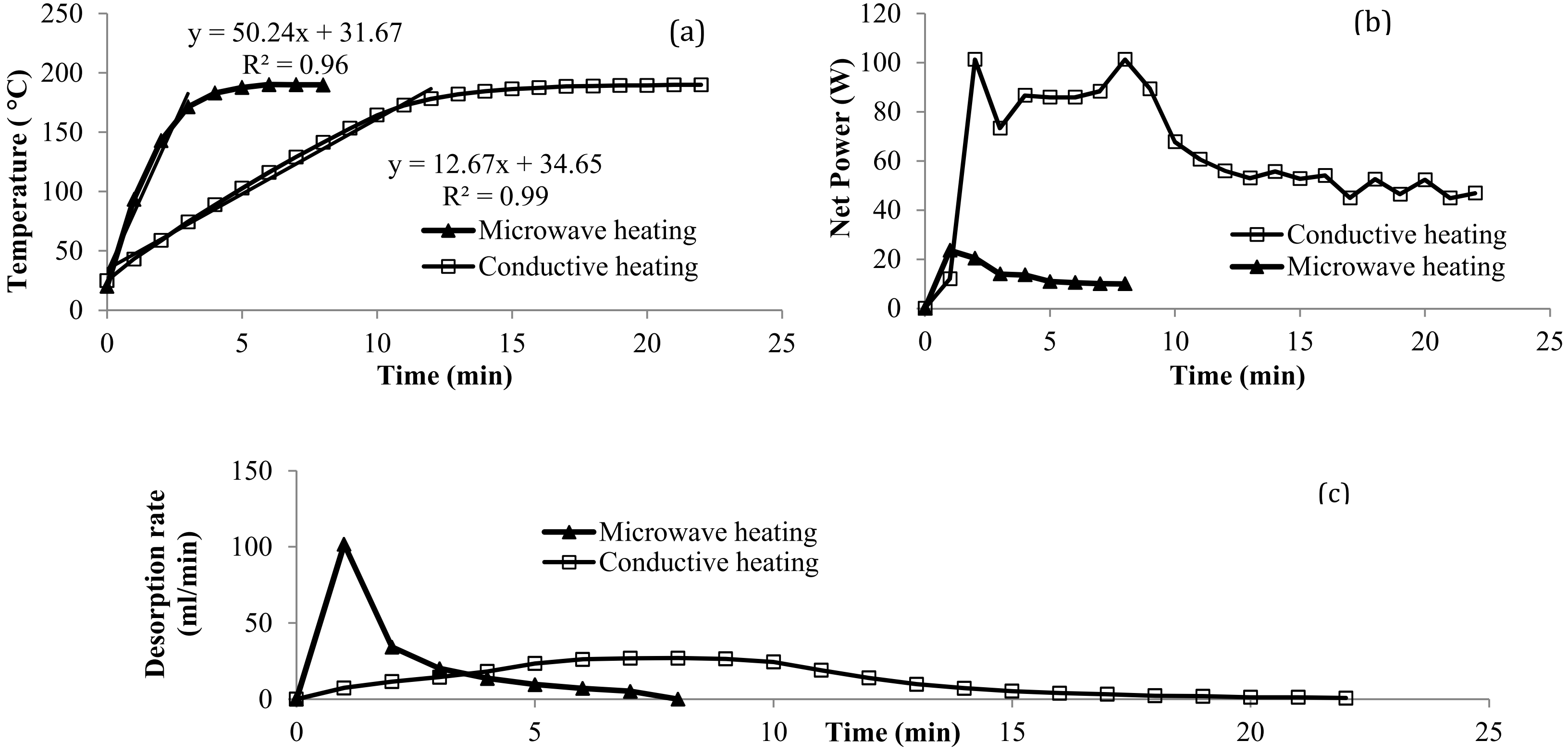

Figure 3-5: Desorption of CO_2/CH_4 saturated Na-ETS-10 with microwave heating and conductive heating: a) temperature; b) net power consumption; and c) desorption rate.

A total of five adsorption/desorption cycles for the CO_2/CH_4 mixture were completed on Na-ETS-10 for both microwave and conductive heating. A comparison of microwave heating and conductive heating over 5 cycles is presented in Figure 3-6 and Table 3-3.

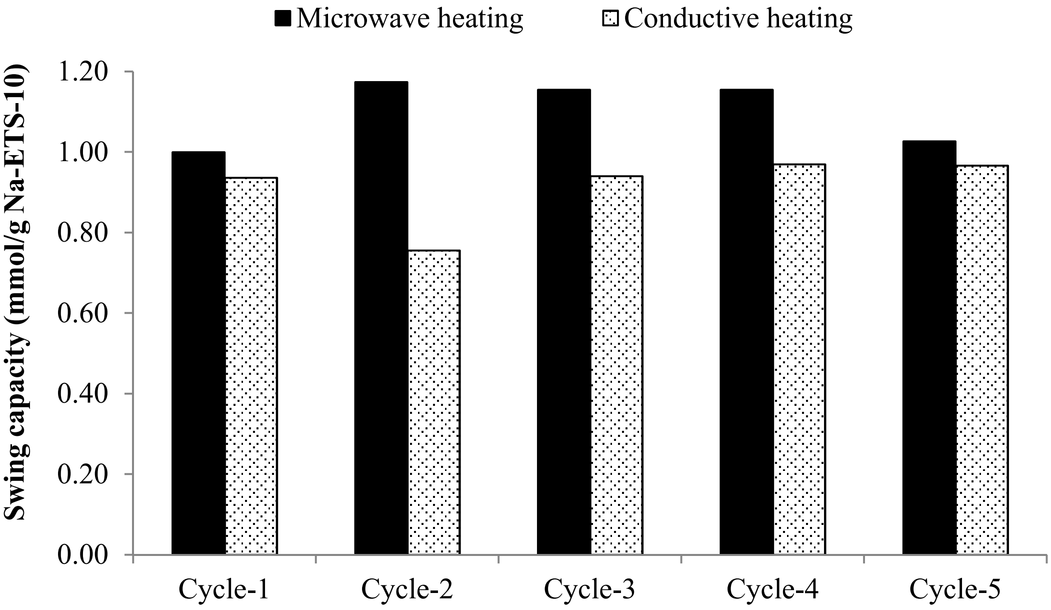

Figure 3-6: Swing capacity of Na-ETS-10 over 5 cycles remains unchanged under microwave heating and conductive heating of CO_2/CH_4 at 190°C.

Based on the gas being recovered, the swing capacity of Na-ETS-10 over 5 adsorption-desorption cycles during microwave heating and conductive heating were stable around 1.10 mmol/g Na-ETS-10 and 0.91 mmol/g Na-ETS-10 (Figure 3-6). Figure 3-6 illustrates that the adsorption capacity of Na-ETS-10 was unchanged during both microwave heating and conductive heating. The results also indicate that swing capacity of microwave is 1.21 times larger than that of conductive heating.

Table 3-3 shows that 70% of the adsorbed CO_2/CH_4 was recovered by microwave heating while only 57% by conductive heating. In microwave desorption, an average net energy of 0.67 kJ/g was consumed to achieve such desorption, however, approximately 7.7 kJ/g was consumed in the case of conductive heating.

On average 25 J of microwave energy and 348 J of conductive energy are needed to release 1 mL of gas adsorbed on Na-ETS-10. Throughout the five adsorption-regeneration cycles, conductive heating requires 14 times more energy than microwave heating in order to desorb the same volume of gas. The higher energy requirement in conductive heating is due to high heat loss as discussed in section 3.3.1. Figure 3-7 illustrates the consistency in energy consumption over 5 cycles of CO_2/CH_4 desorption for microwave heating and conductive heating.

Table 3-3: Comparison of microwave and conductive heating techniques for desorbing CO_2/CH_4 from Na-ETS-10.

	Desorption temperature (ºC)	**Heating time (min)**	**Cooling time (min)**	**Gas recovered (%)**					**Applied energy(kJ/g Na-ETS-10)**				
				Cycles					Cycles				
				1	2	3	4	5	1	2	3	4	5
Microwave heating	190	8	20	63	74	73	73	65	0.6	0.7	0.7	0.7	0.6
Conductive heating	190	22	60	59	47	59	61	60	7.8	7.9	7.6	7.8	7.3

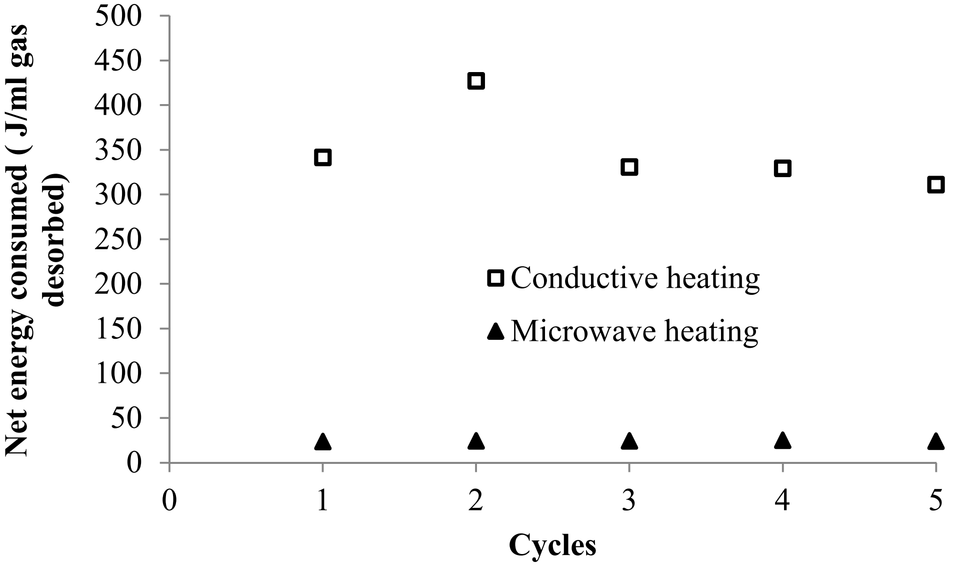

Figure 3-7: Variation in net energy consumption over 5 cycles was insignificant during microwave heating and conductive heating of CO_2/CH_4 on Na-ETS-10.

Table 3-4 summarizes the purity of the recovered CO_2/CH_4 gas for these two heating techniques over five cycles of adsorption/desorption. Based on GC-TCD analysis, the purity of the gas desorbed by microwave heating consisted of 82~83% CO_2 and 17~18% CH_4 while the purity of the gas desorbed by conductive heating contained 81~81.8 % CO_2 and 18~19% CH_4.

Comparing these two different binary systems (C_2H_4/C_2H_6, CO_2/CH_4), the recovery percentage of C_2H_4/C_2H_6 was higher than CO_2/CH_4. In C_2H_4/C_2H_6 separation system, the adsorbed phase is highly enriched C_2H_4 which has a polarizability of 42.52×10^{25} cm^3, while in CO_2/CH_4 separation system, the adsorbed phase is highly enriched CO_2 which has a polarizability of 29.11×10^{25}

cm^3 (Li et al., 2009). Considering in the case of physical adsorption, the adsorbed phase is in a liquid-like phase (Myers et al., 1965), so the adsorbed C_2H_4 consumed the microwave more efficiently than CO_2. By supplying the same amount of microwave energy, a higher recovery rate could be obtained in C_2H_4/C_2H_6 separation system.

Table 3-4: Summary of the desorbed gas purity measured for microwave heating and conductive heating for CO_2/CH_4.

		Purity of the gas recovered (%)				
		Cycles				
		1	2	3	4	5
Microwave heating	CO_2	82.1	83	82	82.5	82.7
	CH_4	17.9	17	18	17.5	17.3
Conductive heating	CO_2	81.3	81	81.8	81	81.5
	CH_4	18.7	19	18.2	19	18.5

3.4 Conclusion

In this work, two binary gas mixtures C_2H_4/C_2H_6 (59:41) and CO_2/CH_4 (10:90) were separated by adsorption on Na-ETS-10 at 22 ºC and 101.325 kPa. Na-ETS-10 was regenerated using microwave and conductive heating desorption and the desorbed gas was collected. Results show that microwave desorption can regenerate Na-ETS-10 more efficiently than conventional temperature swing regeneration such as conductive heating. Swing capacity achieved in microwave heating is higher than that of conductive heating. For both heating techniques swing capacity is not affected by successive heating cycles. During microwave desorption, 94% of the adsorbed C_2H_4/C_2H_6 and 71% of the adsorbed CO_2/CH_4 mixture were recovered. On the other hand, during desorption with conductive heating, 71.4% C_2H_4/C_2H_6 and 57.2% CO_2/CH_4 were recovered. Microwave desorption required an average of 0.7 kJ/g Na-ETS-10 during 8 minutes of heating while conductive heating required 7.7~7.9 kJ/g Na-ETS-10 during 22 minutes of heating. Results show that microwave desorption is characterized by faster heating, higher desorption rate, and lower energy consumption compared to desorption with conductive heating. Therefore, microwave heating can potentially be used as a cheaper energy source to regenerate Na-ETS-10 for adsorptive separation of binary gas mixtures such as C_2H_4/C_2H_6 and CO_2/CH_4.

The regeneration results can be further improved by using a sweep gas that can purge the adsorbent bed during heating. Using steam as purge gas can be a practical approach to enhance the heating both during microwave heating and conductive heating. Another approach can be using previously recovered C_2H_4 / CO_2 to ensure purging without diluting the product gas. It is expected that using C_2H_4 / CO_2 as purge gas would speed up the desorption process and would improve heating and therefore, requires further investigation.

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CHAPTER FOUR: MICROWAVE ASSISTED REGENERATION OF Na-ETS-10

4.1 Introduction

Microwave heating is considered to be an emerging technology in chemical process industries (Bykov et al., 2001). It is a less expensive and time saving desorption technique for adsorbent regeneration (Polaert et al., 2010). It is found to be successful in dehydrating as well as regenerating VOC saturated adsorbents (Roussy and Chenot, 1981; Cha and Carlisle, 2001; Hashisho et al., 2005). In this context, dehydration of adsorbents using microwave heating was studied for zeolite 13X (Roussy and Chenot, 1981), zeolite 3A, 4A, 5A, (Ohgushi et al., 2001), Na-X, and Ca-X (Ohgushi and Nagae, 2003, 2005).

When microwave energy is applied to a material, part of the energy gets stored in the material as electric energy, and part of the energy passes through the material (Meredith, 1998). The fundamentals of microwave heating are unique and opposite to the mechanism of conventional thermal regeneration techniques (Das et al., 2009). For instance in steam regeneration, the thermal energy is transferred from the surface to the bulk of the adsorbent. In contrast, in microwave regeneration, the thermal energy is transferred from the inside to the outside of the adsorbent bed. Microwave propagates through the molecular interaction between material and electromagnetic field (Das et al., 2009).

The control of heating is an emerging concern for industries in order to regenerate the adsorbents in less time and with lower energy. A proportional integral derivative (PID) controller has been used to control the temperature and the outlet volatile organic compound (VOC) concentration during microwave heating and the electro-thermal heating of activated carbon fiber cloth (ACFC) (Emamipour et al., 2007; Hashisho et al., 2007, 2008). The influence of constant power and constant temperature heating has been studied by using various feedback controllers while regenerating ACFC (Johnsen et al., 2011). Constant power microwave heating has been employed to regenerate dealuminated Y zeolite (DAY) (Reuβ et al., 2002; Turner et al., 2000), silicate (Meier, 2009), mordinate (Kim et al., 2005), faujasite (FAU) (Kim et al., 2007) and Engelhard titanosilicate (ETS-10) (Shi et al., 2010). The controlled heating of zeolites still requires extensive research.

Currently, natural gas meets the demand for one-fourth of the world's energy needs and considered to be cleaner than other fuels. Typically, natural gas contains traces of impurities such as carbon monoxide, carbon dioxide, or nitrogen. In Australia and Germany, natural gas contains more than 10% carbon dioxide (CO_2) as an impurity. The percentage needs to be reduced to meet the 'pipeline quality' ($< 2\%$ CO_2 impurity) set for methane (CH_4). Carbon dioxide reduction is important for protecting equipment and pipeline infrastructures (Cavenati et al., 2004). Engelhard titanosilicate (ETS-10) can preferentially adsorb CO_2 over CH_4 and can purify CH_4. Steam desorption and microwave heating techniques were applied to regenerate Na-ETS-10 (Shi et al., 2010).

ETS-10 is a titanosilicate molecular sieve with pores large enough to accommodate CO_2 and lighter hydrocarbons (Kuznicki, 1991; Anderson et al., 1994). ETS-10 can separate CO_2, CH_4 and C_2H_6, and the selectivity of CO_2 is higher than that of the other two hydrocarbons (Anson et al., 2009). Researchers are still trying to develop a successful and efficient regeneration technique to desorb CO_2 and reuse ETS-10. Although microwave heating is more flexible and cheaper than conventional thermal regeneration techniques for regenerating Na-ETS-10, achieving an adequate desorption of gas with less energy and time consumption is still a challenge.

This study investigates water desorption followed by microwave drying as a method for desorption of a binary gas mixture and regeneration of Na-ETS-10 and compares the performance of this method to that of constant power and constant temperature microwave regeneration. In water desorption, a carbon dioxide/ methane (CO_2/CH_4) mixture is adsorbed on a packed bed of Na-ETS-10 and then desorbed by water injection. The wet adsorbent received from water desorption is further dried and reactivated using microwave heating. In microwave regeneration, a carbon dioxide/ methane (CO_2/CH_4) gas mixture was adsorbed on a packed bed of Na-ETS-10 and was later desorbed by using constant power and constant temperature microwave heating. This study compares the swing capacity, gas recovery, and energy consumption achieved in water desorption and the two microwave heating modes for the gas mixture. The regeneration performance of Na-ETS-10 was monitored over five cycles for carbon dioxide/ methane desorption.

4.2 Experimental

Na-ETS-10 was synthesized using the hydrothermal technique as described elsewhere (Kuznicki, 1991). 16-20 mesh pellets were prepared from Na-ETS-10 powder. A detailed method of pellet preparation can be found elsewhere (Shi et al., 2010).

Adsorption-desorption experiments were performed using an adsorbent bed 3.75cm long and 2.9cm in diameter containing 10g of Na-ETS-10 and also using a double ended cylindrical quartz column. The sample was activated at 200°C in a laboratory oven for 16h under 120ml/min helium gas flow. The feed gas mixture (Praxair) of 10%CO_2 and 90%CH_4 was introduced into the fixed bed column with a flow rate of 300 mL/min at 22°C and 101.325 kPa. The outlet gas was sampled and analysed by using a gas chromatograph (Agilent 5890) equipped with a thermal conductivity detector and supelco matrix Heysep Q column, as mentioned in Chapter 3. A continuous flow of feed gas was maintained until saturation when the outlet composition became the same as the feed composition. Na-ETS-10 becomes saturated with CO_2/CH_4 after 90 minutes.

In the water desorption technique, 5ml water was injected into the saturated adsorbent. The desorbed gas flowed to a downstream flask and was collected by water displacement. The desorption experiment was continued until no gas evolution was observed. The volume of the displaced water was equal to the volume of the gas that was collected at the outlet. After desorption with water, a microwave generation and propagation unit was used to dry the adsorbent. The microwave generation and propagation system consisted of a 2 kW switch-mode power supply (SM745G.1, Alter), a 2 kW microwave source (MH2.0W-S, National Electronics) equipped with a 2.45 GHz magnetron, an isolator (National Electronics), a three-stub tuner (National Electronics), and a waveguide applicator connected to a sliding short (IBF Electronic GmbH & Co. KG). The tuner and the sliding short were manually adjusted at the beginning of the experiment to improve the energy transfer to the adsorbent. The isolator was used to protect the microwave head by conducting the reflected power into a water load. The power was monitored with a dual directional coupler with 60 db attenuation (Mega Industries), two power sensors (8481A, Agilent), and a dual channel microwave power meter (E4419B, Agilent). The temperature of the material was monitored by using a fiber optic temperature sensor and a signal conditioner (Reflex signal conditioner, Neoptix). The temperature sensor, power meter, and power supply were connected to a data acquisition and control (DAC) system (Compact DAC, National Instruments) equipped with a Labview program (National Instruments) to record the data and control the power application. The Labview program was used to monitor and control the heating during the drying. During the microwave drying, a 120 mL/min nitrogen flow was used as purge gas to provide uniform heating. After microwave drying, the nitrogen flow was adjusted to 300 mL/min to cool the bed down to room temperature. Once the bed reached the ambient temperature, further adsorption-water desorption-microwave drying cycles were initiated. A block diagram showing adsorption and regeneration by water desorption followed by microwave drying is presented in Figure 4-1.

In the microwave heating technique, after saturation, the microwave generation system was turned on, and the heating was initiated by using the Labview program. The desorbed gas flowed to a downstream flask and was collected by water displacement as before. The desorption experiment was continued until no gas evolution was observed. After desorption, the adsorbent was cooled to room temperature by purging with nitrogen at 120 mL/min. Once the bed reached the ambient temperature, further adsorption-microwave desorption cycles were initiated.

Two techniques of microwave heating were used during regeneration: constant power and constant temperature. In the constant power mode, the adsorbent was exposed to a constant incident microwave power of 60W until the bed temperature reached its set-point. Once the set-point was reached, the heating was stopped. In the constant temperature mode, a proportional-integral-derivative (PID) algorithm was used to control the heating to achieve the set point of the temperature, and the adsorbent was heated at that set point. The maximum incident power was set at 60W. A block diagram showing adsorption and regeneration by constant power and constant temperature microwaves is presented in Figure 4-2.

For water desorption, the swing capacity of Na-ETS-10 is defined as the amount of gas desorbed during water injection. For microwave regeneration, the swing capacity is defined as the amount of gas desorbed during microwave heating from 22°C to 190°C. Gas recovery was calculated based on equation 4-1:

$$\text{Gas recovery } (\%) = \frac{V_{W/M}}{V_W} \times 100\ (\%) \quad \ldots\ldots\ldots\ldots \text{(4-1)}$$

where, $V_{W/M}$ = volume of gas desorbed by water desorption (W) or microwave (M) heating, and V_W = the volume of gas desorbed by water desorption from the fresh adsorbent.

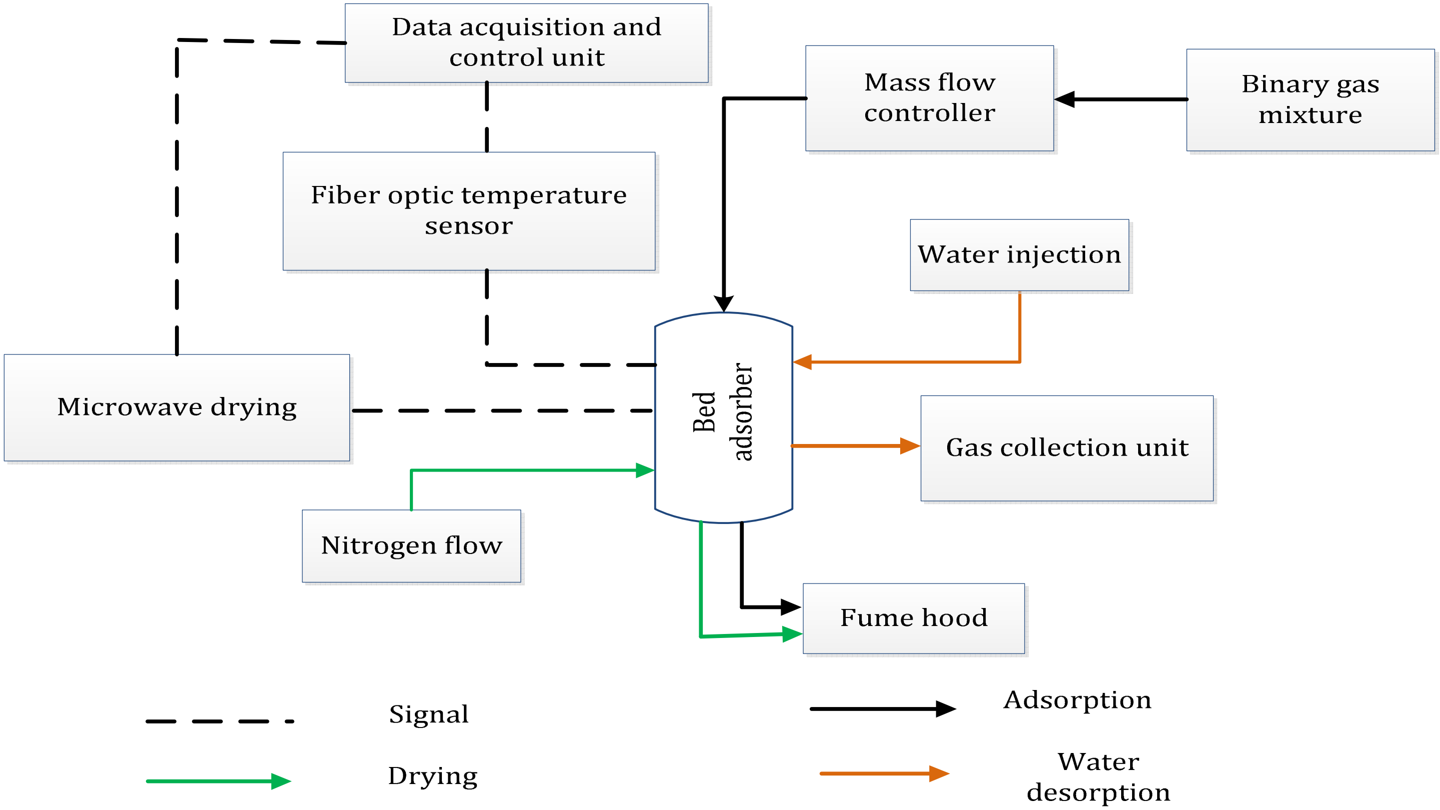

Figure 4- 1: Block diagram showing adsorption and regeneration of Na-ETS-10 using water desorption followed by drying

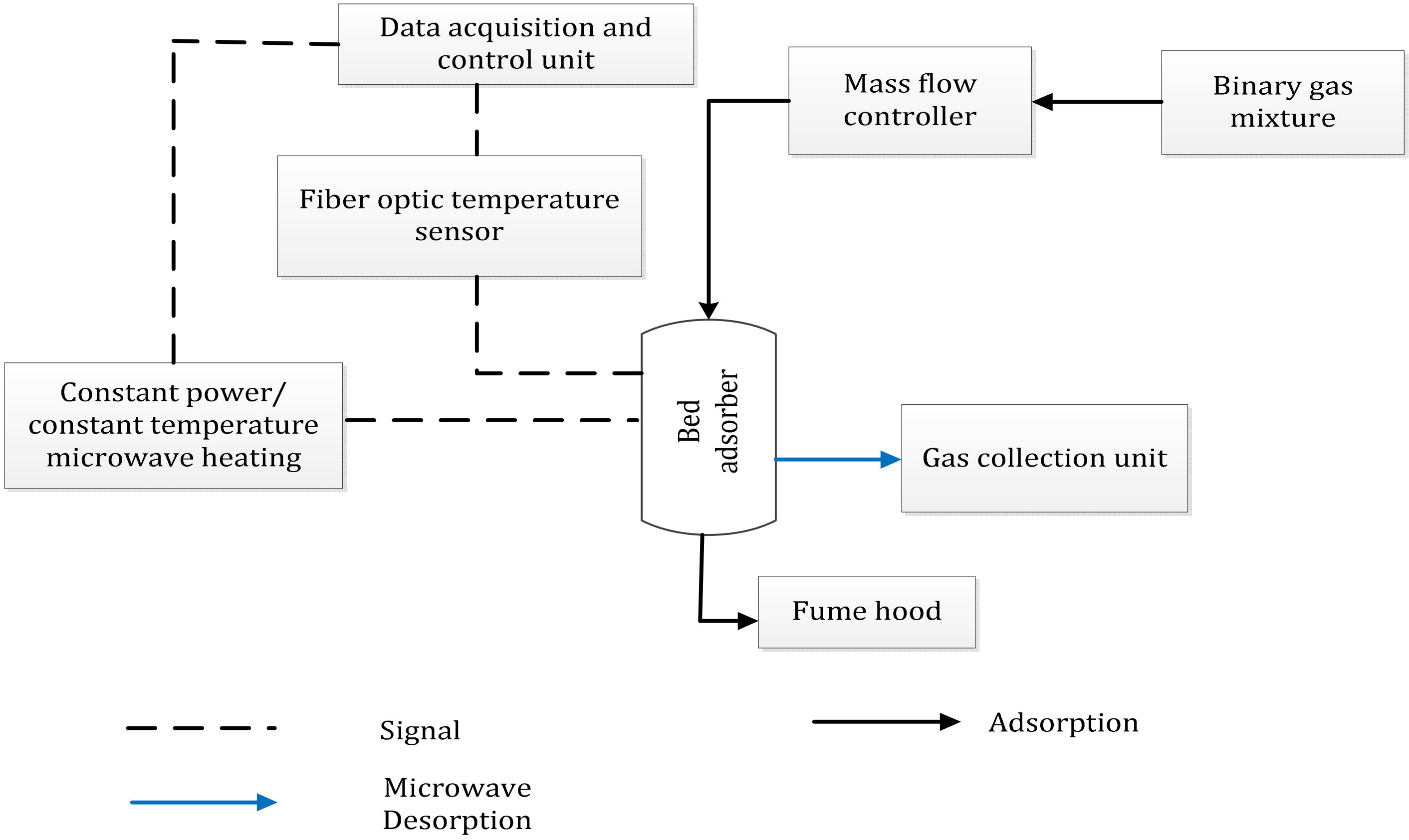

Figure 4-2: Block diagram showing adsorption and regeneration of Na-ETS-10 using microwave heating (constant power and constant temperature).

4.3 Results and Discussion

4.3.1 Water desorption followed by microwave drying

Water desorption applies mass action displacement to achieve complete (100 %) desorption (Shi et al., 2010) and requires 7-8 minutes to complete the desorption process. A total of 410 ml gas was collected from approximately 10g of Na-ETS-10. Based on the GC-TCD analysis, the desorbed gas contained 89% CO_2 and 11% CH_4. Later, the wet Na-ETS-10 was dried by using microwaves.

The wet Na-ETS-10 was heated with microwaves for 20 minutes at 190°C. A total of 2294 J microwave energy was consumed to regenerate 1gram of Na-ETS-10 and restore 20% of the adsorption capacity. Microwave drying desorbed 88% of the adsorbed water and restored 20% of the gas adsorption capacity. Under this operating condition, further drying required more energy and heating-time. Based on the gas being recovered, the swing capacity of Na-ETS-10 during water desorption was 1.58 mmol/g.

The typical temperature and power profile during microwave drying as a function of time is shown in Figure 4-3. Drying occurred in two stages with two different heating rates, 2.9 °C/min and 34.8 °C/min, respectively. The desorbed water coming out from the adsorbent accumulated at the bottom of the reactor during the first stage. The net power consumption varied between 10W to 34W and then became stable at 10W. Most of the power consumption occurred during the first stage of heating (2.9°C/min). This temperature and power profile can be divided into four zones. In zone A, a temperature rise occurred, but no desorption was observed. The adsorbed water molecules diffused from the pores and travelled to the surface of the adsorbent. The net power consumption increased slightly at this stage. In zone B, continuous desorption occurred and the temperature showed very little fluctuation. The power consumption rapidly increased and became constant. In zone C, the temperature sharply increased until the set point was reached. At this stage, the energy consumption could be attributed mainly to adsorbent heating. Therefore, the energy requirement for heating decreased and the power consumption also decreased due to the precise control of the PID controller. Finally in zone D, the temperature stabilized at the set point value. At this stage, the heat gain and heat loss became equal, and very little desorption was observed. For a longer duration of heating, at zone D, drying continued due to vaporization. The drying behaviour of Na-ETS-10 was consistent with that of other zeolites, which have been reported elsewhere (Polaert et al., 2007, 2010).

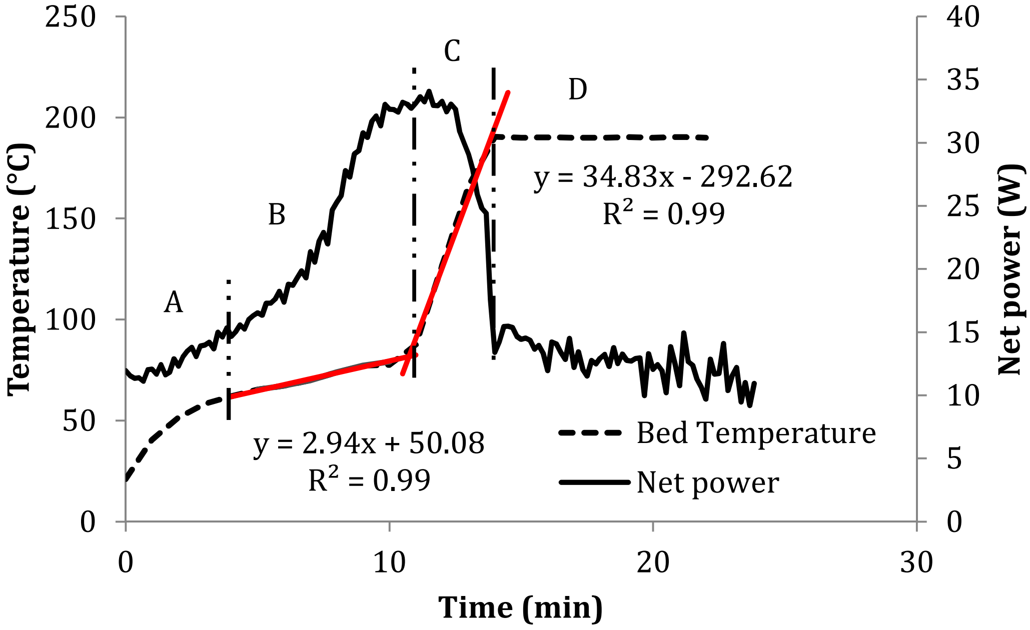

Figure 4-3: Regeneration of wet Na-ETS-10 by microwave heating after desorption of CO_2/CH_4: temperature and power profile.

In microwave drying, electromagnetic energy is converted into thermal energy. The higher the microwave frequency, the larger will be the dielectric loss of water, and the more microwave power will be absorbed. The maximum dielectric loss for water is obtained at a frequency of 20GHz, but the higher the frequency, the shorter the penetration depth. In this experiment, 2.45 GHz was used which is much lower but offers the optimum heating of water (Michael et al., 1991).

Table 4-1 compares the energy requirements for Na-ETS-10 drying and classical zeolites. This table shows that, for Na-X drying, the temperature swing regeneration (TSR) required 1.67 times more energy than the microwaves required to desorb 47% of the adsorbed water. Compared to the microwave drying of Na-X, Na-ETS-10 achieved a 41% higher dehydration with 50% less energy consumption. Similarly, compared to Na-Y, Na-ETS-10 consumed 65% less energy to regenerate 1gram of adsorbent but desorbs 10% less water.

Table 4-1: Comparison of energy consumption during Na-X, Na-Y and Na-ETS-10 drying in laboratory scale.

Adsorbent	Heating technique	Energy consumption (J/g desorbed water)	Energy consumption (J/g adsorbent)	Dehydration (%)
Na-X(Polaert et al., 2007)	TSR	20,300	-	47
Na-X(Polaert et al., 2007)	Microwave	12,200	17,600	47
Na-Y (Polaert et al., 2010)	Microwave	-	6440	98
Na-ETS-10	Microwave	5,909	2,294	88

4.3.2 Constant power microwave heating

In constant power microwave heating, 10 g of saturated Na-ETS-10 was heated under 60 W of constant incident power. The heating started at 22 ºC and continued until the adsorbent bed reached 190 ºC. The bed took 110 sec to reach 190 ºC. Microwave heating required 320 J to regenerate one gram of Na-ETS-10. A total of 6.7 mmol gas was desorbed, which represents 50% of the gas that had been adsorbed.

Figure 4-4 illustrates the temperature, power and desorption rate profiles as a function of time under constant power microwave heating. This heating increased the adsorbent temperature linearly with a heating rate of 1.71ºC/sec. The net power consumption was constantly around 35W in this mode. The desorption rate was 4.1-1.6 ml/sec. As long as adequate power was available to provide a thermal gradient, the desorption continued until it reached completion. Therefore, the desorption rate required adequate net power. More specifically, the desorption rate depended on the absorbed power density (W/m^3 bed). This finding has also been reported elsewhere for other zeolites (Polaert et al., 2007).

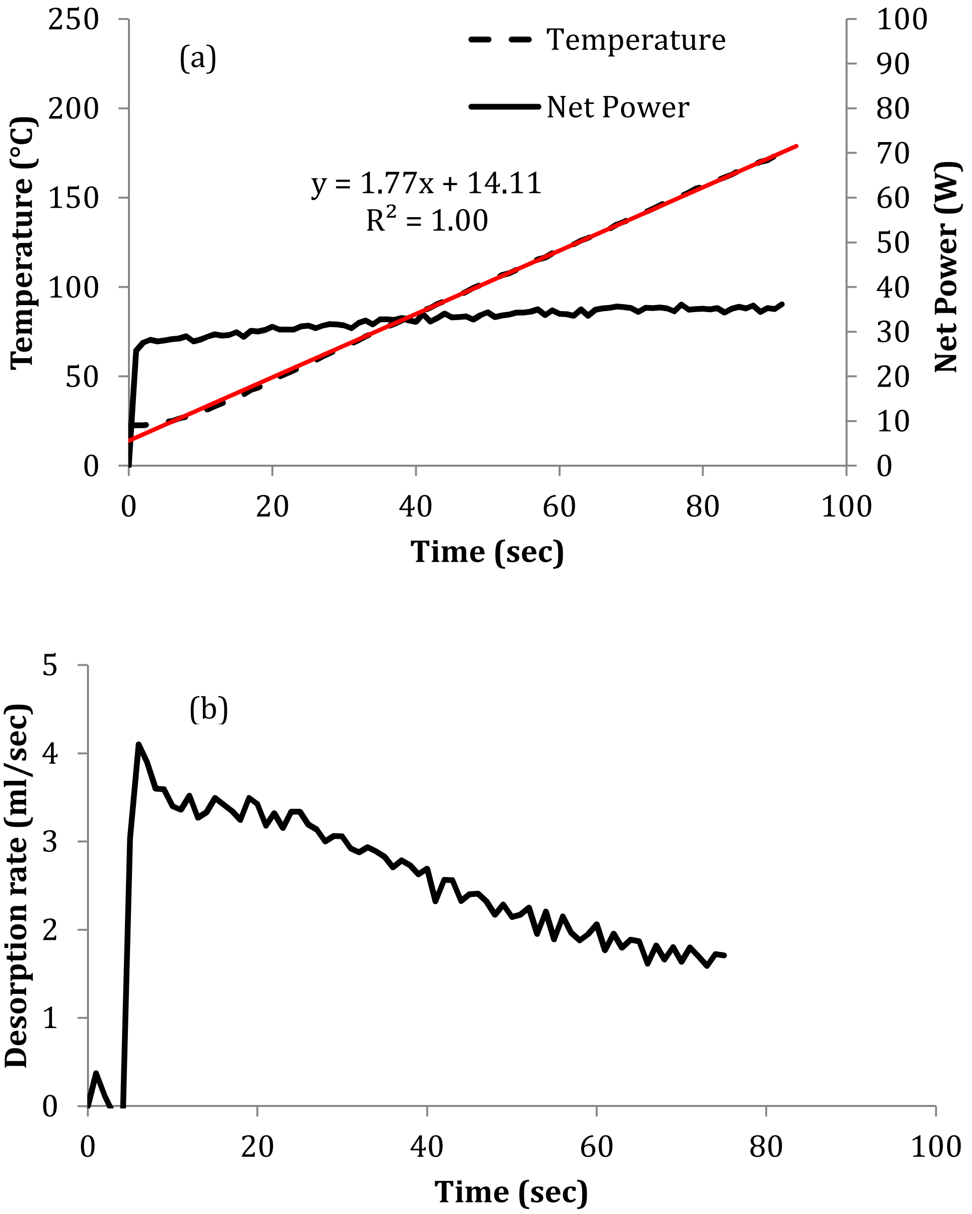

Figure 4-4: Desorption of CO_2/CH_4 and regeneration of Na-ETS-10 with constant power microwave heating; (a) temperature and net power profile and (b) desorption rate

4.3.3 Constant temperature microwave heating

In constant temperature microwave heating, the PID controller maintained a constant temperature at 190 ºC and did not allow the applied incident power to exceed 60 W at any time during heating. The heating started at 22 ºC. The bed was heated for 480 sec, and the temperature was maintained at 190 ºC. Microwave heating required 650 J of energy to regenerate 1gram of Na-ETS-10. 70% of the adsorbed gas was desorbed which represents a total of 12 mmol gas mixture. A detailed description of constant temperature microwave heating including temperature, net power and desorption rate profiles can be found in Chapter 3.

4.3.4 Discussion

A total of five adsorption-desorption experiments was completed with successive microwave cycles for regenerating Na-ETS-10. The comparison of five adsorption-desorption cycles of water desorption (with microwave drying) and microwave regeneration in constant power and constant temperature is presented in Figure 4-5, Figure 4-6 and Table 4-2. For the water desorption case, it was found that 100% of the desorbed phase could be recovered in the first cycle. In the later four cycles, the gas recovery was reduced by 80%. The swing capacity of Na-ETS-10 in the first cycle during water desorption was 1.58 mmol/g (as mentioned in section 4.3.1) and in the other four cycles was 0.28-0.33 mmol/g, which is 5 times lower than the first cycle. On average, 2,463 J microwave energy was needed to regenerate 1g of Na-ETS-10 in water desorption.

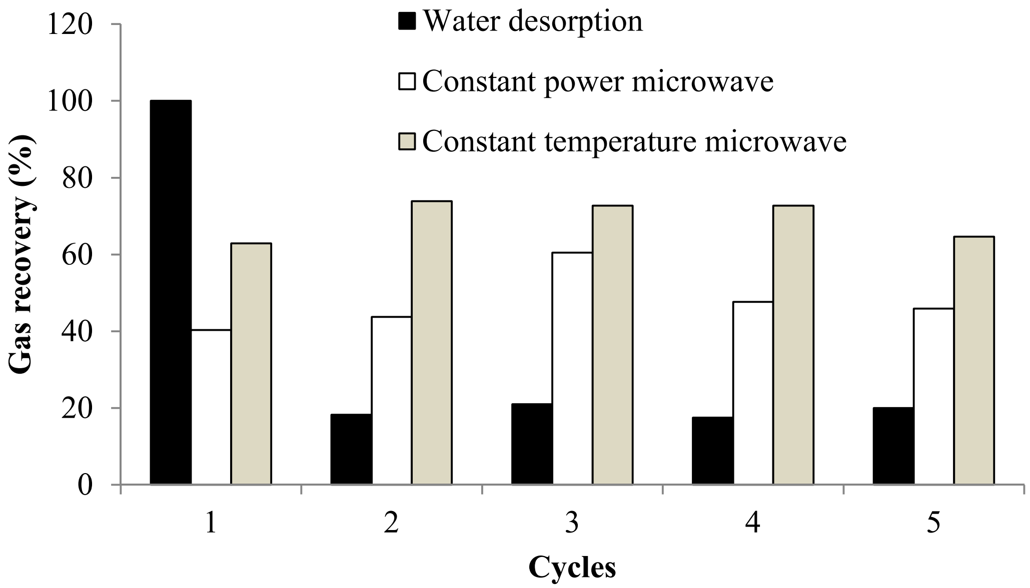

Figure 4-5: Variation in gas recovery (%) over 5 cycles during water desorption and microwave heating of CO_2/CH_4 on Na-ETS-10.

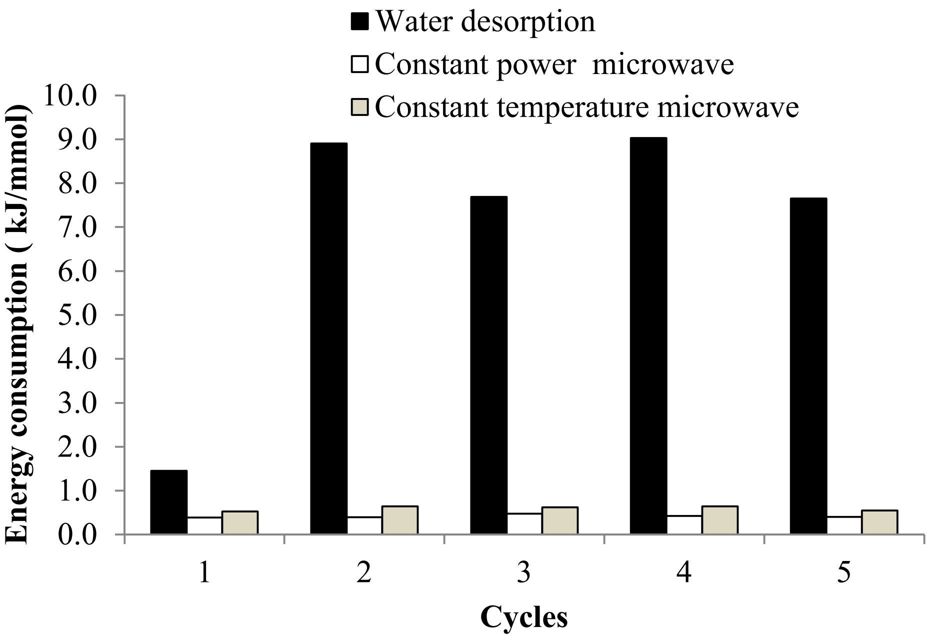

Figure 4-6: Energy consumption in constant power microwave heating was significantly lower than constant temperature microwave heating on Na-ETS-10. However, energy consumption in water desorption was higher than both microwave heating modes.

Table 4-2: Comparison of water desorption with constant power and constant temperature microwave heating techniques for desorbing CO_2/CH_4 from Na-ETS-10 over five cycles.

Water desorption	**Cycles**				
	1	2	3	4	5
Swing capacity (mmol/g)	1.58	0.29	0.33	0.28	0.32
Gas recovery (%)	100	18.25	21	17.5	20
Energy consumed per gram adsorbent regenerated (J/g)	2294	2565	2550	2494	2420
Energy consumed per mol gas desorbed (J/mmol)	1453	8903	7691	9030	7650
Constant Power	**Cycles**				
	1	2	3	4	5
Swing capacity (mmol/g)	0.64	0.69	0.78	0.75	0.72
Gas recovery(%)	40	44	55	48	46
Energy consumed per gram adsorbent regenerated (kJ/g)	300	309	368	332	313
Energy consumed per mol gas desorbed (kJ/mmol)	387	399	476	428	404
Constant Temperature	**Cycles**				
	1	2	3	4	5
Swing capacity (mmol/g)	1	1.17	1.15	1.15	1.03

Water desorption	**Cycles**				
Gas recovery (%)	63	74	73	73	65
Energy consumed per gram adsorbent regenerated (J/g)	576	700	682	703	602
Energy consumed per mol gas desorbed (J/mmol)	528	641	625	644	551

In constant power microwave heating, the average swing capacity, gas recovery (%), and net energy consumption over 5 cycles were 0.72mmol/g, 50% and 324 J/g, respectively. Similarly, in constant temperature microwave heating, the average swing capacity, gas recovery, and net energy consumption were 1.10 mmol/g, 70% and 652 J/g, respectively. The swing capacity, gas recovery, and net energy consumption over five cycles of adsorption and desorption remained unchanged for both the constant power and constant temperature microwave heating. Hence, the repetitive microwave heating did not affect the adsorption capacity of Na-ETS-10. However, for all cycles, the energy consumption and heating time in the constant power mode was lower than the constant temperature mode. The results show that, to achieve 50 % gas recovery, the constant power mode required 110 seconds while the constant temperature mode required 460 seconds. Therefore, the constant power mode provided faster and more energy efficient regeneration of Na-ETS-10 within the same maximum allowable temperature limit.

Typically, the dielectric loss factor of gases is negligible, but in the adsorbed phase, the gases act as a liquid-like phase (Chapter 3). Therefore, the absorbed power must have dissipated into both Na-ETS-10 and CO_2/CH_4 mixture. Hence, it was expected that, as soon as the desorption became close to completion in a constant power microwave regeneration cycle, the power consumption would become lower. In this experiment, at up to 50% recovery, no change in power consumption was observed. Therefore, the amount of energy that dissipated into the liquid-like phase either was not significant, or could be studied if a higher recovery were achieved. The dielectric loss factor of Na-ETS-10 has not been measured yet and requires further investigation.

Qualitatively, water has higher adsorption strength than CO_2 and CH_4 (Li et al., 2009). Therefore, higher microwave energy is required to reactivate the adsorbent in water desorption. Microwave power can induce dipole moments into adsorbates that are typically non-polar and have low adsorptive strength but carry quadrpole moments. CO_2 is quadrupolar and therefore can introduce polar behaviour into the desorption experiment. This issue requires further attention (Li et al., 2009; Maryott and Birnbaum, 1962).

4.4 Conclusion

In this work, water desorption followed by microwave drying was studied and compared with microwave heating as two potential regeneration techniques for Na-ETS-10. 10g of adsorbent was saturated with a CO_2/CH_4 mixture and then was desorbed by injecting water and using microwave heating. 100% gas recovery was achieved in the first water desorption cycle, but was reduced to 20% in the successive cycles. The swing capacity of Na-ETS-10 was reduced from 1.58 mmol/g in the first cycle to 0.28-0.33 mmol/g in the successive cycles in water desorption. On average, 6,940 J/mmol energy was required to recover 20% of the adsorption capacity. In microwave regeneration, microwave heating was applied in two modes: constant power and constant temperature. During constant power microwave heating, 50% of the adsorbed gas was recovered in 110 seconds, while during constant temperature microwave heating the same amount of recovery took 460 seconds. The constant power microwave heating required 320 J/mmol, while the constant temperature microwave heating mode required 610 J/mmol to achieve 50% gas recovery. Therefore, the brief application of the constant power mode provided a quicker and larger recovery compared to the longer and lower power recovery from the microwave application. On average a 70% gas recovery was achieved by the constant temperature microwave heating over 5 cycles of adsorption- desorption. In the constant power and constant temperature microwave heating, the swing capacity of Na-ETS-10 over 5 cycles remained stable at 0.72 mmol/g and 1.10mmol/g, respectively. The heating time for water desorption was 11 and 2.14 times higher than the constant power and constant temperature microwave heating. These results show that the adsorption capacity of Na-ETS-10 remained unchanged under successive microwave cycles in both modes of heating. In summary, water desorption is energy-intensive and is therefore an inefficient regeneration technique compared to microwave heating. Constant power microwave heating is the least energy-consuming microwave heating technique.

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CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

5.1. Conclusion

This research contributes to the understanding of how microwave heating can be used as an alternative mechanism for adsorbent regeneration. The comparison with conventional heating and water desorption show that microwave heating has the ability to provide faster and cheaper regeneration of petrochemical separating molecular sieves. This study is important because it provides information for how the energy need for gas separation and purification process can be reduced by applying a novel adsorbing material in C_2H_4/C_2H_6 separation and removal of CO_2 from CH_4 (natural gas).

This study demonstrates that microwave heating can desorb the adsorbed phase of C_2H_4/C_2H_6 and CO_2/CH_4 and regenerate Na-ETS-10. Na-ETS-10 preferentially adsorbs C_2H_4 over C_2H_6 and CO_2 over CH_4 while separating C_2H_4/C_2H_6 and CO_2/CH_4 respectively.

5.1.1 Comparison of microwave heating and conductive heating

The performance of microwave heating was compared to a conventional regeneration technique (conductive heating) for regenerating gas saturated Na-

ETS-10. Two industrially used gas mixtures C_2H_4/C_2H_6 and CO_2/CH_4, were separated by using a packed column of Na-ETS-10. The swing capacity, energy consumption, gas recovery (%) and purity of the recovered gas were determined and compared between microwave heating and conductive heating. A total of five adsorption-desorption experiments were performed for the two gas mixtures in both heating techniques. The conclusions based on the performance-comparing experiments are summarized below.

5.1.1.1 Ethylene/ ethane (C_2H_4/C_2H_6) desorption

1. The swing capacity achieved in microwave heating was 1.33 times higher than that in conductive heating. During microwave heating and conductive heating, the swing capacity of Na-ETS-10 was stable at 1.16 mmol/g and 0.87 mmol/g, respectively over five cycles of adsorption/desorption. Therefore, the successive application of microwave does not affect the adsorption capacity of Na-ETS-10.

2. On average, conductive heating requires 14.8 times higher energy to desorb the same amount of gas compared to microwave heating. 25 J microwave energy was needed to desorb 1mL of adsorbed gas, while 370 J of conductive energy was needed to do the same. The energy-consumption results are consistent over five cycles of adsorption and desorption.

3. Microwave heating recovered 94%, while conductive heating recovered 71.4% of the adsorbed gas. Microwave heating took 8 minutes, and conductive heating

took 22 minutes to recover this percentage of adsorbed gas repeatedly over five cycles of adsorption-desorption.

4. Based on GC-TCD analysis of the desorbed gas composition, 87~87.5% C_2H_4 and 12.5~13% C_2H_6 could be obtained during the microwave desorption, and 85~85.5% C_2H_4 and 14.5~15% C_2H_6 could be obtained during the conductive heating. Therefore, the desorbed gas had similar compositions.

5.1.1.2 Carbon dioxide/ methane (CO_2/CH_4) desorption

1. In the five cycles of adsorption-desorption, the swing capacity of Na-ETS-10 was repeatedly stable at 1.10 mmol/g Na-ETS-10 in microwave heating, and 0.91 mmol/g Na-ETS-10 in conductive heating. These results show that microwave heating provides a 1.21 times higher swing capacity than conductive heating and the capacity remains unchanged over five cycles.

2. On average, 25 J and 348 J were required to desorb 1mL of adsorbed gas with microwave and conductive heating, respectively. Therefore, the conductive heating requires 14 times more energy than microwave heating to achieve the same amount of desorption.

3. The microwave heating desorbed 70% while the conductive heating desorbed 57% of the adsorbed CO_2/CH_4. The microwave heating took 8 minutes, and the conductive heating took 22 minutes to achieve this much desorption. Therefore, the microwave heating was faster and more productive.

4. The gas desorbed by the microwave heating consisted of 82~83% CO_2 and 17~18% CH_4, while the gas desorbed by the conductive heating contained 81~81.8 % CO_2 and 18~19% CH_4, as determined by GC-TCD analysis. Hence, the purity of the desorbed gas collected from these two heating techniques is similar.

These results indicate that the microwave heating is a faster and less energy intensive regeneration method compared to conductive heating. The absorption of microwave is closely related to the polarizability of gases and solids. Due to the lower polarizability of CO_2, less gas gets desorbed while absorbing the same microwave energy compared to C_2H_4.

5.2.1 Comparison of water desorption and microwave heating

The performances of water desorption and microwave heating were compared as potential regeneration techniques for Na-ETS-10 saturated with a CO_2/CH_4 mixture. Microwaves was used to dry and reactivate the Na-ETS-10 after each water desorption cycle. Two modes of microwave heating were studied; constant power and constant temperature. A total of five cycles of adsorption-desorption experiments was studied to determine and compare the swing capacity, net energy consumption, and gas recovery achieved by these two regeneration techniques. The results obtained from the experiments are summarized below.

5.2.1.1 Swing capacity

Except for the first cycle of water desorption, the swing capacity of Na-ETS-10 was stable at 0.28-0.33 mmol/g. In the first cycles of water desorption, the swing capacity was 1.58mmol/g, which was reduced by 5 times in the later cycles. Therefore, 20 minutes of microwave drying was not sufficient to restore the gas adsorption capacity of Na-ETS-10. In the constant power and constant temperature microwave heating, the swing capacity remained stable at 0.72mmol/g and 1.10mmol/g, respectively, over five repetitive cycles.

5.2.1.2 Net energy consumption

On average, 2,463J, 320J, and 650J microwave energy were consumed by Na-ETS-10 to regenerate 1gram of adsorbent in water desorption, constant power and constant temperature microwave heating, respectively. The heating time for the water desorption was 15.8 and 2.14 times higher than that for the constant power and constant temperature microwave heating.

5.2.1.3 Gas recovery

Except during the first cycle, only 20% gas was recovered by the water desorption within 8 minutes. 100% recovery was achieved in the first cycle of water desorption. In contrast, a total of 50% and 70% gas recovery was achieved by the constant power and constant temperature microwave heating over five cycles of adsorption- desorption. Due to water injection, the adsorbent lost its capacity, and, therefore, the gas collection was reduced in the later cycles of water desorption.

Since the adsorptive strength of water is greater than the gas, energy required to break the water- Na-ETS-10 interaction was found higher than the gas-Na-ETS-10 interaction. Hence, the water desorption required more energy and time and therefore is not appropriate as a regeneration technique for Na-ETS-10. The results indicate that constant power microwave heating was the cheaper and more efficient option for the separation of CO_2/CH_4 on Na-ETS-10.

5.2 Recommendation

The future work should focus on optimizing the microwave system and the gas collection system to improve energy efficiency. The following experiments can be a starting point:

1. Adjusting the sliding short and wave guide through trial and error may further minimize the reflection. A further adjustment of the stub tuner is expected to provide even better results.

2. The microwave heating was found to be successful in regenerating Na-ETS-10 in a bench-scale system. Further investigation should be scaled up and completed on a pilot scale system.

3. Previously recovered C_2H_4 / CO_2 can be used as sweep gas in the adsorbent bed to ensure purging without diluting the product gas. It is expected that using C_2H_4 / CO_2 as a purge gas will speed up the desorption process.

4. The amount of energy consumed by Na-ETS-10 can be measured by heating the activated dry adsorbent under the heating condition used in this research. This measurement will reveal how much energy is consumed by the desorbed gas during microwave regeneration of saturated adsorbent.

APPENDIX A: MASS AND ENERGY BALANCE UNDER MICROWAVE HEATING

Table A-1: Mass balance for adsorption- desorption experiments of C_2H_4/ C_2H_6 mixture on Na-ETS-10 using microwave heating.

Cycles	Before adsorption	After adsorption	Weight gain		After microwave heating	Weight lost	
	g	g	g	g/g	g	g	g/g
1	97.440	97.824	0.384	0.036	97.542	0.282	0.026
2	97.517	97.810	0.370	0.035	97.517	0.293	0.028
3	97.524	97.817	0.377	0.035	97.524	0.293	0.028
4	97.497	97.810	0.370	0.035	97.497	0.313	0.029
5	97.507	97.807	0.367	0.034	97.507	0.300	0.028

Table A-2: Energy balance for microwave regeneration of Na-ETS-10 and desorption of C_2H_4/C_2H_6 gas mixture over five cycles.

Cycles	Input energy		Energy consumed	
	J	J/g	J	J/g
1	13,076	1,228	7,473	702
2	13,191	1,239	7,563	710
3	12,125	1,139	7,056	663
4	13,713	1,288	7,854	738
5	13,724	1,289	7,842	736

Table A-3: Mass balance for adsorption- desorption experiments of CO_2/CH_4 mixture on Na-ETS-10 using microwave heating.

Cycles	Before adsorption	After adsorption	Weight gain		After microwave heating	Weight lost	
	g	g	g	g/g	g	g	g/g
1	97.422	98.103	0.681	0.064	97.609	0.494	0.046
2	97.609	98.109	0.687	0.065	97.541	0.568	0.053
3	97.541	98.101	0.679	0.064	97.558	0.543	0.051
4	97.558	98.115	0.693	0.065	97.623	0.492	0.046
5	97.623	98.098	0.676	0.064	97.601	0.497	0.047

Table A-4: Energy balance for microwave regeneration of Na-ETS-10 and desorption of CO_2/CH_4 gas mixture over five cycles.

Cycles	Input energy		Energy consumed	
	J	J/g	J	J/g
1	11,304	1,175	6,126	583
2	14,033	1,335	7,437	707
3	13,723	1,306	7,254	690
4	14,115	1,343	7,472	710
5	11,914	1,133	6,395	608

APPENDIX B: MASS AND ENERGY BALANCE UNDER CONDUCTIVE HEATING

Table B-1: Mass and energy balance for adsorption- desorption experiments of C_2H_4/C_2H_6 mixture on Na-ETS-10 using conductive heating

Cycles	Before ads.	After ads.	Weight gain		After Conductive heating	Weight lost		Energy consumed		
	g	g	g	g/g	g	g	g/g	J	kJ	kJ/g
1	309.90	310.28	0.38	0.04	309.90	0.38	0.04	80,873	81	7.58
2	309.91	310.29	0.38	0.04	309.91	0.38	0.04	82,483	82	7.73
3	309.91	310.29	0.38	0.04	309.91	0.38	0.04	86,113	86	8.07
4	309.91	310.29	0.38	0.04	309.91	0.38	0.04	86,407	86	8.10
5	309.91	310.28	0.38	0.04	309.91	0.37	0.04	87,573	88	8.21

Table B-2: Mass and energy balance for adsorption- desorption experiments of CO_2/CH_4 mixture on Na-ETS-10 using conductive heating

Cycles	Before ads.	After ads.	Weight gain		After Conductive heating	Weight lost		Energy consumed		
	g	g	g	g/g	g	g	g/g	J	kJ	kJ/g
1	310.10	310.72	0.61	0.06	310.10	0.61	0.06	85,047	85	7.82
2	310.09	310.70	0.60	0.06	310.09	0.61	0.06	85,853	86	7.89
3	310.09	310.71	0.61	0.06	310.09	0.62	0.06	82,712	83	7.61
4	310.09	310.71	0.61	0.06	310.09	0.62	0.06	84,911	85	7.81
5	310.10	310.71	0.60	0.06	310.10	0.60	0.06	79,934	80	7.35

APPENDIX C: MASS AND ENERGY BALANCE IN WATER DESORPTION FOLLOWED BY MICROWAVE DRYING

Table C-1: Mass balance for adsorption- desorption experiments of CO_2/CH_4 mixture on Na-ETS-10 using water desorption coupled with microwave drying

Cycles	Before ads.	After ads.	Weight gain		After water des.	Weight gain		After microwave drying	Weight lost	
	g	g	g	g/g	g	g	g/g	g	g	g/g
1	97.42	98.06	0.65	0.06	102.01	4.59	0.44	97.95	4.05	0.39
2	97.95	98.16	0.21	0.02	102.23	4.81	0.46	97.90	4.33	0.41
3	97.83	98.02	0.19	0.02	102.28	4.86	0.47	97.99	4.29	0.41
4	97.99	98.16	0.16	0.02	101.74	4.32	0.41	97.93	3.81	0.36
5	97.93	98.09	0.17	0.02	102.11	4.69	0.45	98.01	4.10	0.39

Table C-2: Energy balance for adsorption- desorption experiments of CO_2/CH_4 mixture on Na-ETS-10 using water desorption coupled with microwave drying

Cycles	Input energy		Energy consumed	
	J	J/g	J	J/g
1	56,880	5,445	26,790	2,565
2	56,250	5,385	26,700	2,556
3	65,980	6,316	26,630	2,549
4	58,520	5,602	26,050	2,494
5	63,140	6,044	25,230	2,415

APPENDIX D: MASS AND ENERGY BALANCE IN CONSTANT POWER MICROWAVE HEATING

Table D-1: Mass balance for adsorption- desorption experiments of CO_2/CH_4 mixture on Na-ETS-10 using constant power microwave heating

Cycles	Before adsorption	After adsorption	Weight gain		After microwave heating	Weight lost	
	g	g	g	g/g	g	g	g/g
1	97.553	98.053	0.500	0.047	97.608	0.445	0.042
2	97.609	98.056	0.503	0.047	97.615	0.441	0.041
3	97.541	98.060	0.507	0.048	97.562	0.498	0.047
4	97.558	98.043	0.490	0.046	97.606	0.437	0.041
5	97.623	98.039	0.486	0.046	97.601	0.438	0.041

Table D-2: Energy balance for adsorption- desorption experiments of CO_2/CH_4 mixture on Na-ETS-10 using constant power microwave heating.

Cycles	**Input energy**		**Energy consumed**	
	J	J/g	J	J/g
1	6,779	638	3,525	332
2	6,475	609	3,328	313
3	7,691	723	4,074	383
4	7,494	705	3,915	368
5	7,576	713	3,963	373