

A STUDY ON HIGH-PRESSURE ADSORPTION AND DESORPTION  
OF METHANE, ETHANE, PROPANE AND THEIR MIXTURES ON POROUS  
ADSORBENTS

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## ABSTRACT

This work investigates the high pressure adsorption and desorption of methane, ethane, propane and their mixtures on different types of adsorbents in both equilibrium and dynamic systems. A treatment based on thermodynamic concepts was considered to further study the equilibrium system. Meanwhile, a thermodynamic modeling was performed to calculate the experimentally immeasurable adsorption quantities. The results demonstrated that activated carbons provide better adsorption capacities than molecular sieve zeolites and silica gel due to their highly developed porosities. Gas residual amount was observed to be related proportionally to gas molecular weights and bed temperature drop during desorption. Excess adsorption calculated for mixture on the basis of pure gases mole fractions was always higher than that obtained from the mixture within 10-30 % depending on adsorbent and gas mixture properties. This was found to be raised from the competition behavior between dissimilar species in the mixture. Methane maximum discharge rate of 5 L/min resulted in the most severe reduction in steady state delivery capacity, represented by a factor between 8.8-13.5 % compared to that delivered at 1 L/min. This was due to the extremely high temperature drop of  $-51.3$  °C, a net drop of  $78.3$  °C, corresponding to an increase in drop range of about 40% compared to that at 1 L/min. Ethane and propane have potential impacts on all types of delivery capacities within a reduction factor between 19.4 to 37.1 % for discharge rate of 1 L/min. From the results of this work, it can be concluded that the presence of ethane and propane in the mixture substantially reduced the adsorption of methane. In addition, temperature drop in the dynamic system is unavoidable even when the chamber is discharged at the lowest possible rate, causing an increase in gas retention and consequently loss in storage delivery capacity. The introduction of the nonideality assumption into the conventional Kelvin equation has enhanced the applicability of the equation to describe the capillary condensation of subcritical gases at high pressures.

## ABSTRAK

Kerja penyelidikan ini tertumpu kepada penjerapan dan penyahjerapan bertekanan tinggi sampel metana, etana, propana serta campuran-campurannya, terhadap beberapa jenis penjerap di dalam keadaan keseimbangan dan sistem dinamik. Rawatan berdasarkan konsep termodinamik digunakan untuk mengkaji sistem keseimbangan. Sementara itu, model termodinamik digunakan untuk mengira kuantiti penjerapan yang tidak dapat diukur secara ujikaji. Keputusan kajian menunjukkan bahawa karbon teraktif mempunyai kapasiti penjerapan yang lebih tinggi berbanding penapis molekul zeolit dan gel silika, disebabkan oleh keliangannya yang lebih tinggi. Semasa penyahjerapan, jumlah gas tertinggal, di dapati berkadaran dengan berat molekul gas dan kejatuhan suhu pematid. Lebihan penjerapan yang dikira bagi campuran berdasarkan pecahan mol gas-gas tulen adalah sentiasa lebih tinggi daripada nilai yang didapati secara ujikaji bagi campuran yang sama, dalam julat 10-30%, bergantung kepada sifat-sifat penjerap dan campuran gas. Perbezaan ini disebabkan oleh persaingan di antara spesis-spesis gas di dalam campuran. Kadar pengeluaran maksima metana pada 5 L/min menyebabkan penurunan kapasiti pengeluaran mantap yang paling ketara, dalam faktor 8.8-13.5% berbanding penurunan pada kadar pengeluaran 1 L/min. Ini disebabkan oleh kejatuhan suhu yang terlalu ekstrim, iaitu  $-51.3^{\circ}\text{C}$ , kejatuhan bersih  $78.3^{\circ}\text{C}$ , bersamaan dengan peningkatan kejatuhan sebanyak lebih kurang 40% berbanding pada kadar 1 L/min. Etana dan propana mempunyai potensi memberi kesan terhadap semua jenis kapasiti penghantaran dengan faktor penurunan di antara 19.4 hingga 37.1% bagi kadar pengeluaran 1 L/min. Dari keputusan yang diperolehi daripada kajian ini, dapatlah disimpulkan bahawa kehadiran etana dan propana di dalam campuran amat mengurangkan penjerapan metana. Tambahan lagi, kejatuhan suhu di dalam sistem dinamik tidak dapat dielakkan walaupun pada kadar pengeluaran terendah yang boleh dicapai, mengakibatkan peningkatan gas yang tertahan dan seterusnya kejatuhan kapasiti penghantaran storan. Pengenalan terhadap andaian ketidak-unggulan di dalam persamaan konvensional Kelvin telah meningkatkan kebolehan persamaan tersebut untuk menerangkan kondensasi kapilari gas-gas subkritikal pada tekanan tinggi.

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**LIST OF SYMBOLS**

$A$	Specific surface are
$D$	Chamber external diameter
$d$	Chamber internal diameter
$f$	Fugacity
$M$	Molecular weight
$G$	Gibbs free energy
$H$	Enthalpy
$m_A$	Mass of the adsorbent
$m_e$	Mass of the chamber equipped with basic installation
$m_g$	Gas mass
$m_t$	Mass of the empty chamber
$n$	Gas mole in the system
$P$	Pressure
$q$	Heat of adsorption
$R$	Ratio or gas constant
$S$	Entropy
$T$	Temperature
$t$	Chamber wall thickness
$V_e$	External volume of the chamber
$V_{tm}$	Volume of the chamber material
$V_t$	Internal volume of the chamber
$v_i$	Gas specific volume
$x$	Mole fraction in the liquid (adsorbed) phase
$y$	Mole fraction in the gas phase
$Z$	Compressibility factor

**Superscripts**

$Ab$	Absolute adsorption
$Ex$	Excess adsorption
$g$	Gas phase
$ig$	Ideal gas
$R$	Residual property
*	Pure state
$\wedge$	Specific property on mole basis
-	Partial property
$\beta$	Refers to phase $\beta$
$\alpha$	Refers to phase $\alpha$

**Subscripts**

$i$	Species $i$ in the mixture
int	Integral quantity
c	Critical condition
m	Molar property
$r$	Reduced condition
sp	Specific property on mass basis

**Greek letters**

$\mu$	Chemical potential
$\omega$	Acentric factor
$\varphi$	Fugacity coefficient
$\Gamma$	Adsorption
$\rho$	Density
$v^0$	Total void volume in the entire system

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

The development of an extensive traffic system such as the one existing today was only possible because of the discovery and exploitation of sufficient energy resources. The current transportation systems are inconceivable without the widespread availability of liquid hydrocarbons. But the fossil resources are finite and the environmental changes due to the release of the carbonaceous combustion products give causes to think about them. A large number of alternative fuels, in either liquid or gaseous form, are being considered with increasing interest (Manoj, 1994).

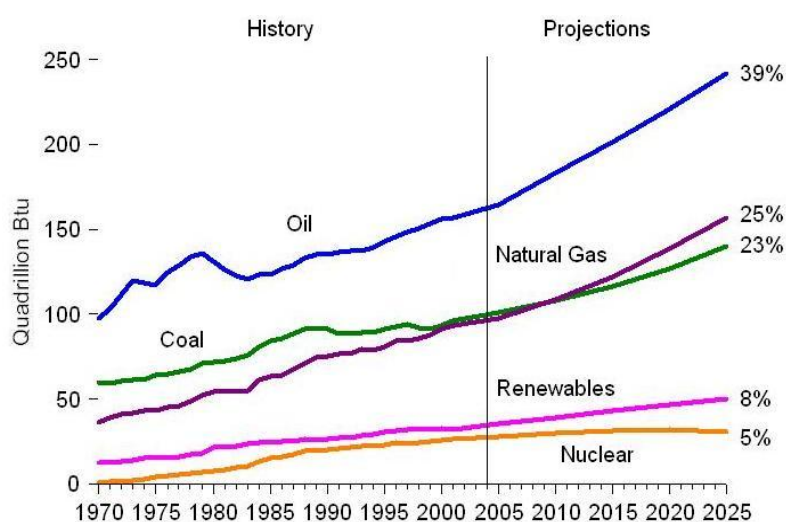
The size of the carbon chain of the molecules determines the calorific power of the gas in an indirectly proportional rate. Petroleum hydrocarbon gases are major source of fuel and they have been utilised widely in industry and automotives. One of the main hydrocarbon fuel gases is natural gas which is used in vehicles as an automotive fuel in Italy since 1938. Natural gas is clean burning since engines running on natural gas produce acceptance amounts of pollutants that do not significantly contribute to photochemical smog as shown in Table 1.1 which compares natural gas in compressed storage mode to petroleum liquid fuel. Furthermore, it is low in cost relative to both gasoline and diesel fuels in spark ignition engines without major modifications. In many applications, the use of natural gas as a motor vehicle fuel offers, and is expected to continue to offer, substantial fuel cost savings to natural gas vehicle owners, as well as greater

efficiency of energy resource utilization and lower air emissions, than does conventional gasoline, methanol, or electric vehicles alternatives (Hay, 1985).

**Table 1.1** Full fuel cycle emissions in g/ mile for the 1995 Chrysler Mini Van operating on petrol and compressed natural gas (The emission standards for passenger cars and light trucks in the United State in 1996) (EIA, [www.eia.doe.gov](http://www.eia.doe.gov), access: June 2004)

Fuel Type	NO <sub>x</sub>	Non-methane Hydrocarbon	CO	Particulate Matter	SO <sub>x</sub>	CO <sub>2</sub>
Natural Gas (CNG)	0.093	0.085	0.420	0.002	0.004	371
Petrol	0.626	0.698	3.462	0.013	0.044	468
Emission Standards	0.400	0.125	3.400	0.080	---	---

The major use of natural gas at present is for combustion in stationary applications, such as space heating. Figure 1 shows the worldwide current energy consumption distribution and the expectation for the coming two decades. Furthermore, it shows the percentage of share taken by natural gas in world total energy consumption.



**Figure 1.1** World primary energy consumption by fuel type (EIA, [www.eia.doe.gov](http://www.eia.doe.gov), access: June 2004)



One of the most common hydrocarbon gases is Methane which is the major component in natural gas and can be found in many industrial hydrocarbon gases mixtures. Methane is a supercritical gas that cannot be liquefied at ambient temperature. Various approaches can be used to store methane (or natural gas) for use as a vehicular fuel, in order to increase the energy storage density at ambient temperature. However, advancements in storage systems for natural gas are necessary because storage systems limit the vehicle's driving range. Two methods for storage of natural gas are common in use: Compressed natural gas (CNG) at pressure up to ~20 MPa is the currently used fuel storage technique for natural gas vehicle (Balassiano, 1997) while liquefied natural gas (LNG) is the conventionally large-scale natural gas storage at about atmospheric pressure and -162 °C (Hanlin, 2006). Although they are in use, these storage methods suffer from limitations due to their heavy and expensive instalations to maintain their extreme operating conditions (Elliott and Topaloglu, 1986; Horstkamp *et al.*, 1997).

From this point of view it is obvious that physical adsorption of light hydrocarbon gases and their mixtures on microporous materials measured at pressures above 0.1 MPa is of great practical importance not only for natural gas storage but also for industrial separation and purification processes. In recent years, moderate and high pressures are more often used in different industrial adsorption processes utilising natural gas or its individual hydrocarbon gases (Salem *et al.*, 1998).

To design and maintain these adsorption and desorption base industrial units, adsorption predictive tools are essential. The most basic common information required to obtain these predictive tools is the amount of pure gas (i.e. methane) adsorbed at a specified temperature and pressure. In other words, the functional form of the adsorption isotherms (i.e. adsorbed density versus pressure at constant temperature) for a given system. To gain a satisfactory representation, several theoretical issues must be taken into consideration regarding the influence of confinement induced by the adsorbent structure on adsorption, and the role of adsorbate molecular volume (i.e. molecular size) on adsorption behavior and capacity. Moreover, the use of thermodynamic concepts to explore the adsorption

phenomenon is a powerful tools and represents a solid ground for better understanding of the fundamental aspects involved in the system.

For a particular hydrocarbon gas mixture such as natural gas, knowledge on the amount of each species adsorbed from the mixture to the solid is of great importance, or at least the ratios of the amounts adsorbed (i.e. the selectivity). For the modeling and prediction of mixture adsorption, it is of basic information to figure out the role of the unequal adsorption affinities among the species on the adsorption (Kaminsky, 1993). Knowing these aspects can provide sufficient information not only on adsorption but also on desorption. The knowledge of desorption behavior of loaded adsorbents is of interest for characterisation of the adsorbate and for design of adsorbing plants (Seewald *et al.*, 1984).

## 1.2 Problem Statement

Designs of adsorption processes for the separation and purification industrial units, heterogeneous chemical reactors and gas storage require extensive information on the adsorption equilibria. One of the major obstacles to development of efficient design methods of adsorption processes is the lack of convenient and reliable equilibrium data at pressure above atmospheric pressure (moderate and high pressure ranges). Pure gas equilibrium data at moderate and high pressures are of great importance since they are required for design purposes even when the adsorption system involves mixture of gases. In the literature, attentions were paid on the adsorption of supercritical hydrocarbon gases (i.e. methane) only. No records were found among those literatures regarding the adsorption of subcritical gases (i.e. ethane and propane) at moderate and high pressures that involves capillary condensation phenomenon. Ethane and propane are the major species present in many hydrocarbon gases mixtures especially the petroleum ones such as natural gas. Therefore, the adsorption of subcritical hydrocarbon gases at moderate or high pressures is essential to understand the process of natural gas and other industrial hydrocarbon gases mixtures. Natural gas as adsorptive media consists of mixture of

super- and subcritical gases that should be taken into account in studying natural gas adsorption and desorption.

The most common case in adsorption industrial units is that the desired equilibria are for a mixed rather than for a pure gas since gas streams are almost carrying mixtures of gases with constant compositions coming in/out of units operating at steady state conditions (chemical reactors working at steady state conditions, natural gas production from the reservoir, effluent gases from petroleum refineries working at steady state conditions...etc.). Unfortunately, limited attention has been paid for such conditions in previous studies. Those studies had assumed, in predicting the adsorption equilibrium of gas mixture systems, that gas phase composition is varying in equipments operating in batch mode, which is valid only for limited industrial conditions. No record among the author's hands dealt with constant gas-phase composition approach in calculating mixed gas equilibria utilizing methane, ethane and propane as hydrocarbons gases as those gases are the common hydrocarbon components in many industrial hydrocarbon gases mixtures.

Since constant gas phase composition mixtures are the most common conditions in effluent streams of different industrial units, it is therefore of considerable practical interest to use theoretical techniques for estimating the adsorption equilibria of pure gases from the known adsorption isotherms of gaseous mixture and vice versa. The most attractive theoretical technique is the thermodynamic-based technique which is necessary to develop industrial adsorption devices. Limited attention has been focused on the exact and absolute adsorption thermodynamic quantities at moderate and high pressures that are of great usefulness for thermodynamic-based equipment design. The estimation of those exact and absolute thermodynamic quantities for mixtures involving supercritical (methane) and subcritical (ethane and propane) gases were not studied properly raising the need for a comprehensive investigation.

The heart of any adsorption and desorption processes is the porous media itself. Therefore, the influence of adsorbent properties of porosity, chemical nature of adsorbents surface and densities are crucial to draw a clear picture on the involved process and the feature of the applications. However, no investigation on the

influence of adsorbents' properties on light hydrocarbon gases mixtures (i.e. methane, ethane and propane) is available in the literature. Furthermore, a considerable shortage in literature is found dealing with the influence of properties of light hydrocarbons gases mixtures on the adsorption and desorption processes behavior. The incomplete information has led to unclear understanding of the adsorption of special gases mixtures such as natural gas.

The adsorption of natural gas for the purpose of storage at moderate pressure could be expected to significantly widen the utilisation of natural gas as alternative fuel for vehicular usage. This technology composes several problems related to residual amount of hydrocarbon gases left in the bed after each cycle leading to bed deactivation (residual amount can be as high as 30% of the storage amount (Mota *et al.*, 1997a,b)) and heat fluctuation problems during operation. Although a considerable number of studies can be found in the literature on natural gas storage, most of these studies focused on the preparation of adsorbents and their test for maximum storage capacities paying limited attention to the dynamic behavior of the system and the influence of gas composition and adsorbent properties on the dynamic performance of the system. These shortages led to incomplete description of the dynamic conditions of charging and discharging of natural gas storage, which represent the major performance parameter in this application.

The deactivation function of the adsorbent due to adsorption of heavy hydrocarbon gases is of great deal in refineries (thermal cracking of heavy hydrocarbon mixtures and gas separation filters) and natural gas storages by adsorption. It holds an important role in adsorbent selection for any industrial unit involving adsorption process as desorption is a major part in their functional sequence. Even though almost there was no study focused on the deactivation although many studies were investigating adsorbents performances. These problems have a strong negative impact on the process performance by reducing the amount of gas that could be stored or delivered during operation cycles. Unfortunately, random and limited studies on these systems could be found in the literatures leading to a shortage in information required to develop this technology. Much research work is still needed before commercial utilisation can be realized for this promising technology.

### 1.3 Objective and Scope

The objective of this research is to study the adsorption and desorption equilibrium and dynamic processes of hydrocarbon gases mixtures at high pressures on different types of adsorbents and to evaluate the important equilibrium thermodynamic parameters. In order to achieve this objective, the following scopes have been adopted:

- 1- To design and construct a reliable experimental rig that provides the capability of measuring the desired parameters for high-pressure natural gas adsorption and desorption process in both equilibrium and dynamic operation modes.
- 2- To study the adsorption and desorption equilibria of pure methane, ethane and propane on ten different adsorbents of activated carbons, molecular sieve zeolites and silica gel at moderate pressures. This collection of adsorbents was chosen in such a way that covers a wide range of chemical and physical properties for conventional adsorbents used in different industrial applications.
- 3- To study the adsorption and desorption equilibria of binary and ternary mixtures of methane, ethane and propane at moderate pressures on four selected different adsorbents of activated carbons, molecular sieve zeolite and silica gel. The four adsorbents have close properties to the common industrial adsorbents which gives an interesting possibility for comparison.
- 4- To study the effect of adsorbent porous structure, surface chemical nature, adsorbent density and particle size on the behaviors and characteristics of hydrocarbon gases mixtures adsorption and desorption equilibrium isotherms at moderate pressures.
5. To investigate the influence of gas physical properties (in pure and mixed states) on the behavior of adsorption and desorption equilibrium isotherms.

6- To evaluate the enthalpy of adsorption of methane, ethane and propane on the four powder adsorbents on the basis of adsorption equilibrium isotherms measured at two different temperatures.

7- To investigate the effect of gas type, adsorbent type and discharging flow rate in the dynamic adsorption and desorption cycles on the total delivered gas volume, pressure- and temperature-time dependency functions.

8- To study the effect of gas and adsorbent types on adsorbent deactivation as a function of number of operation cycles at ambient temperature and moderate pressures.

9- To model the capillary condensation phenomenon occurring during adsorption in such systems, on the basis of thermodynamic concepts by re-deriving the original Kelvin equation for capillary condensation of vapors to be capable to describe the capillary condensation of subcritical gases at high pressures.

10- To model the high-pressure adsorption and desorption equilibria of pure and mixed gases on the basis of thermodynamic concepts and evaluate different thermodynamic quantities of Gibbs residual, excess and absolute energies.

#### **1.4 Thesis Outlines**

As has been discussed in the previous sections, this work focused on the high pressure adsorption and desorption of methane, ethane and propane in their pure and mixture states on different porous adsorbents. Theoretical description and experimental work that have been undertaken were specified in this thesis. This thesis is organized as follows: an introduction of the process along with the problem statement and the objectives are presented in Chapter 1. In Chapter 2 the basic theory of the solid-gas interface associated with some related aspects on adsorption phenomena, such as porous solids description, adsorption and interaction forces causing adsorption are presented. Chapter 3 outlines the basic thermodynamic

concepts of adsorption phenomenon taking into consideration the non-ideal phase behavior. Chapter 4 reviews the previous studies on adsorption that dealt with adsorption and desorption of methane, ethane and propane on different types of adsorbents. Equilibrium and dynamics adsorption studies are reviewed in this Chapter. The experimental work including chemicals used, equipment description, experimental procedure and measurements are presented in Chapter 5. The results and discussion of this thesis are divided into three chapters. In Chapter 6 the results of adsorption equilibria for pure, binary and ternary systems are presented. Chapter 7 discusses the results of the dynamic adsorption for pure and mixture systems. Thermodynamic modeling of capillary condensation and adsorption equilibria are presented in Chapter 8. Finally, the conclusion from the current work and recommendations for further researches are gathered in chapter 9.

## **1.5 Summary**

Adsorption into solid adsorbents has a great industrial significance in separation and purification processes, and gas storage. Adsorption of pure gases and their mixtures on porous solids at high pressures plays an important role in low-energy separation processes and storage processes. An understanding of the adsorption and desorption phenomena of these processes can be helpful in determining the mechanisms involved as well as in identifying further valuable applications. Hydrocarbon gases mixtures are common in industry and cover a wide range of components and concentrations. One of special interest hydrocarbon gases is natural gas. The adsorption and desorption processes of natural gas and its individual gases on most common industrial adsorbents such as activated carbon, molecular sieve zeolite and silica gel, are not fully understood due to limited studies causing a delay in understanding of several aspects involved in high-pressure adsorption and desorption. It is therefore, of great importance to study the high-pressure adsorption and desorption processes of natural gas from both static and dynamic points of views. This could provide promising hopes for more development regarding this area of research.

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