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Alternative Methods of Storage and Transportation of Natural Gas

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Abstract

Comparing alternative methods to store and transport natural gas and some suggestions for improvement of the same will be described in this paper. Compressed Natural Gas (CNG), was, until recently, a reasonable storage alternative and could at the same time be used as an alternative fuel for Natural Gas Vehicle (NGV). But due to its high risk and expensive infrastucture, applications of this method will have to be reduced slowly. For liquified natural gas (LNG) applications, the natural gas is stored as a liquid at around 112 K inside a cryogenic vessel. Such cryogenic system, bec~~o~~ause of its extremely low temperature, is inferior in its safety characteristics, particulary in the presence of a fire. Other possible methods are:

- *Gas-hydrate form ; optimal condition and suitable additives may be added to improve the stability and to reduce the refrigeration cost.*
- *Adsorbed Natural Gas (ANG) ; a cheap, high surface area adsorbent and low bulk density activated carbon may be developed to increase the storage- and delivery capacity of the ANG system.*
- *Liquid Storage of Natural Gas (LSNG) ; collecting data of solubility,miscibility of natural gas in liquid hydrocarbon and optimal design of the fuel tank are necessary for an optimal design of liquid storage natural gas as vehicular fuel.*

CONTENTS

CHAPTER 1:

Natural Gas ; an energy resource for tomorrow

1.1 Why natural gas ?

Increasing demand of energy, clean environmental policy and a growing awareness of ecological problems over the last decades provide oppurtunities for natural gas to be used as an potential energy resource. The overall excellent properties of natural gas are the main reason for its wide acceptance as the cleanest of fosil fuels. Natural gas is often almost sulfur free and yields considerably less nitrogen oxides (NO_x) emissions than both oil and coal per unit of energy produced. Carbon dioxide (CO_2) production per unit of energy used is also less than fossil fuels (40 to 50% less than coal and 20 to 25% less than petroleum products).

Natural gas demand has also increased over the last five years (figure 1.1). It has increased at a rate of 2% per year, reaching a level of 2.158 10^9 m^3 in 1993. The forecast is that natural gas demand growths with 1.8 to 2.2% per year by the year 2010. By this year, the contribution of gas to the worldwide demand for primary energy needs could reach 24 to 25%, compared to 22.5% in 1993.

Use of natural gas for heating is the traditional business of the gas utilities. It is also used as an industrial and transportational fuel and for domestic purposes. Gas for power generation is the fastest growing sector of the gas market and accounts for about 50% of the expected worlwide demand growth. The main competition to gas , nuclear-and hydro electic power generation, are being increasingly scrutinised and suppressed. Public concern on nuclear safety prevents a major short-term development.

Natural gas was also being used as fuel for natural gas vehicle (NGV) engines. Gaseous fuels like compressed natural gas (CNG) and liquefied petroleum gas (LPG) demonstrate very high anti-pollution performance, especially at low temperatures. However, they require special engines to reach their full potential. Some applications such as fuel for taxi's (LPG)-or city buses (CNG) has been implemented in the United States. Their 'nearly zero emission' potential make these engines the great challenge of common fuel engine.

Natural gas has been discovered mainly in Western Europe and the Middle East, two gigantic areas which own 70% of world gas reserves. Natural gas was also discovered in Asia/Oceania give a third world wide position. As an example, Australia, Indonesia and Malaysia own more than 50% of the gas potential in the region.

Natural gas is also being discovered in more difficult areas. Offshore reserves now represent 24% of world reserves and 30% are located in Arctic areas and Siberia. Hence, operating conditions are more difficult and natural gas will be more and more costly to produce and transport from the resource areas.

1.2 Problem arising by the use of natural gas.

The increasing distance from reserves to the major consuming regions has led to regional gaps between domestic supply and demand. These imbalances are sharpening and will entail a substantial increase in the natural gas trade.

Some storage and transportation methods have been developed to eliminate this problem. Pipeline transportation between countries or nearby continents and liquefying of natural gas were major transportation methods in the past. However, the high cost of investments to build adequate infrastructure is the major problem to apply these methods.

Compressed natural gas is a new alternative and well known method to transport natural gas and used for NGV application. The main disadvantage of this method is the high pressure of the storage vessel. Storage of natural gas as its frozen hydrate requires much lower pressures than the compression of natural gas. Another possibility of storage, transportation and use of natural gas resources is storage in activated carbon (Adsorption Natural Gas, named ANG) and blending with liquid hydrocarbon (Liquid Storage of Natural Gas, named LSNG).

This paper will describe the characteristics, advantages, disadvantages and provide some examples and possibilities to improve each method of the storage and transportation of natural gas. The summary of this paper is presented in figure 1.2.

CHAPTER 2 :

Compressed Natural Gas

Compressed Natural Gas (CNG) can be used as fuel for the internal combustion engines (Ali Mansoori, 1994). In general the gas will be transported at about 22 MPa and stored in the vehicle at about 16 MPa (Wilby, 1986). The major disadvantage of this application is the high pressure storage of CNG, but low emission of CO, high octane number compared to gasoline and other fuel possibilities are favourable.

2.1 Characterisation and safety of CNG compared with other fuel sources.

To evaluate the safety aspect of various potential fuels with reference to their suitability as engine fuels the following characteristics need to be considered (Karim and Wierzba, 1992):

- Storage and portability characteristics
- The tendency to form a combustible mixture following an accidental discharge.
- Ignition, explosion and flame spread characteristics.
- Environmental consequences of their use and discharge.

It is recognized that there are potential safety problems arising from the fact that alternative fuel such as CNG are usualy fed from high pressure. The fuel storage tank must meet all the appropriate safety regulations and must be retested at regular intervals. All fuel tubing and fittings, pressure switches, indicators, regulators, etc and associated equipment must also be of appropriate design and comply with the required regulations. Great care is taken to ensure that the fuel gas is at an acceptable level of purity. Neither should it contain significant amounts of material such as sulphur compounds or be excessively wet to avoid possible corrosion problems within the cylinder interior that may undermine the strength of the container. Increasing the ambient temperature may result in increase of pressure, that is why venting is also required.

When a typical gaseous fuel leaks from a cylinder into the surrounding, it can form only a certain maximum volume of combustible mixture. Due to its narrow range of the methane flammability limits (table 1), it can generate only a small amount of combustible mixture relative to other fuels. The discharge of one unit volume of methane in air would generate a maximum volume of combustible mixture that is 40% of that following the release of an equivalent volume of propane and at 20% the volume of the mixture formed following release of a similar amount of gasoline vapour. On the other hand its relatively high flammability limit will result in considerable amount of methane leakage into the air to render the mixture combustible, especially in view of the dispersive nature of the fuel.

The rate of discharge of a gaseous fuel following an accident will depend on the nature of the leak and the associated area of discharge. The discharge from a high pressure cylinder or lines into the atmosphere will be at rates that are proportional to the size of the area and inversely proportional to the density of the gas. Accordingly, hydrogen will leak relatively faster than methane or propane.

The tendency for the CNG fuel to disperse in the surroundings from a leak is governed by the role of the resulting turbulent jet mixing, bouyancy and diffusional effects. Bouyancy effects are dominant in the dispersion of methane and hydrogen in air, unlike the much heavier-than-air vapour of gasoline and propane. These vapours will tend to linger on following a discharge and disperse far too slowly, thus retaining the hazard for longer time and spreading the potential for fire and explosion away from the leakage zone.

The rate of change of fuel concentration due to the diffusion is proportional to the characteristic diffusion coefficient of the gas and the concentration gradient. The diffusion of methane is far faster than the corresponding diffusion of gasoline or propane. In the case of CNG leak , because of the gaseous nature of methane, it will be discharged with a high velocity into the surroundings, aiding greatly in the rapid dispersion of the fuel. Gasoline and propane, which will discharge in a liquid form, requiring a significant period of time to vaporize and disperse, thus adding to the risk and the potential for damage. It is certain that the dispersion rate of methane will be very much faster than those of gasoline vapours.

The minimum energy required to effect a successful ignition of a fuel-air mixture within the flammability range is relatively large for mixtures involving methane. Hence, such mixtures are much more difficult to ignite than other fuels. Ignition is usually assured in the presense of thermal sources, since very large energies are provided by sources such as sparks and hot surfaces. An effort should always be directed first at eliminating the generation of a potentially combustible mixture rather than the mere elimination of ignition sources.

Higher ignition and autoignition temperatures are required to start a fire with methane. The quenching of methane-air flames by cold surfaces, such as through metallic meshes, is much easier than in the case of flames involving propane or hydrogen-air mixtures.

The detonational characteristics of any fuel in air are of far reaching significance as far as safety is concerned. The detonable range of a fuel in air is significantly narrower than the flammability limits under the same operating condition. Considarably more energy is required to start a detonation than to start a deflagration under the same condition. The maximum burning and detonation velocities are different by order of magnitudes. The pressure rise generated in an enclosure following combustion is at least twice as high as that generated following normal flame propagation. The reflected pressure from detonation is yet much greater than the detonation pressure rise.

Since the detonation velocity is greater than the corresponding speed of sound, the walls of a confining structure will be exposed to the pressure generated by the detonation without prior warning, rendering the pressure relief devices ineffective. Hence, detonation situations must be avoided at all cost. Methane in this regard is supremely superior to fuels as hydrogen, gasoline vapour and propane.

The extent of fire damage involving the combustion of any fuel is governed by a number of factors that include the extent of the thermal radiation, flame engulfment and smoke production. Thermal radiation depends mainly on the combustion temperature distribution, emissivity and energy release rate. A fire involving methane contributes significantly less thermal damage than gasoline or propane fires because of its relatively low combustion temperatures and emissivity. Due to the buoyant and dispersive nature of methane, and its low combustion temperatures, its fire hazards do not persist and the flame engulfment period and intensity are reduced.

Methane flames tend to be luminous with relatively small smoke production over a very wide mixture range, making their detection much easier than in the case of flames involving hydrogen, with their low luminosity.

2.2 Engines performance and emission of Compressed Natural Gas.

Natural gas source fuel produces far less CO and other pollutants compared to gasoline and diesel fuels (100 times reducing CO emission and 30% of due to reactive hydrocarbon). Natural gas engines, which have been used for years in industry and agriculture, are mostly spark-ignated.

CNG mixes with air more completely and is distributed more evenly to the cylinders than gasoline. Consequently, CNG engines run more smoothly and quitely. CNG has also a highest octane rating and thus allows for higher compression ratios and greater power compared to gasoline engines.

Anyway, reduced emission of carbon dioxide and compatibility with other fuel efficieny, low emission lean-burn technology makes CNG as one of the most attractive alternative fuel for petroleum based fuels in the transportation sector.

2.3 Major drawbacks of Compressed Natural Gas application.

CNG storage is several times bulkier and more expensive than gasoline storage, on an equal-range basis. Since CNG is a gaseous fuel, it must be compressed and stored at 16 to 20 MPa on board in heavy, bulky,specially designed steel or alumunium cylinders. Due to this, the valuable space in the vehicle would be lost and the distance that a vehicle can travel would be limited. This aspect is often cited as a major drawback to CNG use. However, advanced storage technology, namely adsorption storage, could make CNG less cumbersome to use in vehicle. The potential advantage of adsorption is that a given energy density can be attained at a pressure required to compressed natural gas to the same volumetric energy density. This result in lower capital and operating costs for compression.

Refueling with CNG is a more difficult process than with other fuel sources. Like gasoline or diesel fuel, CNG is dispensed at filling stations. Refueling takes longer and would require a completely new infrastucture for widespread distribution to vehicle. CNG refueling can be carried out either in the 'slow fill' method or 'fast fill' method. In a typical 'slow fill' method, the gas from the pipeline is compressed to the desired storage pressure and is fed directly to the vehicle's storage cylinder over 6-8 hour (Bechthold and Timbario, 1983). Typical 'fast fill' system delivers CNG in 4-6 minutes at 20 MPa from a cascaded array of large cylinders pre-pressurized with natural gas to about 25 MPa (Aerospace Corporation, 1982).

CHAPTER 3:

Frozen hydrate as an alternative to store and transport of natural gas

Hydrates are solid materials that form when liquid water and natural gas are brought in contact under pressure. The formation of this hydrate is a well known problem in petroleum industry and natural gas industries cousing blockage and pressure drop.

On the contrary, hydrate formation can be an advantage. Because of its composition, about 15% gas and 85% water by mass, it can be used as alternative storage of natural gas. Early in the year 1942 Banesh et al. proposed using hydrate to improve the load factor of natural gas system. He suggested that hydrate could be produced by bringing liquid water into contact with natural gas at appropiate temperature and high pressure. The hydrate then would be stored at a temperature and pressure when it was stable. When gas was needed for the supply system, the hydrate would be melted at low pressure.

This chapter will describe an advanced method (storage at higher temperature), based on work from Banesh et al., which is developed by Gudmundsson (Gudmundsson, Parlaktuna and Khokar, 1994) and an example of transporting of natural gas stored in hydrate developed by Chersky et al.

3.1 Characterisation of gas/hydrate system.

A single gas mixture,consisting of 92 mol% methane, 5 mol% ethane and 3 mol% propane, was used in the experimental work. This mixture composition represent the natural gas from the North Sea. Figure 3.1 shows the calculated equilibrium for this gas mixture for temperature between -20 and 20°C. The addition of 5 mol% ethane and 3 mol% propane reduces the equilibrium pressure with about 1.2 MPa compared with pure 100% methane.

3.1.1 Hydrate formation.

The experimental work consisted of producing a hydrate from gas mixture in high pressure vessel. Vessel pressures ranging from 2-6 MPa were used, then the vessel was placed in a deep freezer at -18 °C for about 24 hours.

Figure 3.2 showed the vessel pressure and temperature as function of time for hydrate production at about 2.3 MPa (named: exp.I). The decrease in vessel pressure was characterized by three distinct region. In the first region, the pressure decreased as a result of a reduction in gas specific volume when cooled. In the second region, the pressure decreased owing to the hydrate formation (gas consumption). In the third region, the pressure again decreased as a result of a reduction in gas specific volume when cooled. Figure 3.3 plotted the pressure and temperature equilibrium data from this run. Line 1 corresponds to the vessel gas-mixture composition at the beginning of the experiment, line 2 corresponds to the vessel gas-mixture at the end of the experiment. It shows that hydrate formation began when gas/water system cooled to about 4 to 5 °C below the equilibrium temperature. Figure 3.4 showed the pressure and temperature equilibrium data from initial vessel pressure of 4 and 6 MPa. This figure showed also that the hydrate formation began when gas/water system cooled below about 4 to 5 °C from its equilibrium temperature.

Exp.I showed that 27% volume of the water was converted to hydrate. The vessel pressure was increased when adding more gas mixture after the first hydrate formation; this resulted in a higher percentage of water converted to hydrate (contains 44% volume of water,named exp.II). The amount of water converted in hydrate depended on the degree of pressurization of the hydrate vessel. It was found that different hydrates were equally stable during refrigerated storage and that they behaved alike when melted to recover the gas mixture.

3.1.2 Natural gas recovery and stability.

Figure 3.5 presented the temperature in the center of the sample and the amount of gas recovered by melting at atmospheric pressure and 20 °C from exp.II after storaged at -18 °C for 2 days. The hydrate/ice sample took about 45 minutes to melt.

The stability of the hydrate produced in exp.I(storage temperature of -5 °C), exp.II (storage at -18 °C) and exp.III (contains about 35% volume of water converted to hydrate and storage temperature of -10 °C) are ploted in figure 3.6. The amount of gas released was calculated with the reference to the samples measured for each run immediately after removal from the hydrate vessel. This figure showed that the natural gas hydrate remained stable during refrigerated storaged for up to 10 days. The hydrate samples of exp.I stored at -5 °C released on average 11.3% of its gas initially; the hydrate stored at -10 °C lost on average 3.4% of its gas initially and hydrate stored at -18 °C,however, lost practically nothing. It should be emphasized that each point in figure 3.6 represents a different sample for the same hydrate formation run. The important observation of this measurement is that samples remained stable during storage at refrigerated conditions.

The gas composition is 69.49% methane, 15.78% ethane and 14.73% propane, of exp.I was plotted in figure 3.7. The hydrate samples were taken immediately after the hydrate vessel was opened after 1,2 and 7 days of storage.

In a large-scale industrial plant producing natural gas hydrates, the gas lost from the hydrate immediatelly after opening (pressure release) of the hydrate vessel can be recovered easily and recycled into the process. In the present context it is necessary to understand the phenomena that give rise to the observed gas release. A possible explanation concerns the formation of a protective layer of ice on the outside of the hydrate particles. This protective layer may form as the hydrate warms up from -18 °C to the storage temperature of -5 and -10 °C. The gas lost most likely originates from the surface of the natural gas hydrate-i.e.,the surrounding exposed to the surrounding air. The hydrate that decomposes will leave behind a layer of ice. This ice forms a protective coating for the hydrate.

3.2 Transportation of natural gas hydrate system.

An example of storage and transporting natural gas in the form of gas hydrate was firstly introduced by Chersky et.al.,1975. Natural gas hydrates are loaded into containers with latter being propelled through a pipeline filled with natural gas, and with the pressure and temperature which will preserve the physical state of the hydrates during the process of transportation.

The natural gas and water are delivered under a pressure from 6-4 MPa to the hydrate producing apparatus (block 1, figure 3.8). The gas is previously cooled to a temperature of -20 °C to -30 °C and divided into two streams. One stream is mixed with sprayed water previously cooled to a temperature of 1 °C or 2 °C. The mixing of natural gas with sprayed water produces finely divided hydrates. Then these hydrates are supercooled by other stream of natural gas which has been previously cooled to -45 °C approximately. The supercooled hydrates are then delivered into loading devices (block 2) in which the containers are loaded with hydrates. In order to preserve the physical state of the natural gas hydrates at a temperature of -20 °C the pressure must be about 1 MPa (point a, figure 3.9).

The containers loaded with hydrates are propelled through pipeline 3 (figure 3.8) filled with natural gas. The propulsion is effected by means of the natural gas which is compressed and cooled at station 4 spaced at certain distances from another throughout the length of pipeline 3. The natural gas used for propelling the containers is compressed at the station 4 to a pressure of about 5 MPa and cooled to -40°C.

At the terminal point of the pipeline 3, the containers are delivered into disintegrating unit 5, where the hydrates are decomposed into gas and water by raising the temperature above the equilibrium temperature (point c, figure 3.8). The gas is then conveyed from the unit 5 to the consuming installation and the water into the industrial water supply system. The empty containers are returned to the loading device 2 and being propelled by natural gas under pressure of 0.12-0.3 MPa.

The pipes used for natural gas by this method are made of common carbon steel which are considerably cheaper than the straight-seam high pressure pipes. Another advantage of this method is the simultaneous transportation of large amounts of commercially pure water required for industry.

CHAPTER 4:

Adsorption of natural gas on activated carbon

Adsorbed Natural Gas (ANG) is stored at relative low pressure (3-4 MPa) in a lightweight cylinder filled with high surface area activated carbon adsorbent. The attractive feature of ANG is that the storage tank can be filled with an inexpensive single-stage compressor. An example application of ANG is to store natural gas fuel onboard automotive vehicles.

The characterization of ANG on activated carbon (i.e: the structure of activated carbon, the adsorption capacity etc.) and the energy density will be compared with the result of a simulation method named Grand Canonical Monte Carlo simulation. The filling processes will be also described briefly.

4.1 Stucture of activated carbon

The maximum adsorptive capacity of activated carbon for methane was estimated using an idealized slit model (Matranga and Myers,1992) , with single planes of graphite ($\rho = 2.28$ g/cm^3, $A = 2620$ m^2/g, $a_s = 0.552$ g/g) covered on both sides with a two dimensional solidified layer of methane at the saturation limit of infinitely high pressure (see figure 4.1). Adsorbed methane is sandwiched between the basal planes of graphite when the spacing of the graphite planes is optimized.

Another example of this activated carbon adsorbent is AX-21 (Chahine and Bose, 1991) developed by Amoco. Solidification method is developed to produce this activated carbon to reach high surface area carbon adsorbent and a low bulk density. This method consists in forming a slurry of a pre-wet carbon adsorbent with an aqueous solution of a thermoplastic binder. Some additives such as plasticizers and internal lubricants can be added to improve the general characteristics of the final products. After spray drying or heating, the coated carbon particles are then molded under pressure (100 to 300 MPa) to any desired shape. Binding of the particles can be enhanced by heating the particles while under pressure up to or slightly above the melting temperature of the binder. As a final step, the retrieved solids are heat treated to remove solvent that the adsorbent may retain and to open some pores that may have been clogged during the process. This heat treatment will improve the specific adsorption of the shape adsorbent but above a certain temperature it could stress the bonds and cause the swelling of the adsorbent. This expensive AX-21 has a high surface area (3000 m^2/g) compared to single planes of graphite. Another activated carbon named BPL ($A=1000$ m^2/g) is much cheaper but has insufficient capacity for methane.

4.2 Computer simulation of methane adsorption in activated carbon

The adsorption affinity or strength depends on intermolecular potentials which used a Grand Canonical Monte Carlo (GCMC) simulation (Allen and Tildesly,1987 ; Tan and Gubbins,1990). Molecular simulations are realistic because the affinity is determined by the actual intermolecular forces between methane molecules and carbon atoms. The idealized slit model described previously was used; the slit width $H=11.4$ Å was determined by maximizing the methane delivered per cycle. As a first approximation, natural gas is assumed to be pure methane. The result of GCMC simulation compared to the perfect affinity (Langmuir isoterm model) and experiments based on some activated carbon adsorbent at 300 °K are presented on figure 4.2. Some idealization assumed at this GCMC simulation (i.e: no inert binder in the adsorbent pellets, isothermal filling of the storage tank; natural gas simulated by pure methane) would give an upper limit for the adsorptive capacity and a consistent basis for comparing the simulations with experimental data.

Pictures of methane molecules in the simulation box for 300°K and pressure respectively 2 , 3 and 5.1 MPa are shown in figure 4.3. It has been shown that H=11.4 Å is the optimum slit width. The pictures (d), (e) and (f) are top views of the simulation box for H=11.4 Å for different pressure.

Figure 4.4 and figure 4.5 presented the methane adsorption capacity for different types of activated carbon at 300°K (Matranga and Myers,1992) at low and high pressure respectively. Especially for AX-21 the thermoplastic binder will influence the adsorption of methane. AX-21 pelletized with 2% weight of binder (called AX-31) are particular interesting (Chahine and Bose, 1991,see figuur 4.6). Table T1 presented the increasing capacity of AX-31 compared to the original activated carbon adsorbent.

Although AX-21 reaches a storage capacity comparable to that of CNG system, it should be pointed out that economically it is not competitive with CNG system;the cost of KOH based adsorbent likes AX-21 is about five times that of regular activated carbon. Another cheaper process possibility is to pelletize coconut carbons with 4% weight of binder. Table 3 shows the results of such process. The storage capacity of such adsorbent (CNS) at 3.45 MPa and 300°K is 40% lower than the capacity of CNG system operating at 17 MPa.

4.3 Delivery of methane and energy density of Adsorption Natural Gas

The difference of the storage capacity at the loading pressure and the amount adsorbed at exhaustion pressure will be influencing the amount delivery of methane. The storage capacity will be expressed as the bulk density (mol/m^3) in a storage tank of actual volume, pressure and temperature divided by its density at standard conditions. Table 4 compares the delivery of methane between CNG at 20.7 MPa and the GCMC simulation of ANG based on an operating cycle from 3.4 MPa down to 0.14 MPa. It can be observed that CNG gives ± 30% more methane than the simulated ANG.

The energy density has been defined as the heat derived from combustion of methane in a tank of volume V, divided by the heat of combustion from gasoline filling the same volume. The results are presented in table 5. For a given storage volume and filling pressure of 3.4 MPa, the molecular simulations predict that the maximum combustion energy delivered by adsorbed natural gas is 25% of that of gasoline. The energy density of CNG loaded at 20.7 MPa is comparible with ANG. This gives some oppurtinities to use ANG instead of CNG.

4.4 The filling process

If a quick process is needed, than an adiabatic filling is recommended instead of isotermal process which is described yet. At this process the undissipated heat of adsorption raises the temperature of carbon and thus lowers its capacity of methane. In figure 4.7 the calculation of adiabatic temperature rise during the filling process (Sincar, 1991) is illustrated. Point 3 is the result of isothermal (slow) filling. Point 1 is the amount of methane molecule corresponding to temperature (300 °K) and pressure (0.14 MPa) at exhaustion.

Point 2, the intersection of the adiabat with the isobar for loading pressure (3.4 MPa), is the state for quick filling. The predicted temperature rise was 74 °K. The adiabatic capacity predicted by GCMC simulation is 45%less than the isotermal capacity (figure 4.8). Remick and Tiller, 1985 determined a temperature rise of 55 °K and a 20% loss in storage capacity as compared to isothermal filling.

Another modern method of speeding up the filling process without loss of capacity is to mix the carbon pellets with capsules containing a solid with a melting point at 30 °C. The heat generated by the adsorption of the methane would then be dissipated more rapidly by heat transfer within the bed from the adsorbent pellets to the capsules.

CHAPTER 5:
Storage of natural gas in liquid hydrocarbon

High pressure storage and expensive adsorbent are the main obstacles of natural gas storage at CNG and ANG system respectively. New development for application of natural gas storage in the transportation sector is to develop a technology to store natural gas in the liquid state by blending it with hydrocarbons and the use of co-solvents to optimize the product, named liquid storage of natural gas (LSNG). This chapter will describe first the advantages of this method and characteristics of blending methane with hydrocarbons, then give an example of natural gas blended in liquid petroleum gas.

5.1 Advantages of storing methane in liquid hydrocarbons.

Interest in natural gas fueled vehicles has continued to grow with the economics of cost and the unpredictable availability of gasoline and diesel liquid fuels. A motivating force for natural gas fueled vehicle has been to clean up air pollution which is threatening air quality in many metropolitan areas. Clean air legislation and regulation are creating a demand for alternative vehicle fuels throughout various areas of the world. Natural gas based alternative fuels (i.e liquid petroleum gas, liquefied natural gas, compressed natural gas) have environmental advantages due to its low emmision compared to another alternate fuels (diesel, gasoline ,etc,see chapter 2). However, significant obstacles remain to be overcome including the challenge of establishing infrastructure for convenient fuel delivery and energy density of proposed fuels. These obstacles can be overcome by providing a technique and a product which incorporates methane into liquid phase fuel for general purpose use but more specially for vehicular fuel decreasing cost with impact to liquefaction of the methane.

Liquid storage of natural gas in hydrocarbons shall need lower storage pressure (for LPG-methane system: 2-3.5 MPa) compared to CNG (about 22 MPa) and ANG (about 4 MPa). This advantage of LSNG reduces the high pressure storage risk and the cost of high pressure storage tanks.

LSNG is also preferred over the ANG becouse the whole content of the tank is combustible in the engine.

5.2. Characterisation of methane in liquid hydrocarbons.

One potential application of natural gas to use as fuel for internal combustion engines is to mix natural gas with other hydrocarbons at low pressure in the presence of co-solvent. This idea is based on experimental data of high solubility of methane in crude oils and the role of solvent/co-solvent in solubility enhancement (Mansoori, 1994).

There are some important aspects needed for an optimal design of liquid storage of natural gas, these are as follows:

- Infinite dilution properties:
  Knowledge of these properties will help to search for the optimum conditions at which it could store the most amount of natural gas in liquid fuel.
- Interfacial properties of partially miscible systems:
  Reducing the interfacial tension is needed to ensure a one phase (miscible) system of liquid storage natural gas at a wide range of pressure and composition. Occurance of two phase mixtures will give a reducing performance of the internal combustion engine. Recent technology with used of propane or butane as hydrocarbon liquid give an alternative solution of this problem (see next section).
- Design of the fuel tank:
  In order to use LSNG as a vehicular fuel, it is necessary to design a fuel

tank so that at all condition of operations only the liquid phase will be consumed as the fuel.

5.3 Liquid solution of methane in Liquid Petroleum Gas

The high solubility of natural gas in liquefied petroleum gas has been used as a storage tool to meet increased consumption requirements and demands on existing storage volume equipment. These studies were primarily directed to 'peak-shaving' wherein the alternative was liquefied natural gas storage. In peaksheaving the end product is desired to be utilized as a gas fuel form for stationary industrial or pipeline utilization.

An example of binary mixtures of the hydrocarbons methane and propane or butane (defined as Prothane and Buthane; Teel,1994) provides a newly conceived fuel substitute for gasoline or liquefied petroleum gas. Mixing propane directly into liquefied natural gas and evaporating part of the liquefied natural gas provides cooling of the propane up to -120°C and enhances the amount of gas (methane) from the pipeline that can be dissolved in the chilled propane. The composition of this mixture (prothane) due to this method can reach about 77% volume of methane (comprised of about 20% volume gas from liquefied natural gas and about 50% volume gas from pipeline natural gas) and 23% volume of propane at 2 MPa.

The economics of attemping to superchill propane by mechanical refrigeration to a temperature low enough to dissolve methane is unattractive. However, chilling of the propane by mixing directly into liquefied natural gas and evaporating a portion of the liquefied natural gas permits such chilling to be achieved with minimum of investment and apparatus. As reported by Teel (1994), the Prothane or Buthane provides a new binary liquid level having an energy density (calories per unit of container interior volume) which provides a practical alternatieve to liquefied petroleum gas,liquefied natural gas or gasoline.

The most significant aspect of Prothane is that it provides a process and product for presenting substantial amounts of methane in liquid phase for storage, transportation and directly use as a vehicular fuel. It offers an opportunity to allow more efficient, economical and environmentally acceptable utilization of natural gas.

5.4 Some futures of liquid storage of natural gas.

Due to its advantages in economical,risk and environment- aspects, some research has been done to optimize the conditions of storage of natural gas in liquid hydrocarbons. Collecting solubility data of methane in different hydrocarbons and determining the optimal condition to dissolve and exhaust methane from hydrocarbon is necessary for the future of this technology. Some further characterizing of this system i.e.: infinite dilution- and interfacial miscible system properties are needed to be determined becouse of the possibilities of using liquid storage natural gas as alternative fuel to gasoline, liquefied petroleum gas and liquefied natural gas.

However, some recent research indicated that two immiscible systems of liquefied petroleum gas and methane (i.e.: Prothane) can be used as an alternate fuel. The main problem arising from this method is to determine the optimal condition to maximize the amount of natural gas and minimizing the 'more expensive' liquid petroleum gas.

CHAPTER 6:

Some suggestions for the improvement of storage and transportation of natural gas

As we have seen in previous chapters natural gas has taken an important place in the industrial and transportational sectors, especially for the next century it may eliminate the use of gasoline as fuel for vehicle engines. The problem arising from this 'new energy source' is the storage and transportation from the source to the consumer. Compressed Natural Gas provided a reasonable answer to the storage problem and at the same time could be used as an alternative fuel for Natural Gas Vehicle (NGV). But, due to its high risk and expensive infrastucture, wide applications of this method is not foreseen.

Natural gas storage in the form of hydrate may give a better alternative when used in industrial sector. However, the stability of natural gas delivery is one of the attractive factor of this method; a better undertanding of this gas-hydrate behaviour and an optimal condition development is required to reduce the refrigeration cost. A suitable agent may be added to improve these aspects.

Adsorption of natural gas on activated carbon (ANG) also offers an alternative method through the usage of natural gas. The major problem of this method is the expense involved in activated carbon, therefor a cheap, high surface area adsorbing and low bulk-density activated carbon must be developed for an optimal use of this method.

Natural gas blending in hydrocarbon is another possibility of storage and transport and at the same time use as engine fuel for the transportational sector. The main advantage of this method is the total combustiblity of the entire engine-content when the LSNG technique is used. Collecting information of solubility, miscibilty and retrogade phenomena of natural gas in hydrocarbon is the main research field for an optimal design of LSNG.

All of these methods ,except CNG, are operational at acceptable pressure range (± 2 MPa until ±5 MPa). Hence, this factor determined the use of ANG, natural gas-hydrate system and LSNG instead of CNG which is operationally at ±17 MPa.

Some suggestions for improvement to store and transport natural gas are:

- Gas-hydrate form; optimal conditions and suitable additives may be found to improve the stability and reduce the refrigeration cost.
- ANG; a cheap, high surface area adsorbent and a low bulk- density activated carbon may be developed to increase the storage- and delivery capacity of ANG system.
- LSNG; collecting data on solubility,misciblity of natural gas in liquid hydrocarbon and optimal design of the fuel tank are necessary for optimum use of liquid storage natural gas as vehicular fuel .

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Nomenclature

A : Specific surface area of activated carbon
ANG : Adsorption Natural Gas
a_s : Saturation capacity
CNG : Compressed Natural Gas
exp.I : Experiment I
exp.II : Experiment II
exp.III : Experiment III
GCMC : Grand Canonical Monte Carlo
H : Slit width
LPG : Liquid Petroleum Gas
LSNG : Liquid Storage Natural Gas
NGV : Natural Gas Vehicle
t_{sto} : Storage temperature of gas hydrate system
ρ : Bulk density of activated carbon

Appendix A: Tables

Table 1. Some properties of methane, propane, hydrogen and gasoline[4–6]

Property	Methane	Propane	Hydrogen	Gasoline
Specific gravity at NTP relative to air	0·55	1·52	0·07	≅0
Normal boiling point (K)	111·6	231	20·3	310–478
Density of gas at NTP (kg/m^3)	0·651	1·96	0·084	≅40
Density ratio, NTP liquid/NTP gas	649	259	845	≅150
Diffusion coefficients in NTP air (cm^2/s)	0·16	0·10	0·61	≅0·05
Quenching gap in NTP air (mm)	2·03	1·78	0·64	2·0
Limits of flammability (vol. %)	5·3–15	2·1–10·4	4–75	1–7·6
Limits of detonation in air (vol. %)	6·3–13·5	3·4–35 (in O_2)	18·1–59	1·1–2·2
Minimum energy for ignition in air (mJ)	0·29	0·305	0·02	0·24
Autoignition temperature (K)	813	740	858	501–744
Maximum flame temperature in air (K)	2 148	2 243	2 318	2 470
Burning velocity in NTP air (cm/s)	37–45	43–52	278	37–43
Energy of stoichiometric mixture (MJ/m^3)	3·58	3·79	3·58	3·91

Table 2: Adsorption storage of methane on AX-31 at 3.5 MPa and 25°C

	Original	Pellets	% Change
Sto.(g/l)	73	103	42
Sto.(v/v)	101	144	42

Table 3: Adsorption storage of methane on CNS at 3.5 MPa and 25°C

	Original	Pellets	% Change
Sto.(g/l)	59	74	25
Sto.(v/v)	82	103	25

Table 4: Comparison of methane delivered by ANG with CNG at 20.7 MPa. ANG delivery based on an operating cycle from 3.4 MPa down to 0.14 MPa.

	Delivered CH_4 (V/V)	
Storage medium	Monolith	Pelletized
GCMC simulations	195	137
Perfect affinity	380	255
CNG	216	

Table 5: Comparison of energy density of ANG at a filling pressure of 3.4 MPa with CNG at 20.7 MPa. Energy density for ANG based operting cycle from the filling pressure down to 0.14 MPa.

	Energy density	
Storage medium	Monolith	Pelletized
GCMC simulations	0.246	0.173
Perfect affinity	0.480	0.322
CNG	0.290	
Gasoline	1.000	

Appendix B: Figures

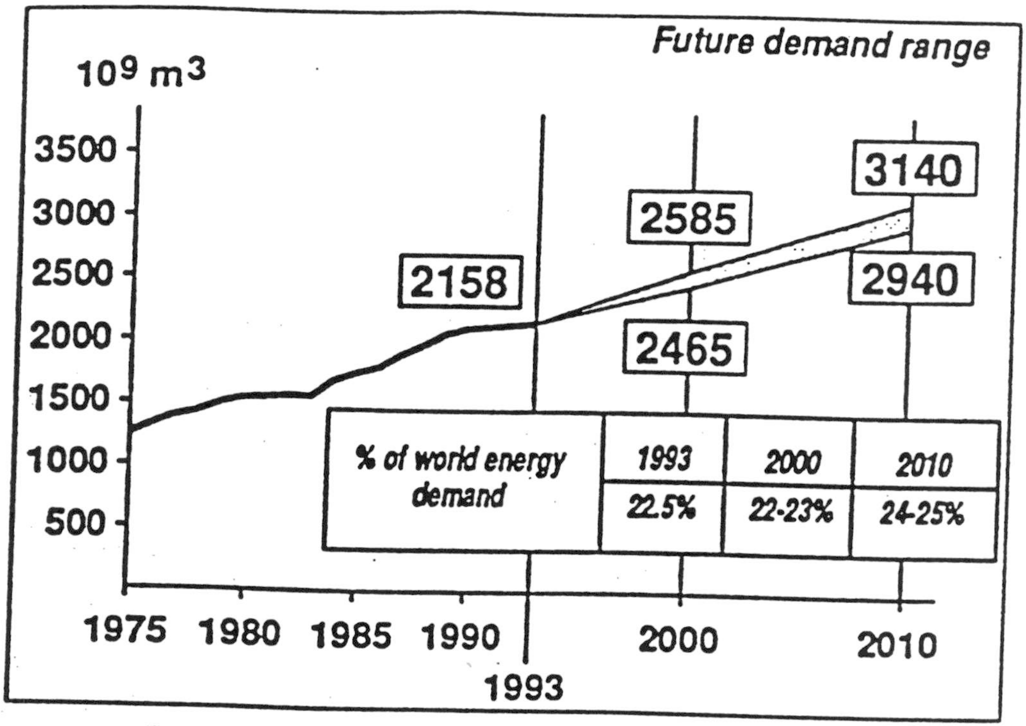


Fig 1.1 : Outlook for world gas demand

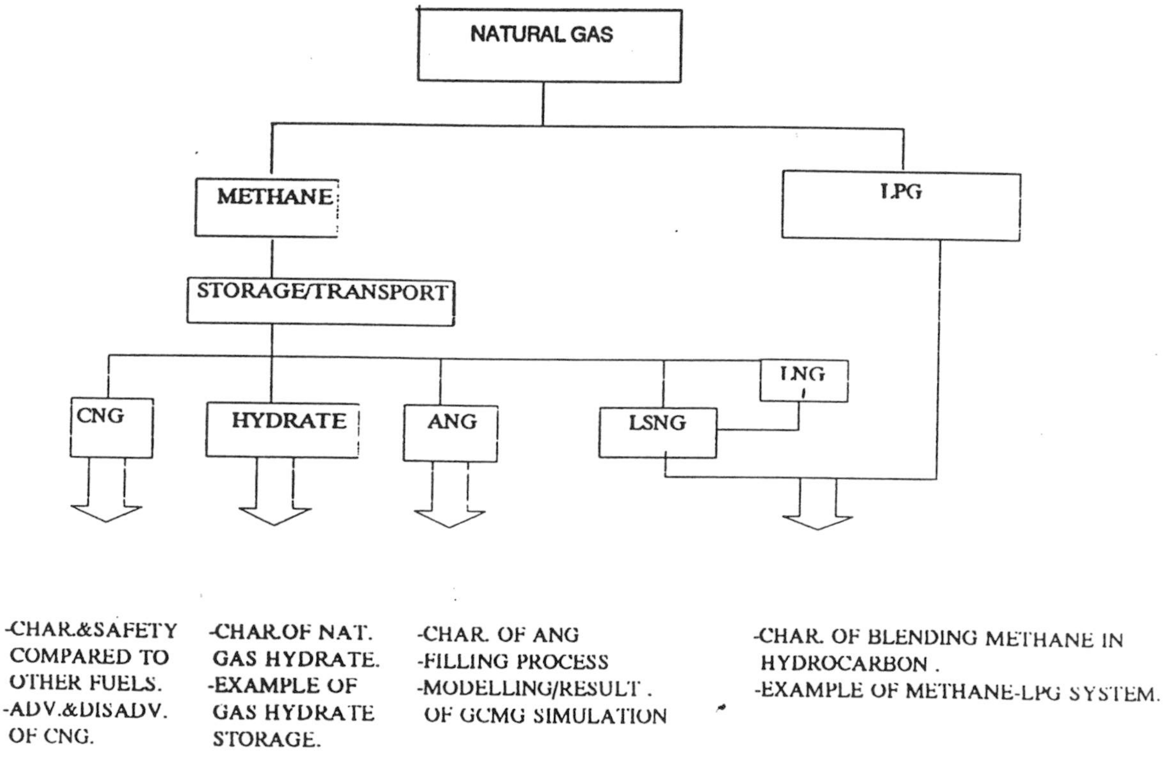


Fig.1.2 Summary of the possibilties to store and transport of natural gas.

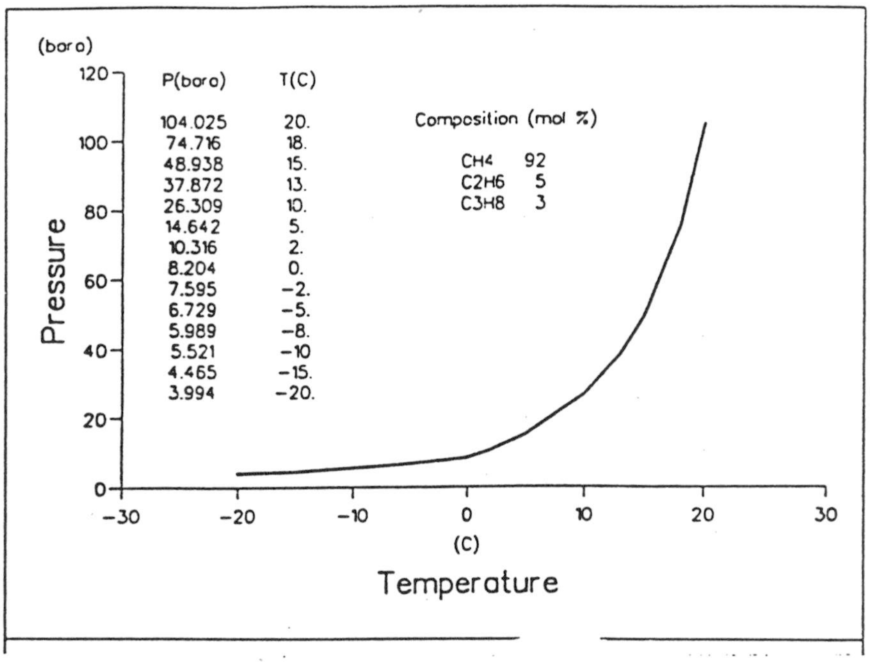


Fig 3.1 : Equilibrium line for a natural gas mixture consisting of 92, 5,and 3 mol% methane ethane, and propane, respectively.

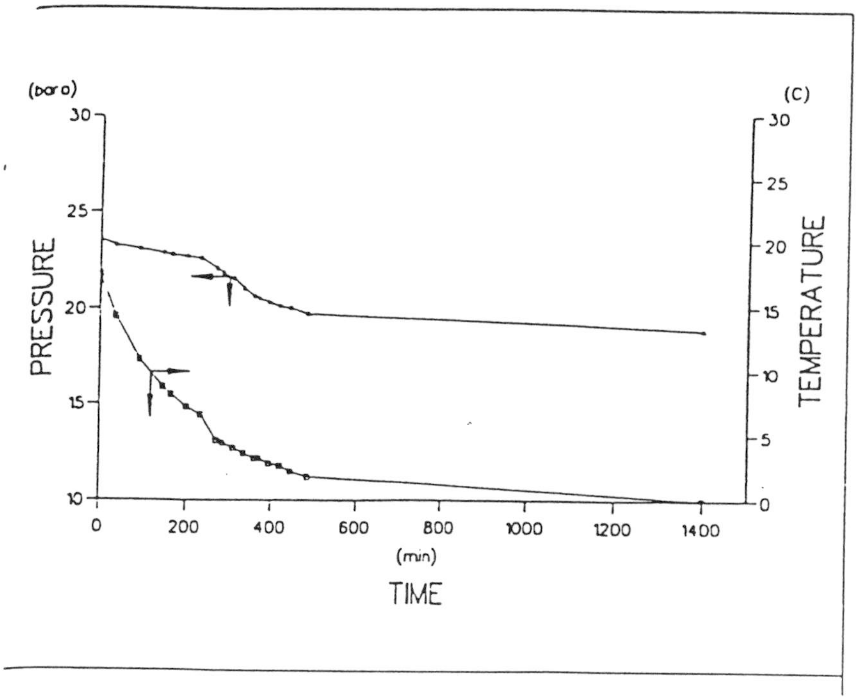


Fig 3.2 : Vessel pressure and temperature with time for hydrate formation of exp I.

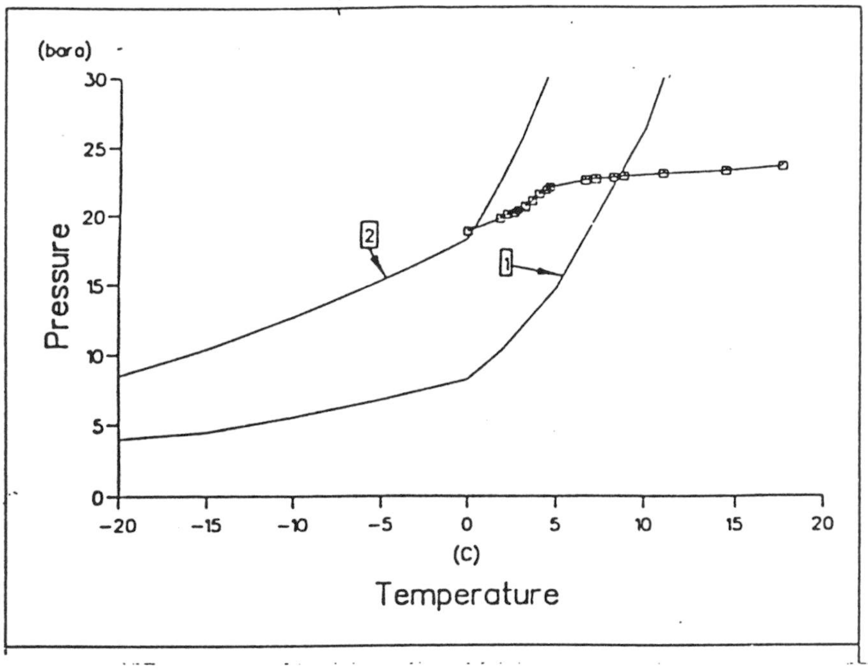


Fig 3.3 : Vessel pressure and temperature for hydrate production exp.I with equilibrium line at beginning (point 1) and end (point 2) of experiment.

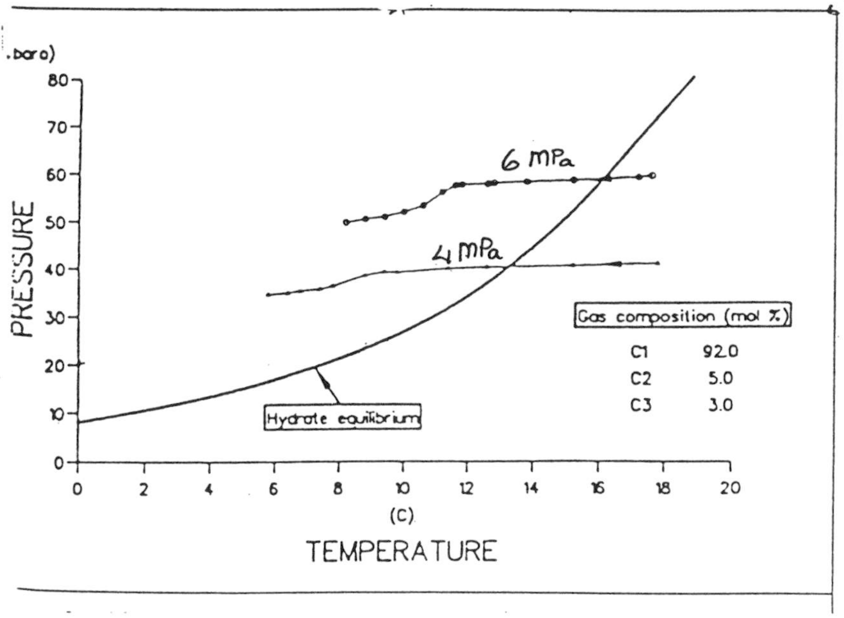


Fig 3.4 : Vessel pressure and temperature for hydrate formation at different pressures with equilibrium line at beginning of experiment.

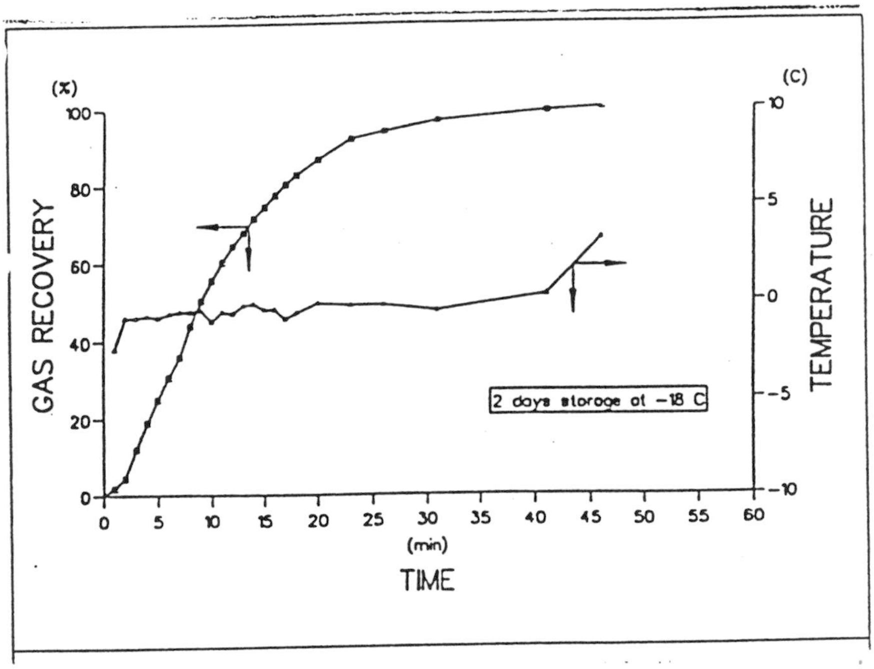


Fig 3.5 : Gas mixture recovered by melting hydrate from exp.I after 2 days of storage at -18°C.

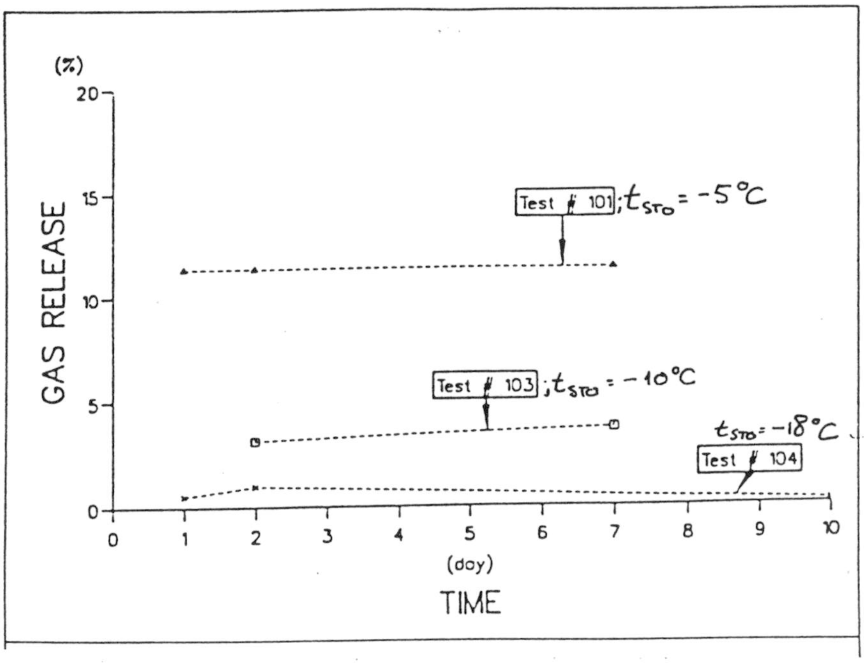


Fig 3.6 : Gas mixture release with time by melting hydrates from exp.I, exp.II and exp.III after storage at -5,-10 and -18 °C, respectively.

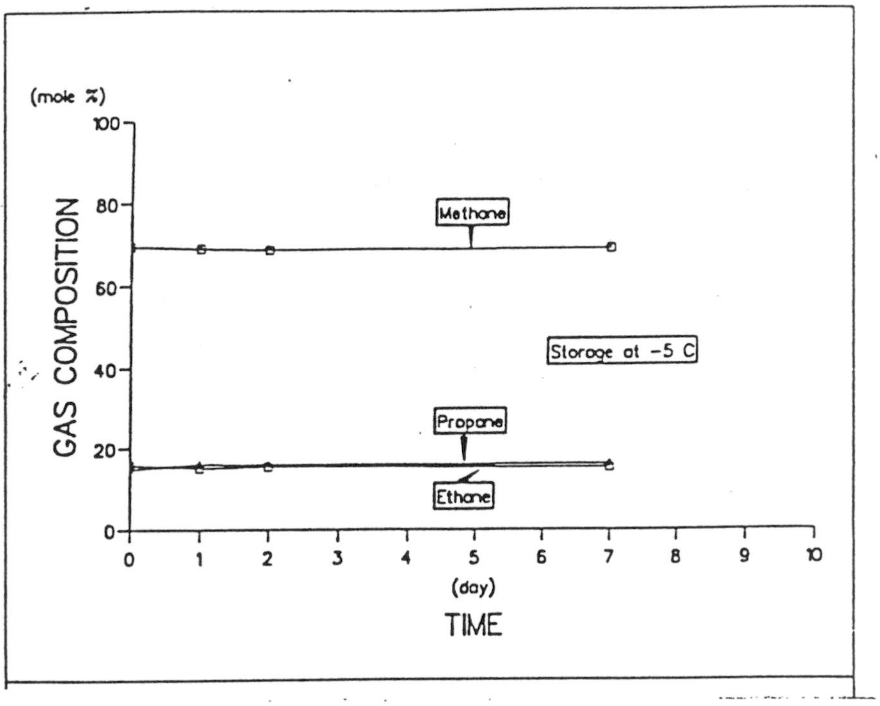


Fig 3.7 : Gas mixture composition at melting of hydrate samples from exp.I.

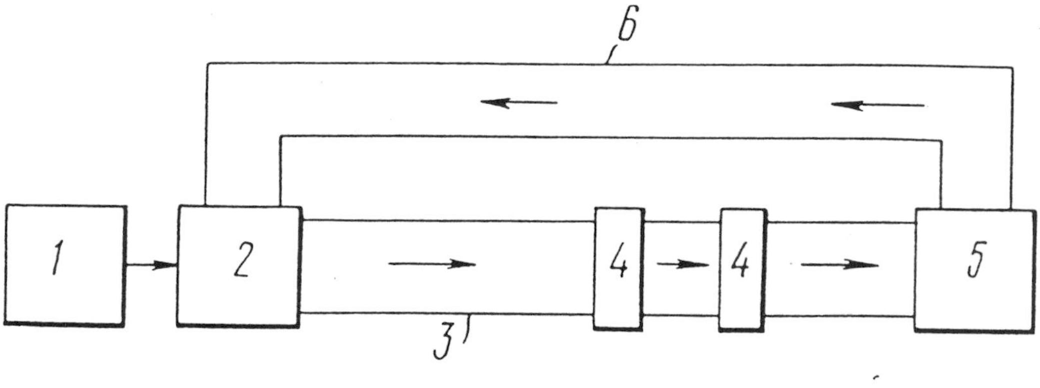


Fig 3.8 : Block diagram of system for transporting of natural gas hydrate.

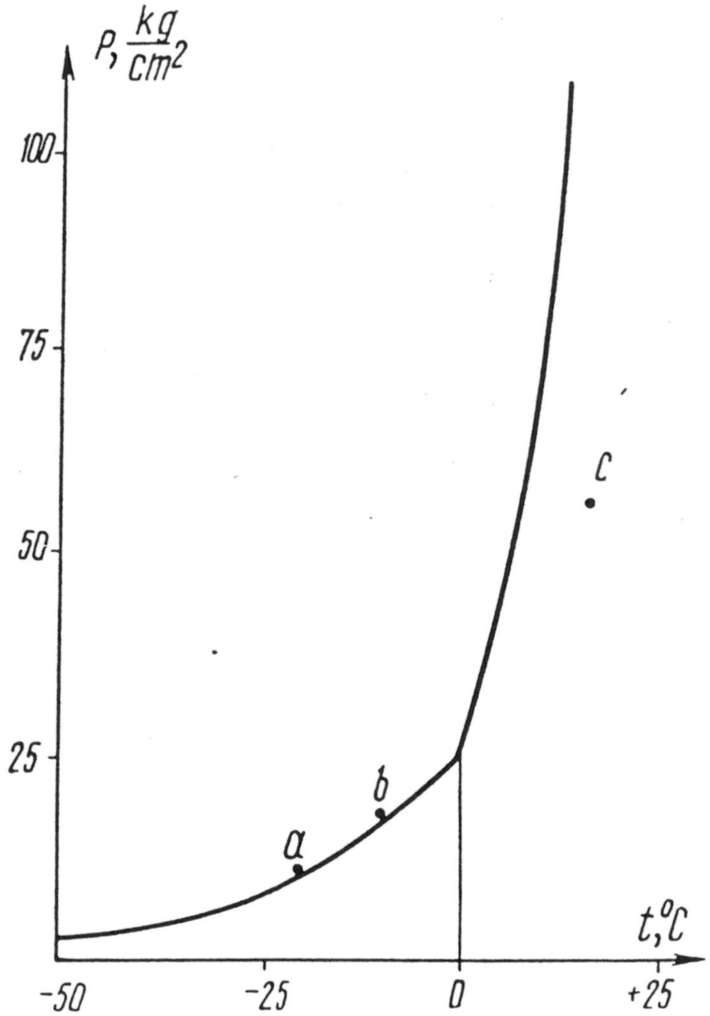
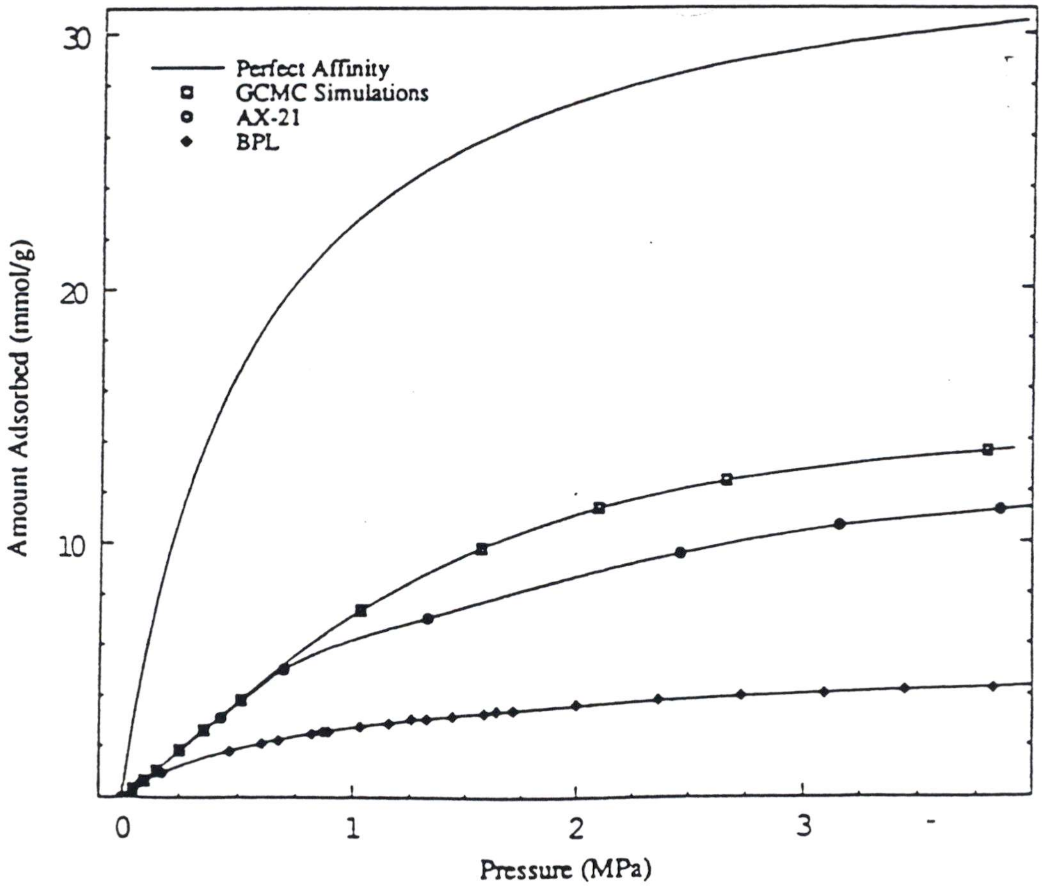
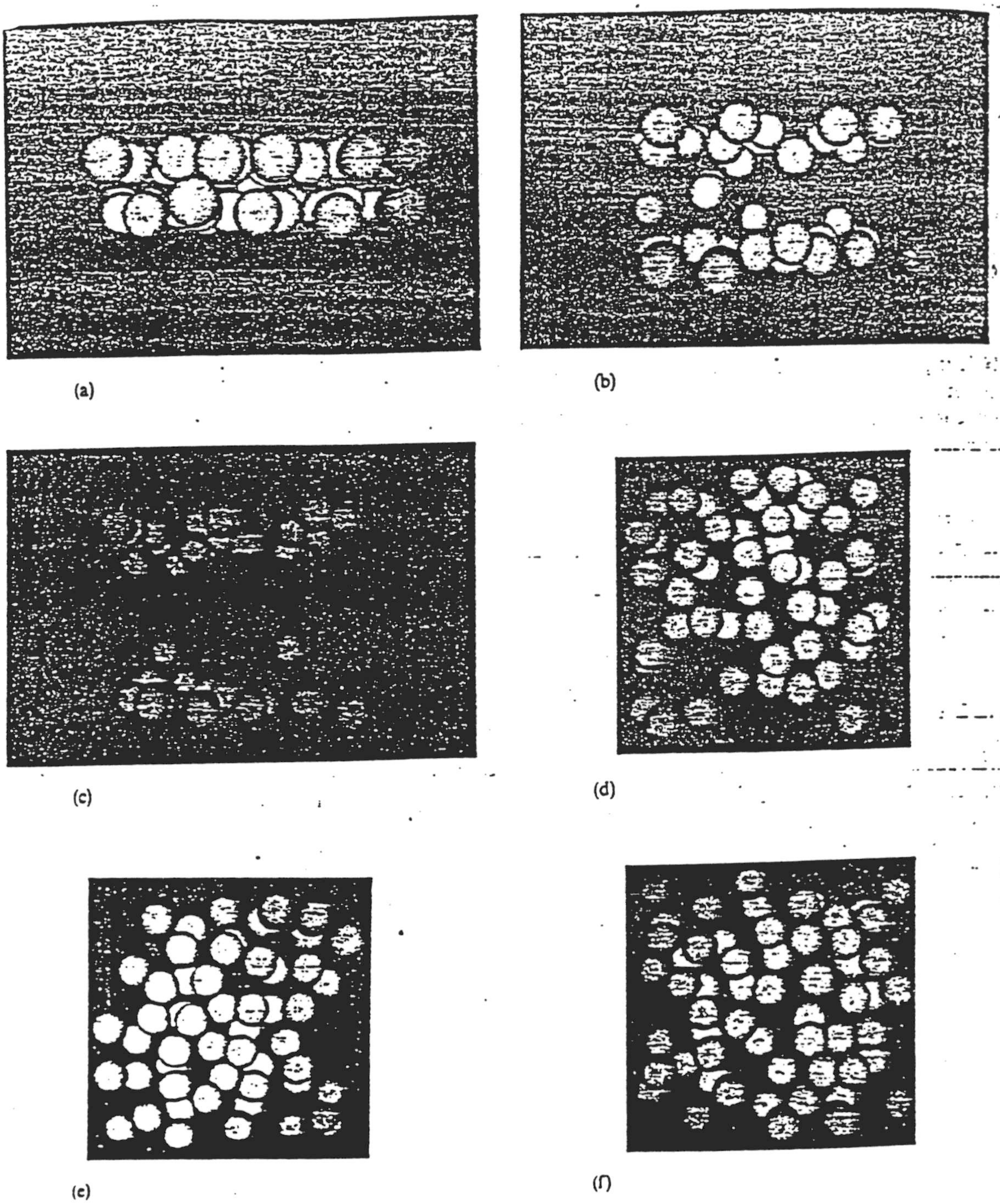


Fig 3.9 : Curve of phase equilibrium of hydrates.

Fig 4.1 : Ide$\overset{a}{\vee}$lized slit model.

Fig 4.2 : Comparison of perfect affinity model & GCMC simulation with experiment adsorption isoterm of methane on carbon at 25 °C.





(a) (b) (c) (d) (e) (f)

Fig 4.3 : Pictures of methane molecules adsorbed in slit for typical equilibrium configurations at 25°C:(a)H=11.4Å, P=2.0 MPa; (b)H=19.1Å, P=2.0 MPa; (c)H=26.7Å, P=2.0 MPa; (d)H=11.4Å, P=2.0 MPa; (e) H=11.4Å,P=3.0 MPa; (f)H=11.4Å, P=5.1 MPa.

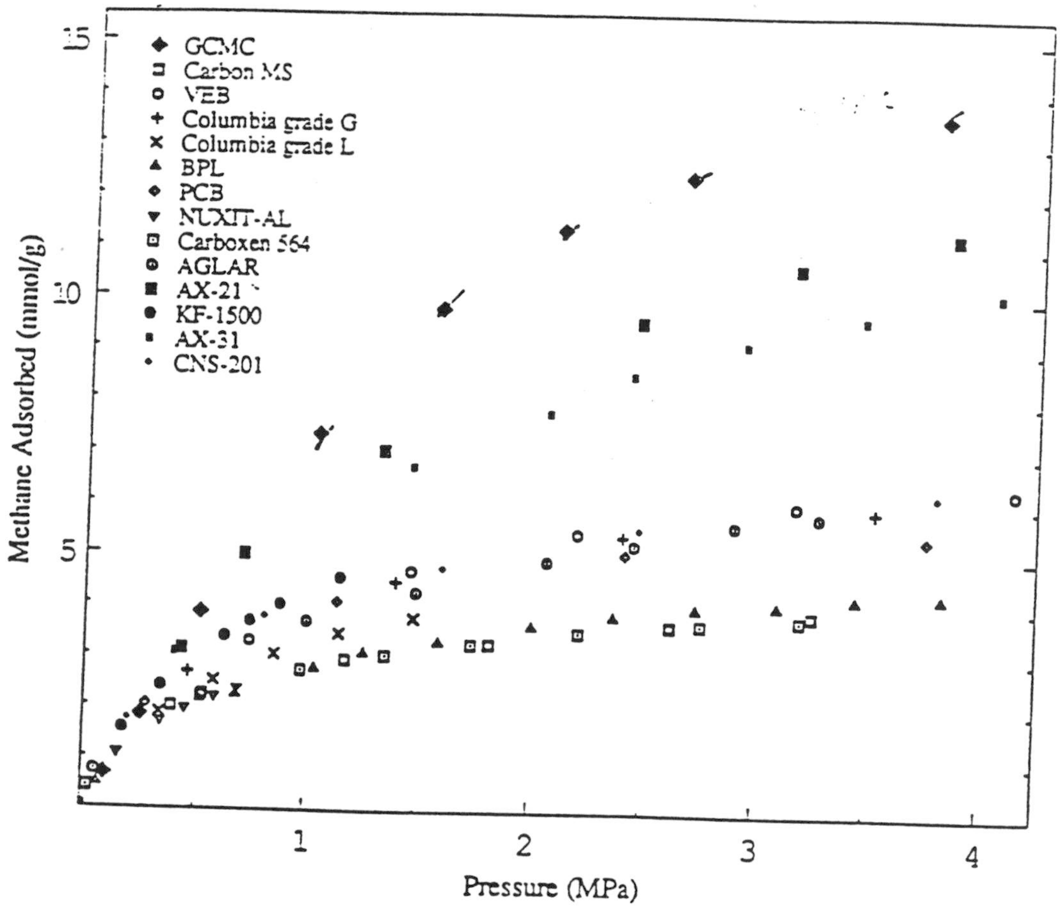


Fig 4.4 : Comparison of GCMC simulations with experimental data for adsorption on methane of carbon at 25°C;low pressure range.

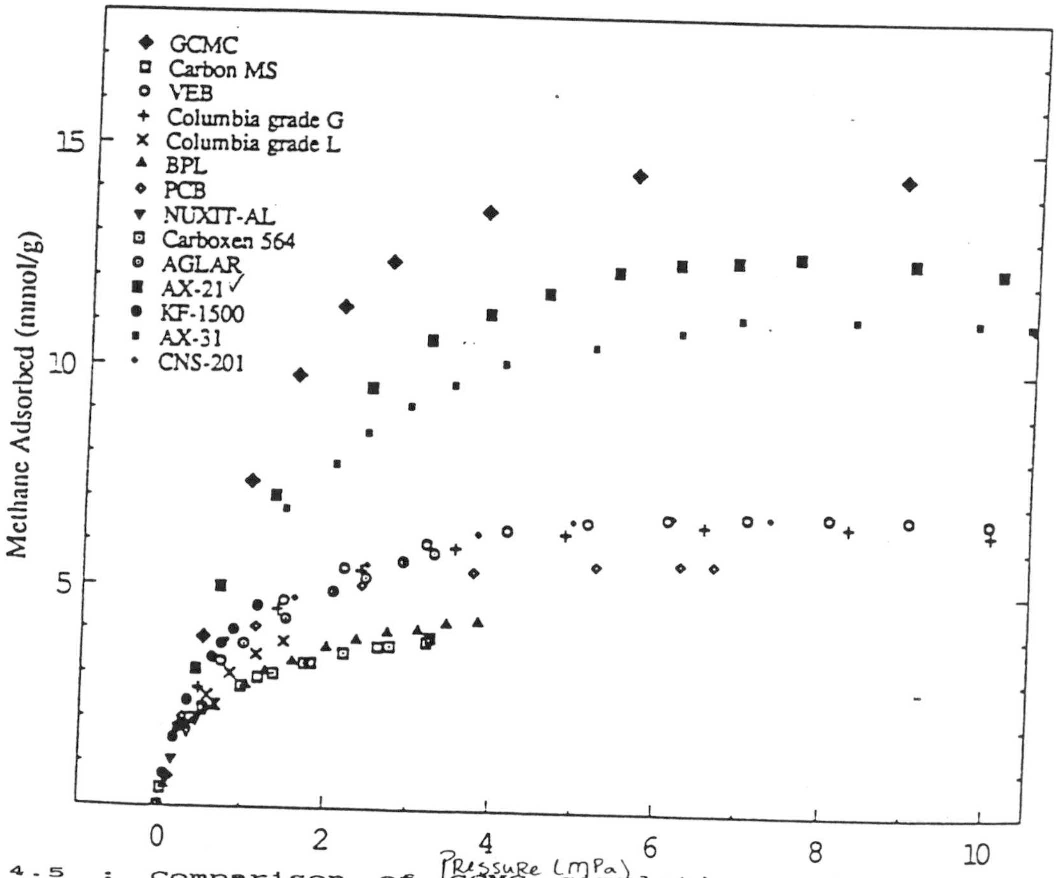


Fig 4.5 : Comparison of GCMC simulations with experimental data for adsorption on methane of carbon at 25°C;medium pressure range.

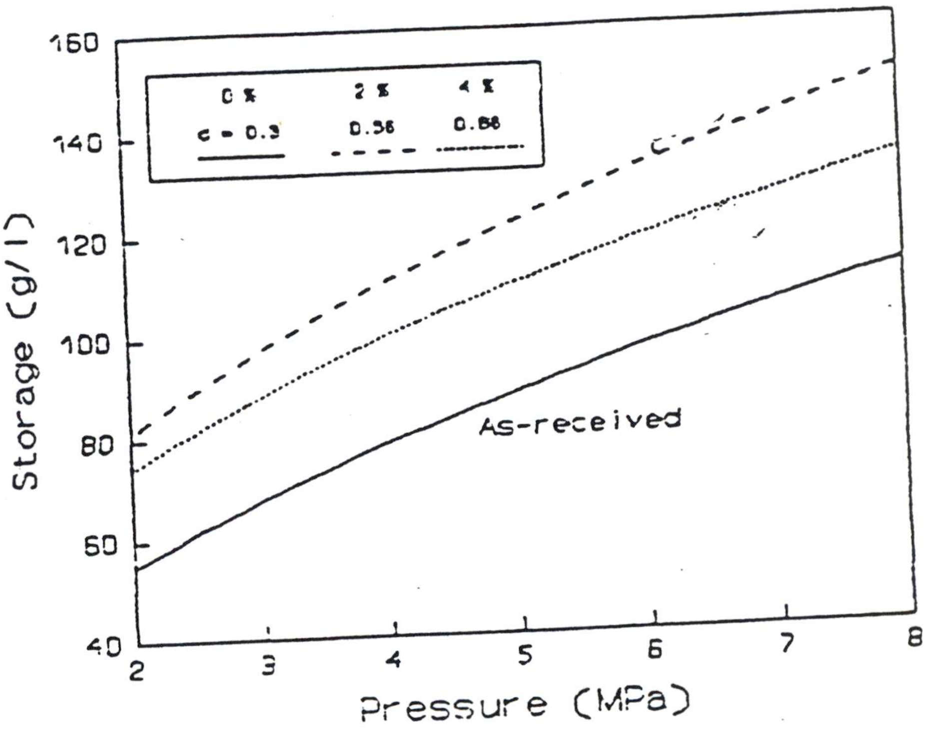


Fig 4.6 : Methane storage capacity ~~in~~ as function of pressure and various binder propotions.

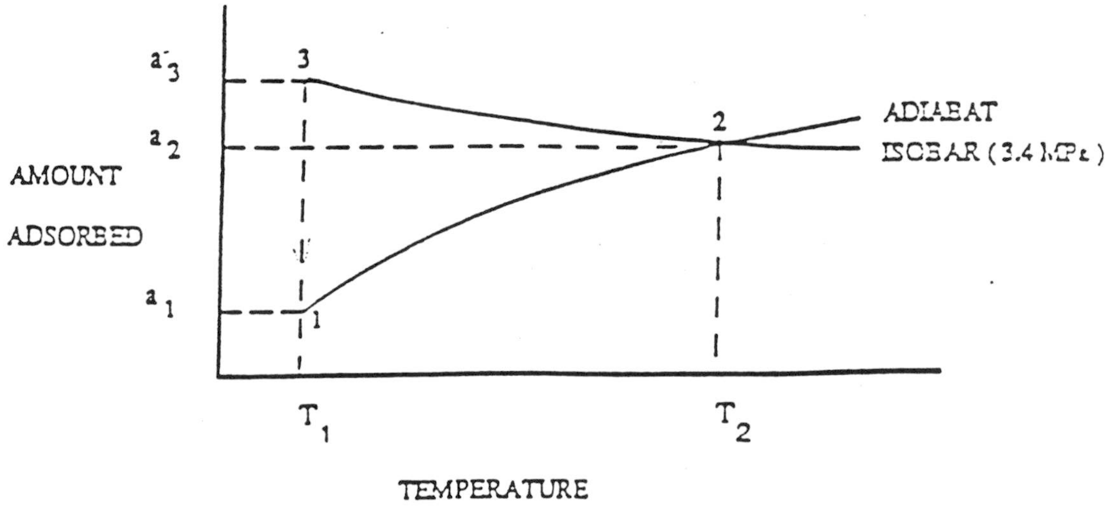


Fig 4.7 : Schematic diagram for adiabatic filling. Point 1 is ambient temperature (25°C) and exhaustion pressure (0.14 MPa). Point 3 is the amaount adsorbed (a_3) for isotermal filling at 3.4 MPa. Point 2 at the intersection of the adiabatic through point 1 with the isobar at 3.4 MPa shows the amount adsorbed (a_2) for adiabatic filling.

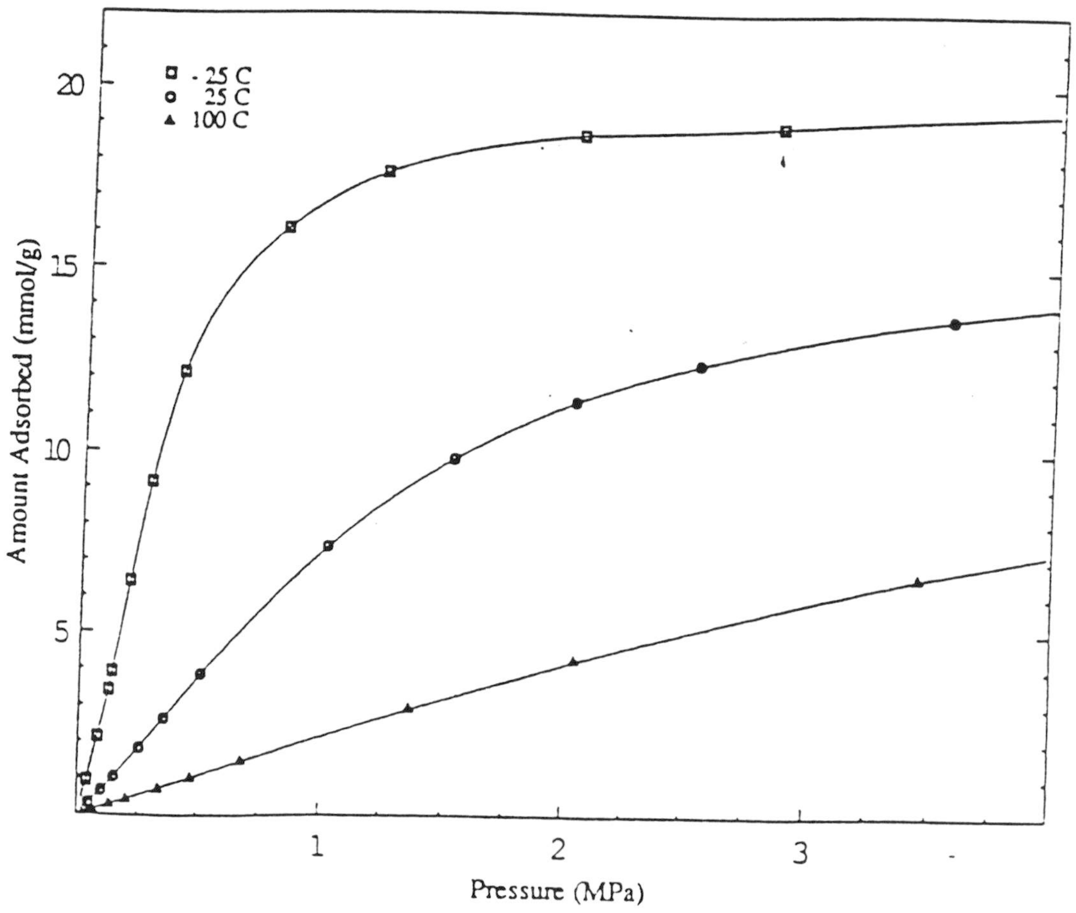


Fig 4.8 : Comparison of GCMC simulation isoterm at various temperatures: -25°C (temperature corresponding to maximum mathane delivery), 25°C (ambient temperature) and 100°C (adiabatic filling temperature)