CHAPTER 2
Pertinent Literature Survey

2.1 General Background

2.1.1 World picture for natural gas [4]

The current status of primary energy sources is summarized in Figure 2. 1. Basically, dry natural gas (natural gas with natural gas liquids [NGLs] removed) is on par with coal in importance.
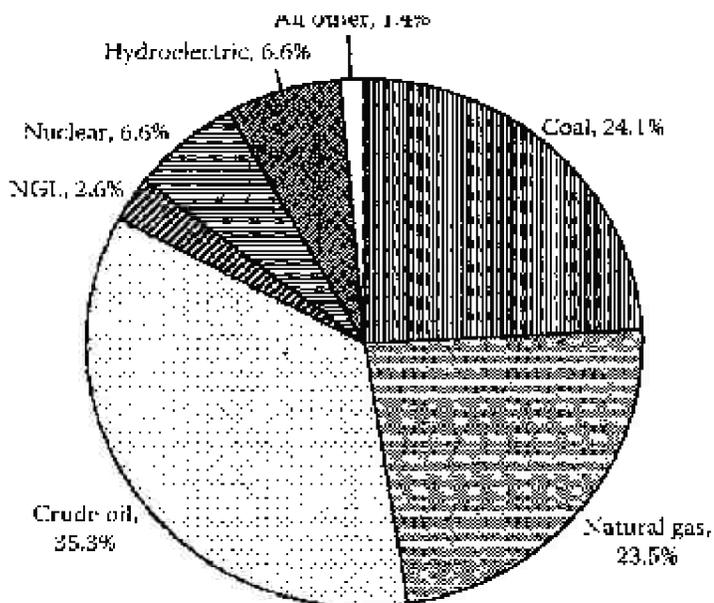

Figure 2.1 Primary sources of energy in the world in 2003.

2.2 What Is Natural Gas?

Natural gas is a subcategory of petroleum that is a naturally occurring complex mixture of hydrocarbons, with a minor amount of inorganic compounds. Geologists and chemists agree that petroleum originates from plants and animal remains that accumulate on the sea/lake floor along with the sediments that form sedimentary rocks. The processes by which the parent organic material is converted into petroleum are not understood.

The contributing factors are thought to be bacterial action, shearing pressure during compaction, heat, natural distillation at depth, possible addition of hydrogen from deep-seated sources, presence of catalysts, and time.

2.3 <u>Sources of Natural Gas</u> [4]

Conventional natural gas generally occurs in deep reservoirs, either associated with crude oil (associated gas) or in reservoirs that contain little or no crude oil (non-associated gas). Associated gas is produced with the oil and separated at the casing head or wellhead. Gas produced in this fashion is also referred to as casing head gas, oil well gas, or dissolved gas. Non-associated gas is sometimes referred to as gas-well gas or dry gas. However, this dry gas can still contain significant amounts of NGL components. Roughly 93% of the gas produced in the United States is non-associated. A class of reservoirs, referred to as gas condensate reservoirs, occurs where, because of the high pressures and temperatures, the material is present not as a liquid or a gas but as a very dense, high-pressure fluid.
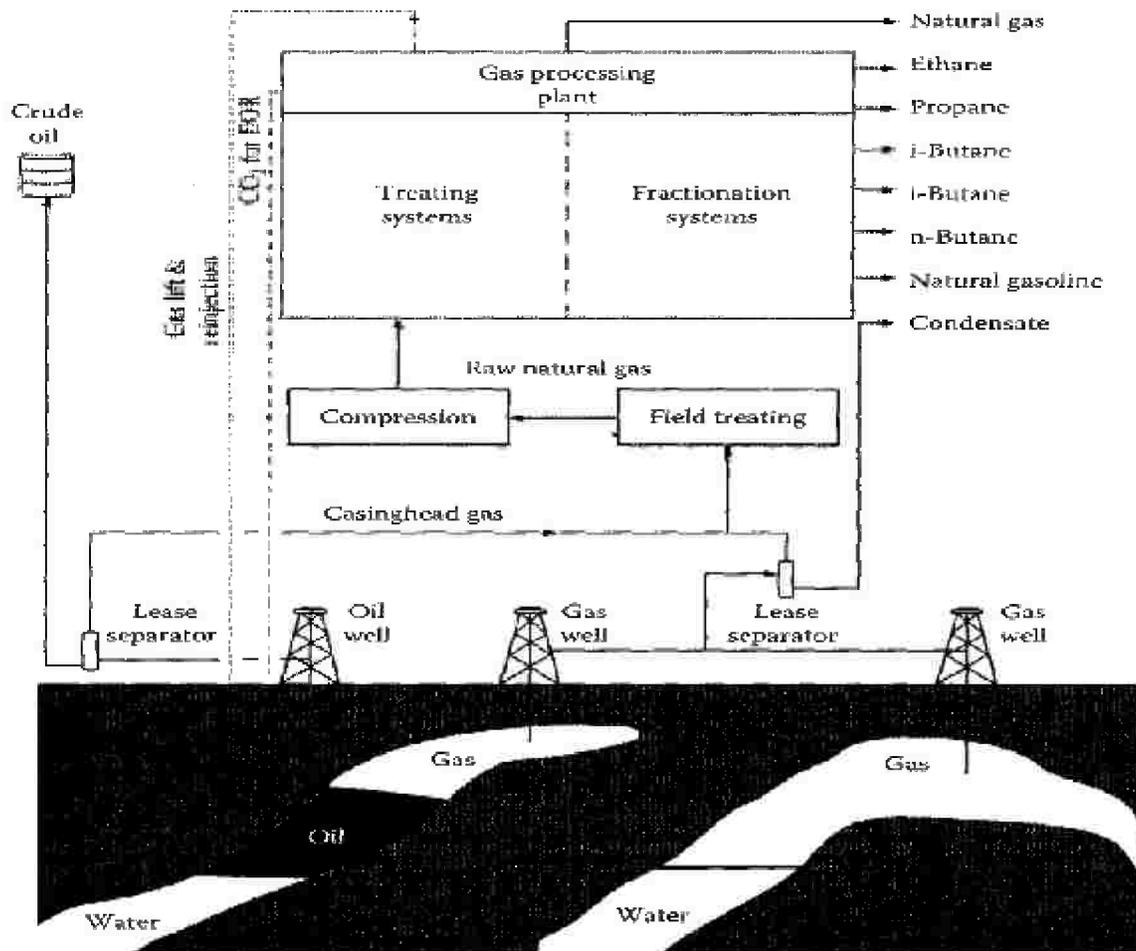

Figure 2.2 Schematic overview of natural gas industry. (Adapted from Cannon, 1993.)

Figure 2.2 shows a simplified flow of material from reservoir to finished Product and provides an overall perspective of the steps involved in taking natural gas from the wellhead to the customer.

2.4 Composition of Natural Gas [5]

Table 2.1 shows the composition of a typical natural gas. It indicates that methane is the major component of the gas mixture. The inorganic compounds nitrogen, carbon dioxide, and hydrogen sulfide are not desirable because they are not combustible and cause corrosion and other problems in gas production and processing systems. Depending upon gas composition, especially the content of inorganic compounds, the heating value of natural gas usually varies from 700 Btu/scf to 1,600 Btu/scf.

Natural gas accumulations in geological traps can be classified as reservoir, field, or pool. A reservoir is a porous and permeable underground formation containing an individual bank of hydrocarbons confined by impermeable rock or water barriers and is characterized by a single natural pressure system. A field is an area that consists of one or more reservoirs all related to the same structural feature. A pool contains one or more reservoirs in isolated structures. Wells in the same field can be classified as gas wells, condensate wells, and oil wells.

Table 2.1: Typical Composition of Natural Gas

Compound	Mole Fraction
Methane	0.8407
Ethane	0.0586
Propane	0.0220
Butane	0.0093
Pentane	0.0052
Hexane	0.0028
Heptanes and Heavier	0.0076
Carbon Dioxide	0.013
Hydrogen sulfide	0.0063
Nitrogen	0.0345
Total	1.0000

Because natural gas is petroleum in a gaseous state, it is always accompanied by oil that is liquid petroleum. There are three types of natural gases; *viz.*, non-associated gas, associated gas, and gas condensate. Non-associated gas is from reservoirs with minimal oil. Associated gas is the gas dissolved in oil under natural conditions in the oil reservoir. Gas condensate refers to gas with high content of liquid hydrocarbon at reduced pressures and temperatures.

2.5 Utilization of Natural Gas [5]

Natural gas is one of the major fossil energy sources. When one standard cubic feet of natural gas is combusted, it generates 700 Btu to 1,600 Btu of heat, depending upon gas composition. Natural gas provided close to 24 percent of U.S. energy sources over the three-year period 2000-2002.

Natural gas is used as a source of energy in all sectors of the economy. Figure 3 shows that during the three-year period 2000-2002, natural gas consumption was almost equitably distributed across all sectors of the U.S. economy (except transportation).
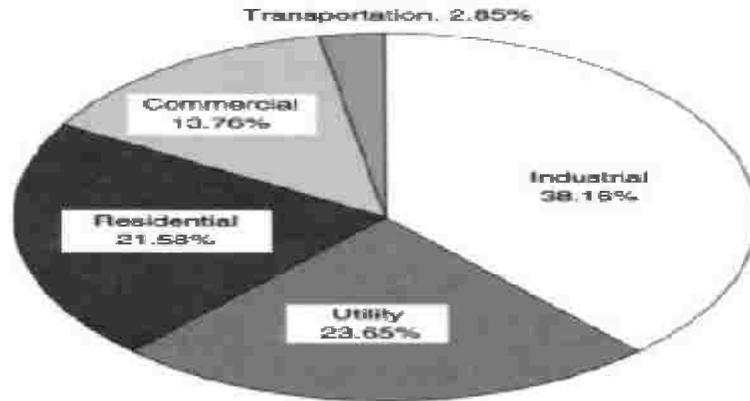

Figure 2.3 Natural gas is used as a source of energy in all sectors of the U.S. economy - 2004.

2.6 Impurities[4]

A number of impurities can affect how the natural gas is processed, for example,

Water. Most gas produced contains water, which must be removed.
Sulfur species. If the hydrogen sulfide (H_2S) concentration is greater than 2 to 3%, carbonyl sulfide (COS), carbon disulfide (CS_2), elemental sulfur, and mercaptans may be present.
Mercury. Trace quantities of mercury may be present in some gases. Levels reported vary from 0.01 to 180 $\mu g/Nm^3$. Because mercury can damage the brazed aluminum heat exchangers used in cryogenic applications, it has to be removed.
NORM. Naturally occurring radioactive materials (NORM) may also be present problems in gas processing. The radioactive gas radon can occur in wellhead gas.
Oxygen. Some gas-gathering systems in the United States operate below atmospheric pressure. As a result of leaking pipelines, open valves, and other system compromises, oxygen is an important impurity to monitor. A significant amount of corrosion in gas processing is related to oxygen ingress.

2.7 Classification [4]

Natural gases commonly are classified according to their liquids content as either lean or rich and according to the sulfur content as either sweet or sour. This section provides some quantification of these qualitative terms.

A. Liquids content
Gas composition plays a critical role in the economics of gas processing. The more liquids, usually defined as C2+, in the gas, the "richer" the gas. Extraction of these liquids produces a product that may have a higher sales value than does natural gas.

B. Sulfur content

Sweet and sour refer to the sulfur (generally H_2S) content. A sweet gas contains negligible amounts of H_2S, whereas a sour gas has unacceptable quantities of H_2S, which is both odiferous and corrosive. When present with water, H_2S is corrosive. The corrosion products are iron sulfides, FeSX, a fine black powder. Again, the terms are relative, but generally, sweet means the gas contains less than 4 ppm_v of H_2S.

2.8 Operational Problems of Water Vapor in Natural Gas [6]

Natural gas dehydration is the process of removing water vapor from the gas stream to lower the dew point of that gas. Water is the most common contaminant of hydrocarbons. It is always present in the gas–oil mixtures produced from wells. The dew point is defined as the temperature at which water vapor condenses from the gas stream. The sale contracts of natural gas specify either its dew point or the maximum amount of water vapor present. There are three basic reasons for the dehydration of natural gas streams:

2.8.1 To prevent hydrate formation. Hydrates are solids formed by the physical combination of water and other small molecules of hydrocarbons. They are icy hydrocarbon compounds of about 10% hydrocarbons and 90% water. Hydrates grow as crystals and can build up in orifice plates, valves, and other areas not subjected to full flow. Thus, hydrates can plug lines and retard the flow of gaseous hydrocarbon streams. The primary conditions promoting hydration formation are the following:

i. Gas must be at or below its water (dew) point with ''free'' water present.
ii. Low temperature.
iii. High pressure.

2.8.2 To avoid corrosion problems. Corrosion often occurs when liquid water is present along with acidic gases, which tend to dissolve and disassociate in the water phase, forming acidic solutions. The acidic solutions can be extremely corrosive, especially for carbon steel, which is typically used in the construction of most hydrocarbon processing facilities.

2.8.3. Downstream processing requirements. In most commercial hydrocarbon processes, the presence of water may cause side reactions, foaming, or catalyst deactivation. Consequently, purchasers typically require that gas and liquid petroleum gas (LPG) feed stocks meet certain specifications for maximum water content. This ensures that water-based problems will not hamper downstream operations.

2.9 Gas Dehydration Processes [4]

Two processes, absorption and adsorption, are the most common and are discussed in more detail.

2.9.1 Absorption processes [4,7]

Water levels in natural gas can be reduced to the 10 ppm_v range in a physical absorption process in which the gas is contacted with a liquid that preferentially absorbs the water vapor. The solvent used for the absorption should have the following properties:-

• A high affinity for water and a low affinity for hydrocarbons.
• A low volatility at the absorption temperature to reduce vaporization losses.
• A low viscosity for ease of pumping and good contact between the gas and liquid phases.
• A good thermal stability to prevent decomposition during regeneration.
• A low potential for corrosion.

In practice, the glycols, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TREG) and propylene glycol are the most commonly used absorbents; triethylene glycol is the glycol of choice in most instances. For operations in which frequent brine carryover into the contactor occurs, operators use EG because it can hold more salt than the other glycols. The solubility of sodium chloride in EG water mixtures is around 20 wt%.

Following the process flow in Figure 2.4, the regenerated glycol is pumped to the top tray of the contactor (absorber).

The glycol absorbs water as it flows down through the contactor countercurrent to the gas flow. Water-rich glycol is removed from the bottom of the contactor, passes through the reflux condenser coil, flashes off most of the soluble gas in the flash tank, and flows through the rich-lean heat exchanger to the regenerator. In the regenerator, absorbed water is distilled from the glycol at near atmospheric pressure by application of heat. The regenerated lean glycol flows through the rich-lean and glycol cooler exchanger for cooling before being recirculated to the contactor by the glycol pump.
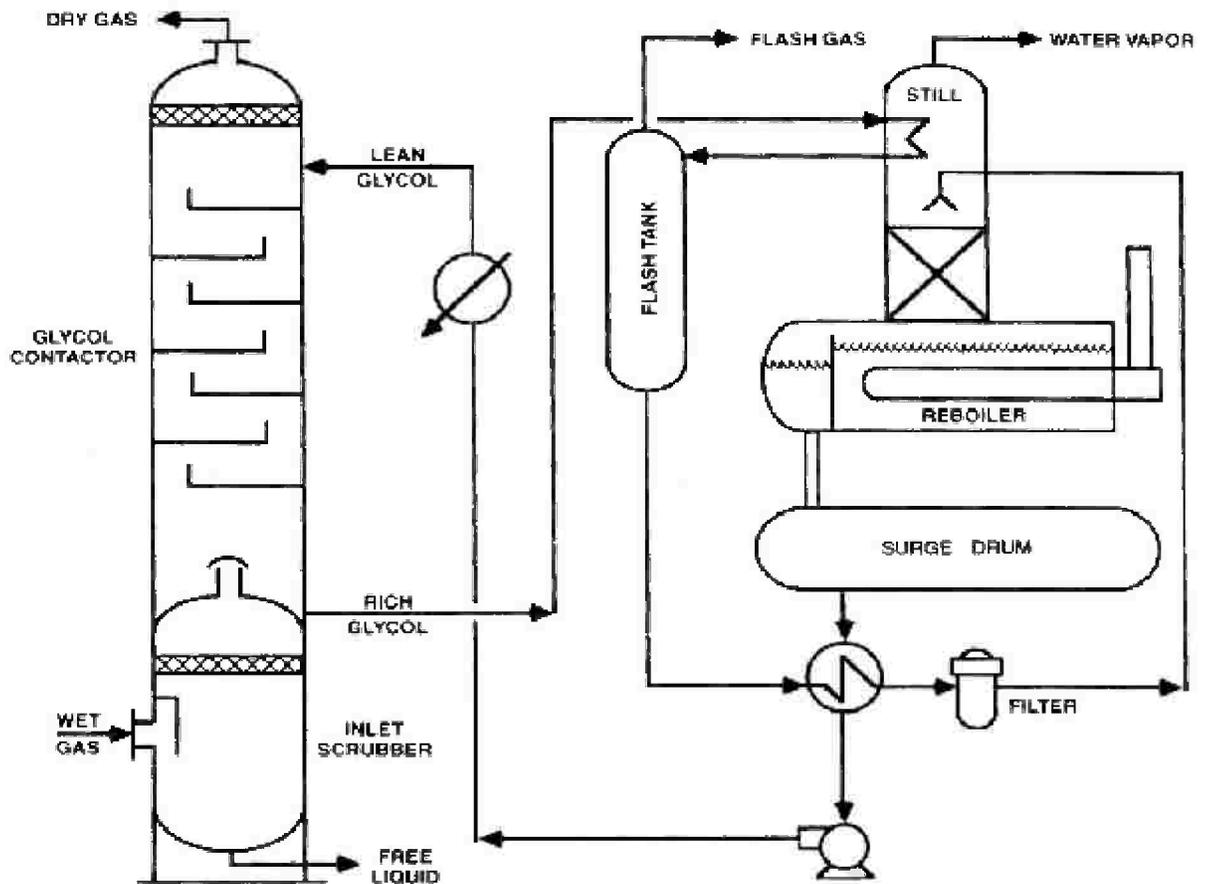
Figure 2.4: Typical process flow diagram for glycol dehydration unit

2.9.2 Adsorption [1, 7 & 8]

The two types of adsorption are physical adsorption and chemisorptions. In *physical adsorption*, the bonding between the adsorbed species and the solid phase is called van-der-Waals forces, the attractive and repulsive forces that hold liquids and solids together and give them their structure. In *chemisorptions*, a much stronger chemical bonding occurs between the surface and the adsorbed molecules.

When wet gas contacts solid desiccant particles, water is absorbed until equilibrium is achieved. This equilibrium is usually described in terms of three variables: the *contact temperature* (°F, °C), the desiccant water content or *static* capacity (wt H20/wt dry desiccant), and the *water content* of the gas (water partial pressure-mmHg or water dew point - °F, °C). Common graphical presentations are those of constant temperature (or *isotherms-Figure 2.* 5.a), constant water partial pressure (or isobars-Figure 2.5.b) and constant desiccant water content (or isosteres-Figure 2.5.c).

When wet gas flows into a fixed bed of regenerated solid desiccant particles, the result is dynamic adsorption (Figure 2.5.d). Particles nearest the gas inlet or top soon become saturated with water - the desiccant water content is in equilibrium with the "wet" inlet

gas. No more adsorption can occur in this saturated zone. All water is now adsorbed in the zone of particles below the top saturated zone. In this mass transfer zone (MTZ), the gas water content is reduced from the inlet concentration, C0, to the value in equilibrium with the regenerated desiccant, Cs. Below this MTZ the desiccant "sees" only dried gas and therefore remains regenerated. Figure 5.d shows how the MTZ moves down the bed and eventually reaches the bottom of the bed. Also shows how the exit-gas water content remains constant at Cs until the MTZ reaches the bottom and then "breakthrough" occurs. If wet gas continues to flow, the exit-gas water content continues to increase until it reaches the inlet value, Co. At this point the entire bed is completely saturated with water and there is no MTZ in the bed.
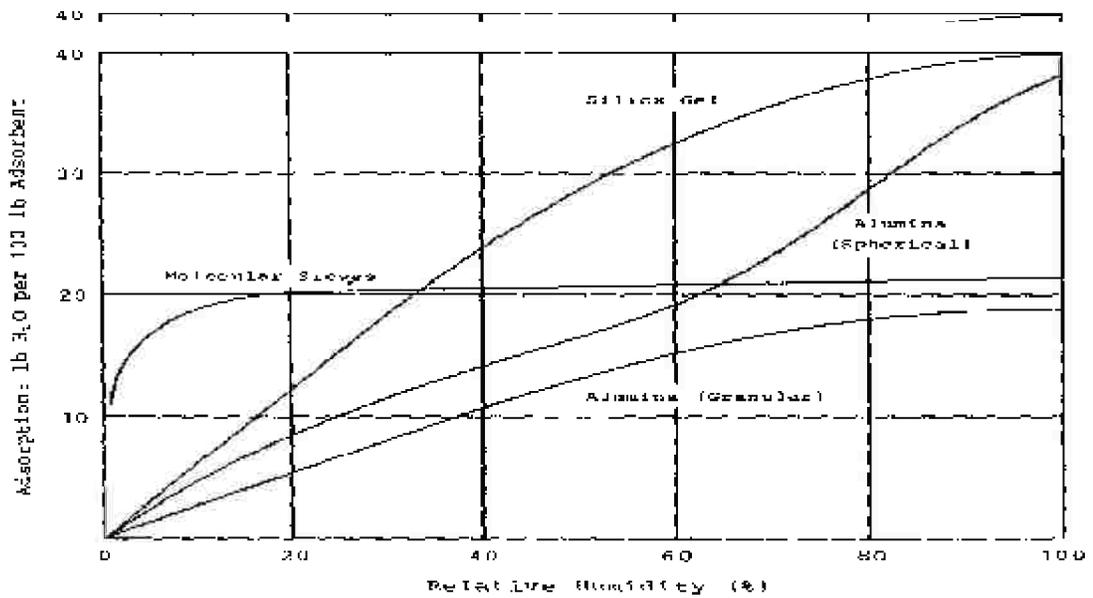

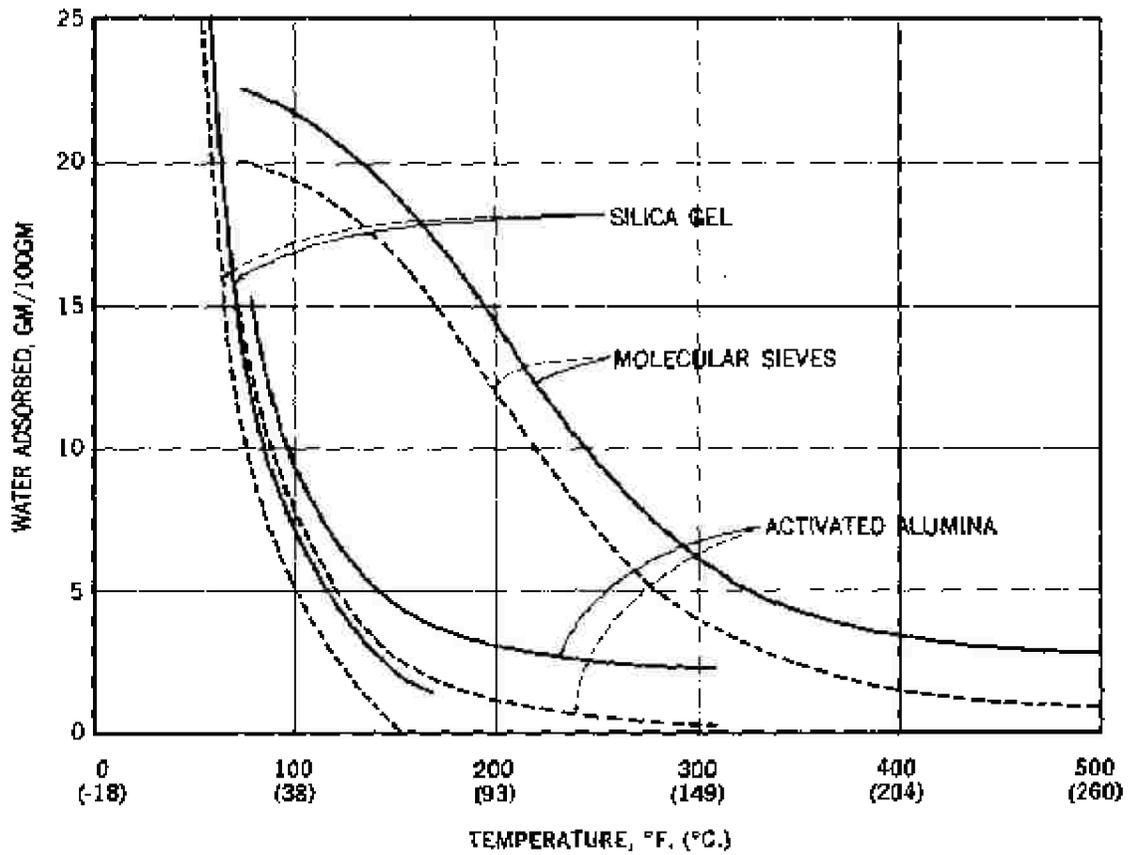**Figure 2.5a:** Water vapor isotherms

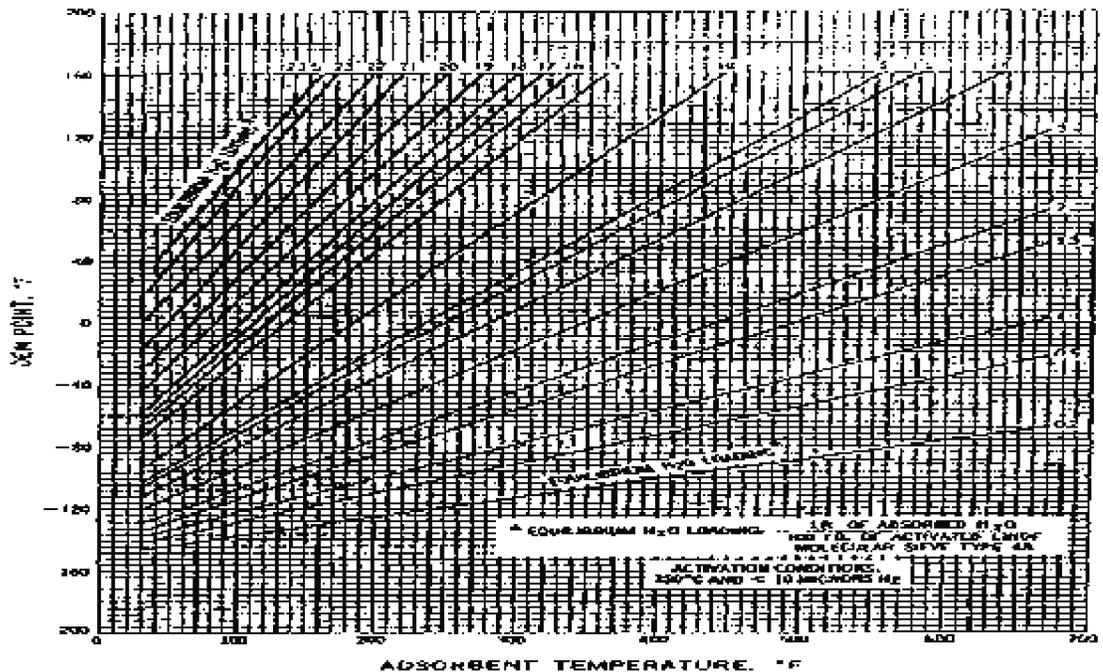**Figure 2.5b:** Water vapor adsorption isobars

Figure 2.5 c : Molecular sieve adsorbent, type 4A water adsorption isostere
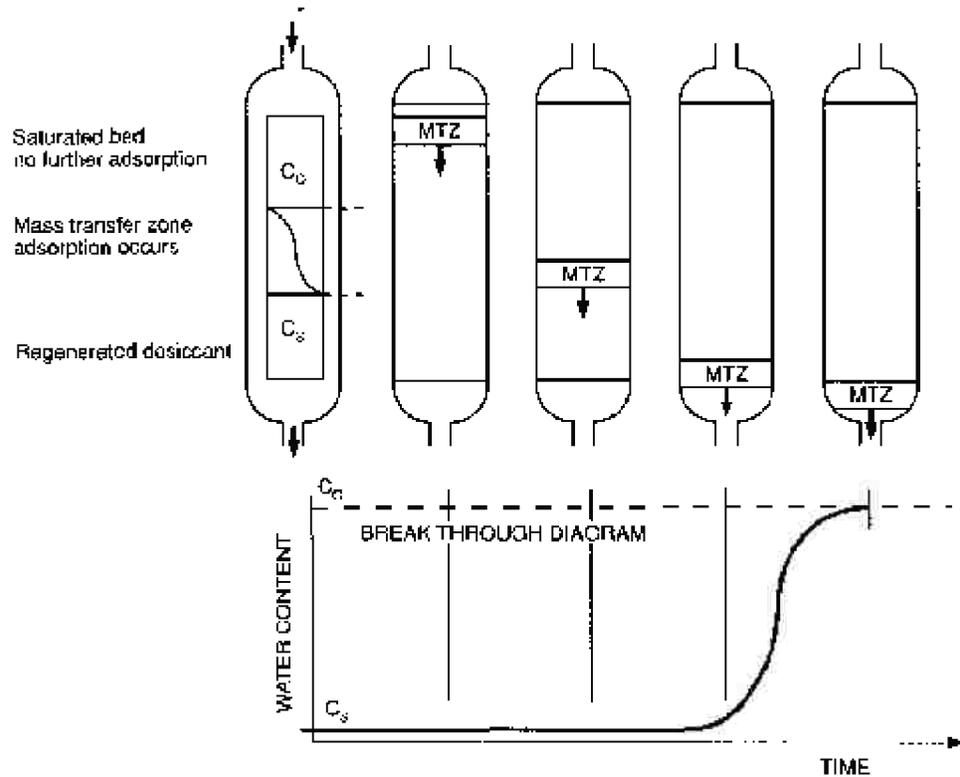

Figure 2.5.d Adsorption of water in a fixed bed.

Figure 2.5.e shows the three zones in an adsorbent bed:
1. The equilibrium zone, where the adsorbate on the adsorbent is in equilibrium with the adsorbate in the inlet gas phase and no additional adsorption occurs.
2. The mass transfer zone (MTZ), the volume where mass transfer and adsorption take place.
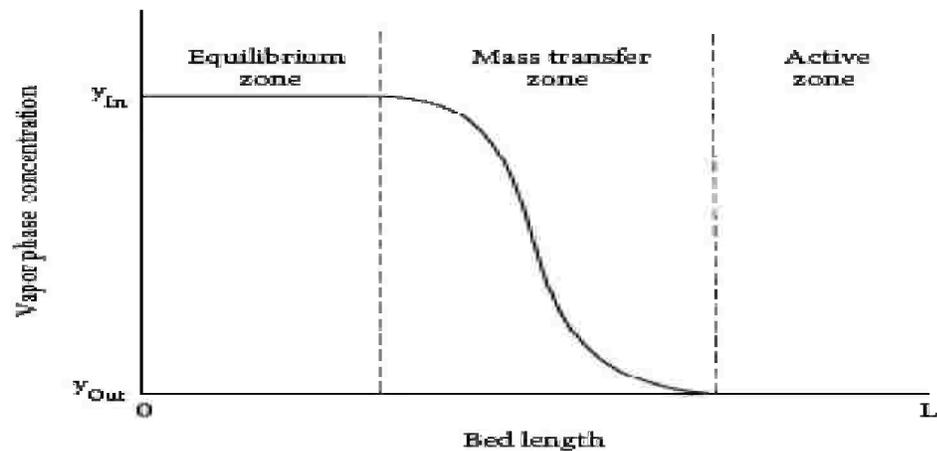3. The active zone, where no adsorption has yet taken.

Figure 2.5.e Vapor-phase concentration profile of an adsorbate in the three zones of an adsorption bed.

In the mass transfer zone (MTZ), the concentration drops from the inlet value, y_{in}, to the outlet value, y_{out}, in a smooth S-shaped curve. If the mass transfer rate were infinite, the MTZ would have zero thickness. The MTZ is usually assumed to form quickly in the adsorption bed and to have a constant length as it moves through the bed, unless particle size or shape is changed. The value of y_{in} is dictated by upstream processes; the y_{out} value is determined by the regeneration gas adsorbate content.

For a point in the MTZ, the gas phase adsorbate content increases in time from y_{in} to y_{out}. In principle, beds can be run until the first sign of breakthrough. This practice maximizes cycle time, which extends bed life because temperature cycling is a major source of bed degeneration, and minimizes regeneration costs. However, most plants operate on a set time cycle to ensure no adsorbate breakthrough.

2.9.2.1 <u>Adsorption tower</u> [1]

As shown in Figure 2.6, the adsorption tower consists of a bed support, gas stream distributors at ends, adsorbent loading and removal connections, and a sample / moisture probe. The bed support must withstand both dead load (weight of desiccant) and live load (flowing pressure drop). One type of bed support is a stainless steel or mantel screen (with openings 10 meshes smaller than the desiccant particles) supported horizontally by 1-beams and a welded ring. The screen should be securely fastened while allowing for thermal expansion and contraction. The annular space between screen and vessel wall should be sealed to prevent desiccant loss. A screen-wrapped slotted pipe or perforated basket is recommended. Also at the top, the desiccant bed should be protected by a 4 to 6 in. layer of ½ to 2 in, balls resting on retainer screen with 1/2 in. openings. This improves distribution of the inlet gas and prevents desiccant damage due to swirling. The adsorption tower is insulated either externally or internally. External insulation is much easier, but internal insulation can save up to 30% of the total regeneration heat load. Properly applied and cured castable refractory lining can be used internally. However, any liner cracks will allow wet inlet gas to bypass the bed.
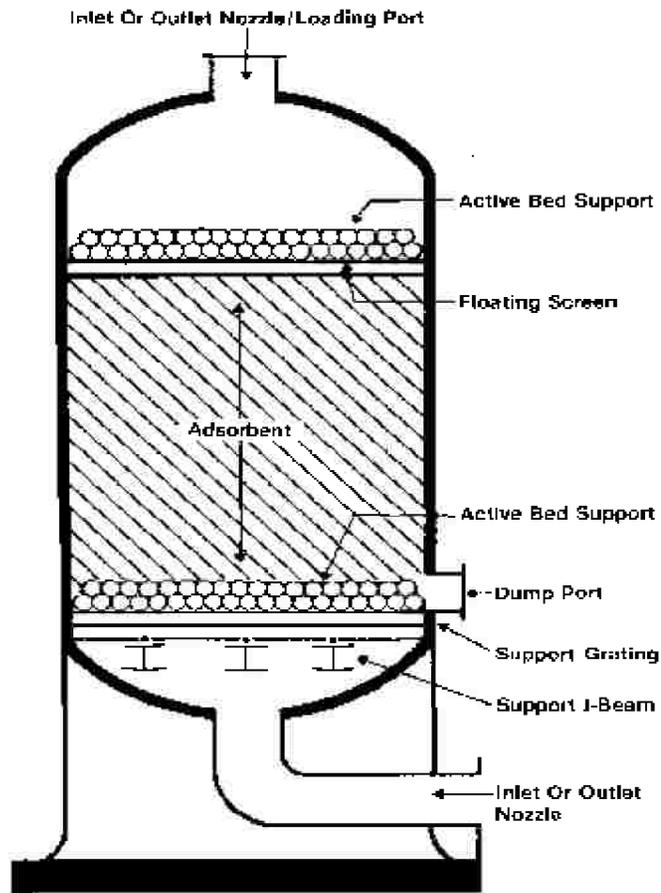
Figure 2. 6: Adsorption tower

2.9.2.2. Basic Adsorption Process System [7]

Although this discussion uses molecular sieve as the example of an adsorbent to remove water, with the exception of regeneration temperatures, the basic process is the same for all gas adsorption processes. Figure 2.7 shows a schematic of a two-bed adsorber system. One bed dries gas while the other bed goes through a regeneration cycle. The wet feed goes through an inlet separator that will catch any entrained liquids before the gas enters the top of the active bed. Flow is top-down to avoid bed fluidization. The dried gas then goes through a dust filter that will catch fines before the gas exits the unit.
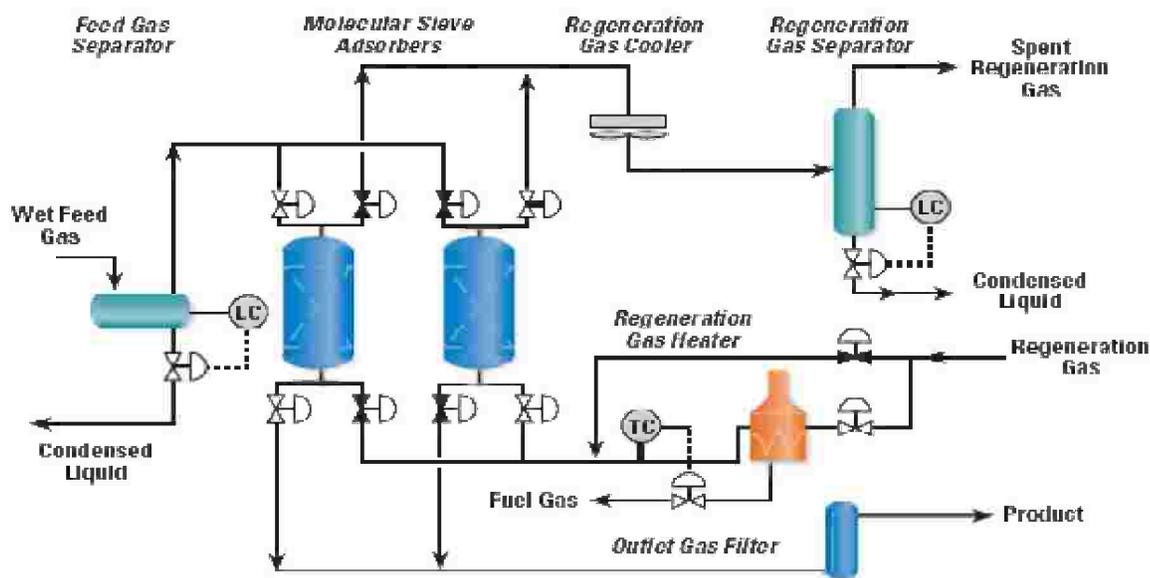
Figure 2.7 Schematic of a two-bed adsorption unit.

This filter must be kept working properly, especially if the gas goes on to a cryogenic section with plate-fin heat exchangers, as dust can collect in the exchangers and reduce heat transfer and dramatically increase pressure drop.

Figure 7 shows a slip stream of dry gas returning to the bed that is being regenerated. (Sales gas is sometimes used instead of a slip stream. The sales gas stream has the advantage of being free of heavier hydrocarbons that can cause coking.) This gas is usually about 5 to 10% of gas throughput. Regeneration involves heating the bed, removing the water, and cooling. For the first two steps, the regeneration gas is heated to about 600°F (315°C) to both heat the bed and remove adsorbed water from the adsorbent. If COS formation is a problem, it can be mitigated by lowering regeneration temperatures to 400 to 450°F (200 to 230°C) or lower, provided sufficient time for regeneration is available, or by switching to 3A. Regeneration gas enters at the bottom of the bed (countercurrent to flow during adsorption) to ensure that the lower part of the bed is the driest and that any contaminants trapped in the upper section of the bed stay out of the lower section. The high temperature required makes this step energy intensive and in addition to furnaces, other heat sources (e.g., waste heat from gas turbines that drive compressors) are used when possible. The hot, wet regeneration gas then goes through a cooler and inlet separator to remove the water before being recompressed and mixed with incoming wet feed. To complete the regeneration, unheated regeneration gas passes through the bed to cool before it is placed in drying service.

The Engineering Data Book (2004b) recommends that the bed pressure not be changed more than 50 psi/min (6 kPa/s). Therefore, if the adsorption process operates at high pressure, regeneration should take place at as high a pressure as possible to reduce the time needed for changing the pressure. The high pressures increase the amount of water and hydrocarbons that condense at the top of the bed and fall back onto the adsorption bed. This unavoidable refluxing is a major cause of bed aging, as it leads to adsorbent breakdown and subsequent fines agglomeration. The caking leads to higher pressure drop. Condensation at the bed walls can also occur, which a cause bed channeling.

2.10 Desiccant processes [9]

2.10.1 Dehydration Using Calcium Chloride

Literally hundreds of calcium chloride dehydration units are currently operating in the U.S. Calcium chloride is most attractive for small (50 Mscfd -2.5 MMscfd) streams in remote locations where low water dew points are not required (e.g., lift gas) and for offshore retrofits with severe space and weight limitations.
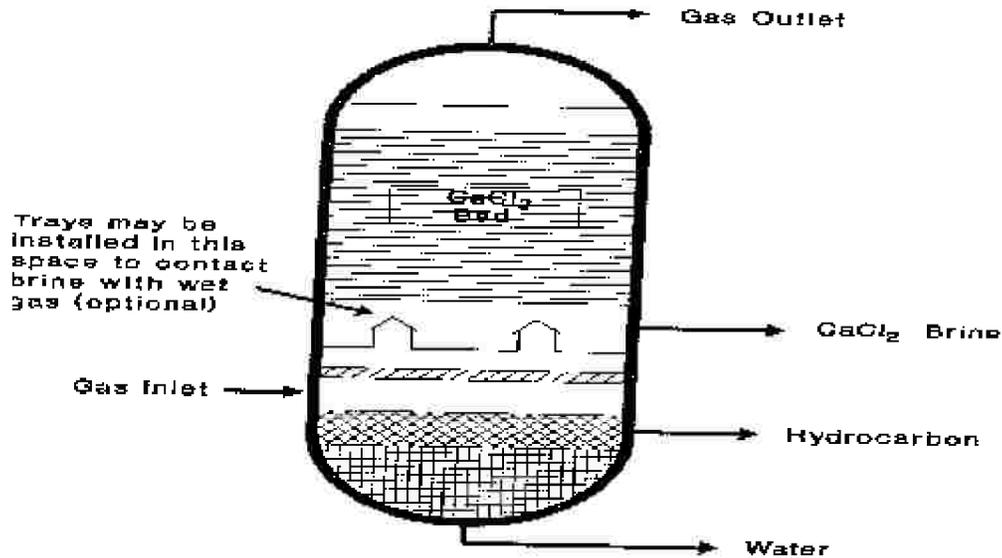

Figure 2.8 Typical CaCl₂ dehydrator

2.10.2 Membrane Processes

Membranes offer an attractive option for cases in which drying is required to meet pipeline specifications. Their modular nature, light weight, large turndown ratio, and low maintenance make them competitive with glycol units in some situations.
Inlet gas temperature should be at least 20°F (10°C) above the dew point of water to avoid condensation in the membrane.
Units operate at pressures up to 700 to 1,000 psig (50 – 70 barg) with feed gases containing 500 to 2,000 ppmv of water. They produce a product gas stream of 20 to 100 ppmv and 700 to 990 psig (48 to 68 barg). The low-pressure (7 to 60 psig [0.5 to 4 barg) permeate gas volume is about 3 to 5% of the feed gas volume.
This gas must be recompressed or used in a low-pressure system such as fuel gas.
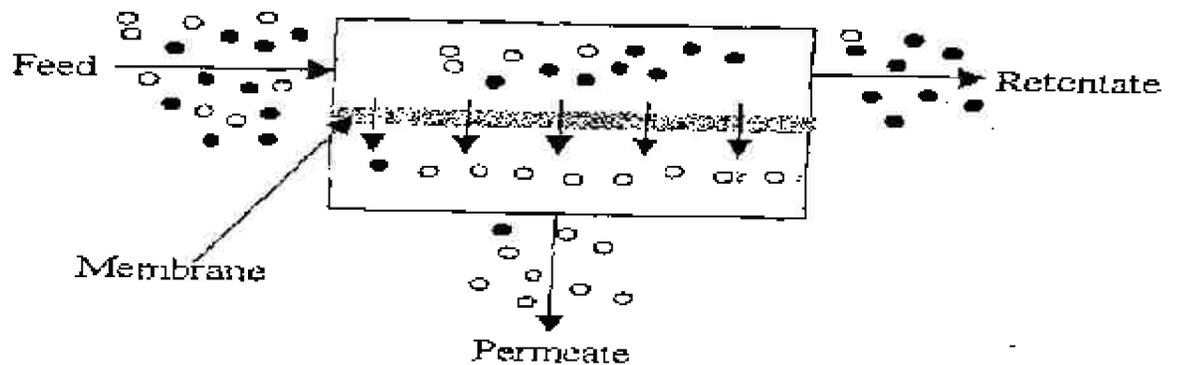
Figure 2.9 a membrane process

2.10.3 Low temperature process

When the wellhead pressure is high enough, low- temperature separation is usually the most efficient method of:

1. Separating liquid hydrocarbons and water
2. Recovering additional liquids (condensate) from the gas stream
3. Dehydrating the gas to pipeline specifications.

If the wellhead pressure exceeds that of the pipeline, then the gas can be passed through a choke or throttled in a constant-enthalpy Joule-Thomson expansion to provide cooling. Low temperature processes may be classified as follows:

1. Those that intentionally form and melt hydrates.
2. Those that use hydrate inhibitors (EG).
3. Those where additional cooling (mechanical refrigeration) is required to obtain the required gas dehydration and/or condensate recovery.

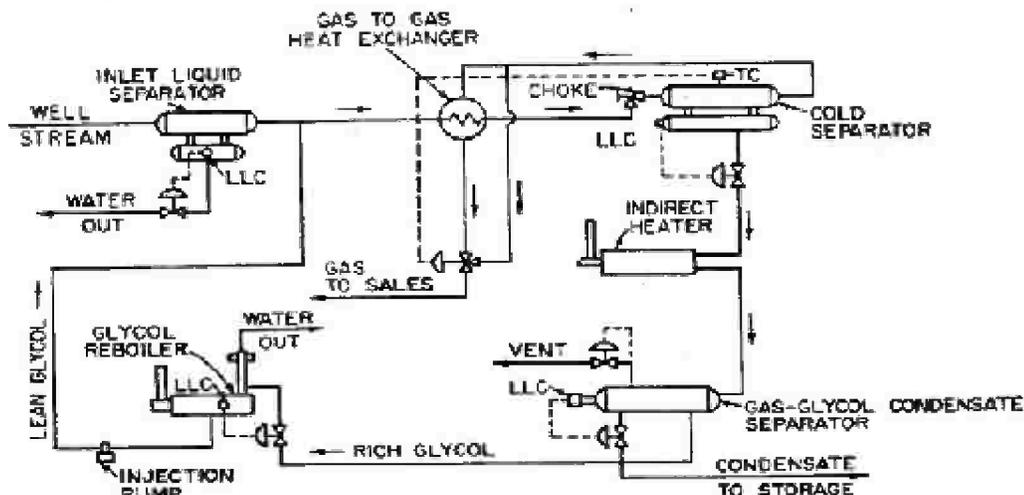**Figure 2.10** Typical LTS system with hydrate inhibitor

2.10.4 Other Processes [9]

Three relatively new processes are worth mentioning.

The first process is a **refrigeration process** that mixes methanol with the gas and cools the gas to very low temperatures. The water-methanol mixture drops out and the methanol is recovered in a stripper column. The process has several major advantages:

• It can obtain dew points in the −100 to −150°F (−70 to −100°C) range.
• It requires no heat input other than to the methanol regenerator.
• It requires no venting of hydrocarbon-containing vapors.
However, it requires external refrigeration to cool the gas, and minimal methanol losses occur in the stripper.
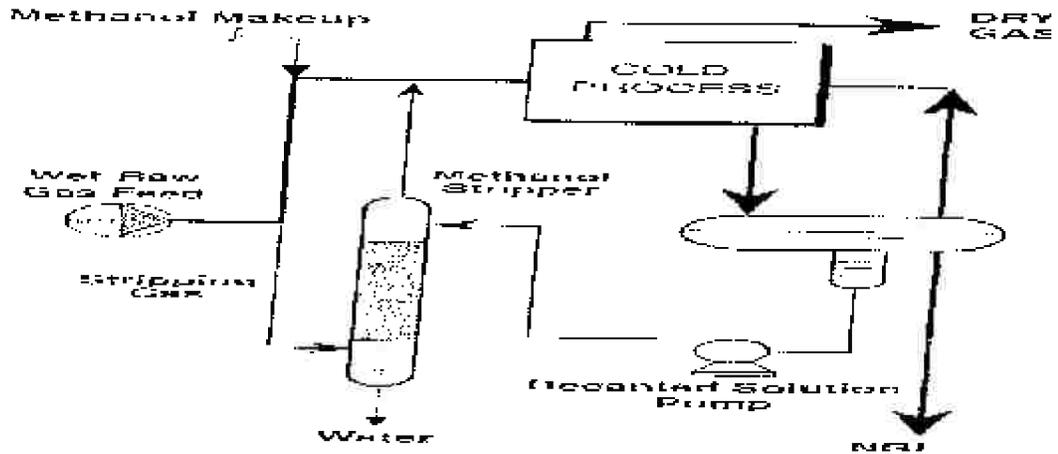
Figure 2.11 dehydration processes by refrigeration

The second process is the Twister technology is simplicity (no moving parts) along with its small size and weight. It is successful implementation is on an offshore platform. Some offshore field pressures are greater than 2,000 psi (140 bar), so recompression is not needed with the unit where overall pressure drop is 20 to 30%.
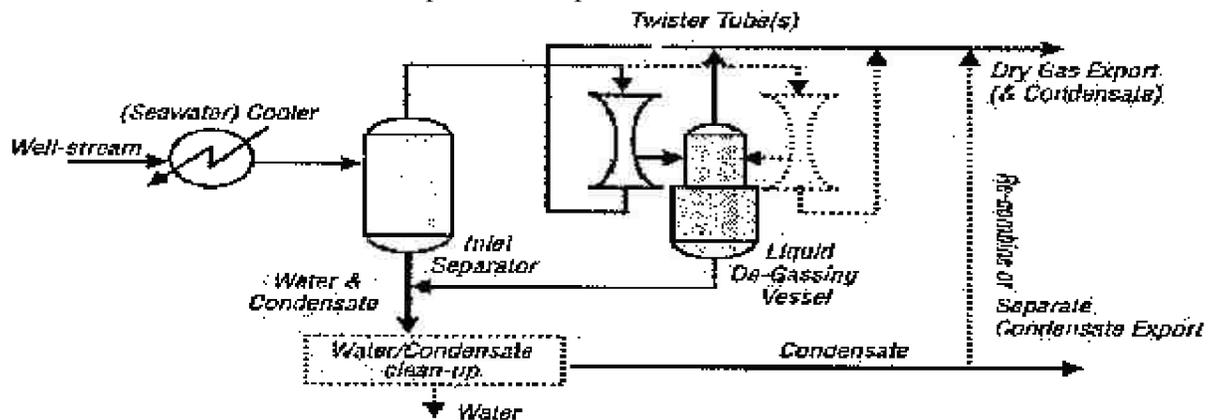
Figure 2.12 process flow diagram of a typical twister system

The third process is the vortex tube technology, also has no moving parts. According to vendor information, it is used in Europe in conjunction with TEG addition to remove water from gas stored underground. We found no examples of its use in gas plants.

Figure 2.13 the process scheme of vortex technology.   **Figure 2.14** the annular gap of the
Vortex tube.

2.11 Pressure Swing Adsorption (PSA) Separation [10]

Pressure swing units are widely used for air separation, both on a small scale for
production of medical oxygen and, increasingly, on a large scale as an alternative to the
cryogenic process for production of industrial oxygen and nitrogen.

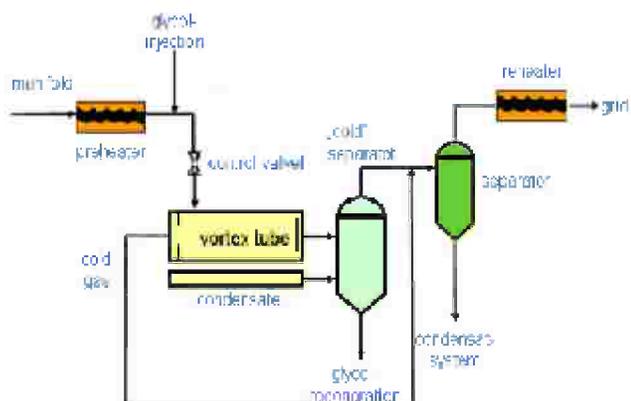There are two different types of process in common use processes which utilize a zeolite
adsorbent depend on the preferential adsorption of nitrogen under equilibrium conditions,
whereas processes which use a carbon molecular sieves depend on a kinetic separation in
which oxygen, the faster diffusing species is preferentially adsorbed. The types of cycles,
the conditions of operation, and the product purities are quite different for these two types
of process.

2.12 Adsorbent material [9 &10]

A. Characteristics

1. Large surface area for high capacity.
2. Possesses **"activity'** for the components to be removed.
3. Mass transfer rate is high.
4. Easily and economically regenerated.
5. Good activity retention with time.
6. Small resistance to gas flow.
7. High mechanical strength to resist crushing and dust formation.
8. Fairly cheap, non-corrosive, non-toxic, chemically inert and possesses a high bulk
density.
9. No appreciable change in volume during adsorption and desorption, and should retain
strength when "wet."

B. Properties of industrial adsorbents for dehydration

Three types of commercial adsorbents are in common use in gas processing plants:

- Silica gel, which is made of pure SiO_2
- Activated alumina, which is made of Al_2O_3
- Molecular sieves, which are made of alkali alumina-silicates and can be altered to affect adsorption characteristics.

Silica gels, are used mostly where a high concentration of water (>1 mol%) vapor is present in the feed, and low levels of water in the dehydrated gas are not needed. They are relatively non catalytic compounds.

Alumina, are very polar and strongly attract water and acid gases. They are used for moderate levels of water in the feed when low levels of water in the product are not required. They have the highest mechanical strength of the adsorbents considered here.

Molecular sieves, Molecular sieves are crystalline metal aluminosilicates having a three dimensional interconnecting network of silica and alumina tetrahedra. Natural water of hydration is removed from this network by heating to produce uniform cavities which selectively adsorb molecules of a specific size. The type forms of the 3A, 4A, 5A and 13X sieves are suitable for specialized applications.

Figure 2.15 Molecular sieves

Table 2.2: Types of molecular sieves

Type	3A
Composition	0.6 K_2O: 0.4 Na_2O : 1 Al_2O_3 : 2.0 ±
Description	The 3A form is made by substituting potassium cations for the inherent sodium ions of the 4A structure, reducing the effective pore size to ~3Å
Major Applications	Commercial dehydration of unsaturated hydrocarbon streams, including cracked gas, propylene, butadiene, acetylene; drying polar liquids such as methanol and ethanol. Adsorption of molecules such as NH_3 and H_2O from a N_2/H_2 flow.

Type	4A
Composition	1 Na_2O: 1 Al_2O_3: 2.0 ±
Description	This sodium form represents the type A family of molecular sieves. Effective pore opening is 4Å, e.g., propane
Major	Preferred for static dehydration in closed liquid or gas systems, e.g., in

Applications	packaging of drugs, electric components and perishable chemicals; water scavenging in printing and plastics systems and drying saturated hydrocarbon streams.

Type	5A
Composition	0.6 K_2O: 0.40 Na_2O : 1 Al_2O_3 : 2.0 ±
Description	Divalent calcium ions in place of sodium cations give apertures of ~5Å, e.g., all 4-carbon rings, and iso-compounds.
Major Applications	Separation of normal paraffins from branched-chain and cyclic hydrocarbons; removal of H_2S, CO_2 and mercaptans from natural gas.

Type	13X
Composition	1 Na_2O: 1 Al_2O_3 : 2.8 ±
Description	The sodium form represents the basic structure of the type X family, with an effective pore opening in the 910¼ r range. Will not adsorb($C4F9$)3N, for example.
Major Applications	Commercial gas drying, air plant feed purification (simultaneous H_2O and CO_2 removal) and liquid hydrocarbon/natural gas sweetening (H_2S and mercaptan removal).

Carbon molecular sieves, most commercial carbon sieves are prepared from anthracite or hard coal by controlled oxidation and thermal treatment. The effective microspores diameters ranging from about 4 to 9 °A. Application of carbon sieves have large-scale in air separation and in the latter application hydrogen purification process based on zeolite molecular sieve.

2.13 Previous Studies

The adsorption process is a vital one in the field of gas processing and mostly done by thermal adsorption process for dehydration of natural gas and pressure swing adsorption for nitrogen production. Many researchers have shown interest in this field of studying the breakthrough curves, mass transfer zone and temperature effects. Their findings and suggestions are summarized in the following table:

Reference /year	Subject	Field	Result
11 / 2012	Predicted the breakthrough curves using a film-pore and surface diffusion (FPSD) model for **adsorption of chloroform** on granular **ZSM-5 zeolite** in fixed-bed columns. It was found that the adsorption rate was enhanced with decrease in particle size. The FPSD model accounted for the effects of axial dispersion, external film transfer resistance, and intra-particle mass transfer resistances. A sensitivity analysis was carried out to investigate the relative impact of kinetic parameters on the FPSD model predicted breakthrough profiles and showed that the model calculations were insensitive to either the effective pore diffusivity coefficient (D_p^e) or the axial dispersion coefficient (E_z), but were sensitive to the external mass transfer coefficient (k_f).	laboratory	1. Comparison between measured concentrations – time data and simulated data at different particle sizes. 2. Breakthrough curves at different bed lengths. 3. Sensitivity analysis at different (k_f) and (E_z).
12 / 2012	The sorption equilibrium of **CO$_2$ and CH$_4$ on 13X zeolites** was investigated between two of temperatures. The value of diffusivity of CO_2 measured experimentally is 5.8×10^{-15} and 1.3×10^{-15} m^2/s at 373°K and 313°K respectively. The diffusivity of CO_2 in 13x can be measured macroscopically by zero length column (ZLC) being the same measurement for CH_4 practically impossible.	Laboratory	1. Relation between partial pressure and the amount adsorbed. 2. Effect of flow rate on ZLC desorption curves. 3. The relation between concentration ratio and time. 4. Effect of temperature on ZLC desorption curves.
13 / 2012	PSA is acyclic process of adsorption / desorption that occur through pressure changes and can be very	Laboratory	- The adsorption dynamics was investigated at several

	suitable for **carbon dioxide separation from exhaust gases** due to its easy application in a large temperature range. The activated carbon used was norit-R2030, however the temperature of CO_2/N_2 mixture in a typical exhaust gas exceeded 100^oC		temperatures and considering the effects caused by N_2. - Breakthrough curves for CO_2/N_2 adsorption were obtained on activated carbon.
14 / 2011	Separated **CO2-N2** mixture through adsorption **on activated carbon** in fixed bed.	Laboratory	Obtained a breakthrough curves at different temperatures.
15 / 2011	Determined modifyied **LDF mass transfer rate** of the adsorption dynamics of N_2-PSA process over carbon molecular sieve by using a mathematical model. Simulation studies are performed to investigate the effect of changing various process variables, such as feed flow rate, bed length, purge to feed ratio and cycle time.	Laboratory	Relation between the following: 1. Flow rate and N2 purity. 2. Flow rate and N2 recovery. 3. Cycle time and N2 purity. 4. Cycle time and N2 recovery.
16 / 2011	**Multi-component (H₂-CO₂-CO-CH₄-N₂)** breakthrough experiments were performed under different operating conditions **on activated carbon** extradites to validate the mathematical model. The mathematical model was employed to assess the effect of operating conditions in PSA unit.	Laboratory	1. Adsorption equilibrium data was predicted for multi-component (H_2-CO_2-CO-CH_4-N_2). 2. Breakthrough curves for mixture were performed.
17 / 2010	Developed a mathematical model to simulate an adsorption process for dehydration of gas stream by using **zeolite 5A**.	Laboratory-data collected from literature	Relation between the following: 1- Bed length and water concentration. 2-time and temperature. 3- Bed length and particle diameter.
18 / 2010	Model simulated a PSA cycle for **hydrogen purification** in fixed bed by using activated carbon and zeolite.	Laboratory and its key industrial application	Compared the columns having activated carbon and zeolite packing.
19 / 2009	**A review paper** for mathematical modeling of single and multi component adsorption fixed beds to rigorously predict the mass transfer zone and breakthrough curves. This paper compared various	Laboratory-data collected from literature	Breakthrough curves for multi-component adsorption in either gas or liquid phase.

	mechanisms of mass transfer in the adsorbers. The model can predict experimental mass transfer zone and breakthrough curves in adsorption and desorption mode for different adsorbents such as molecular sieves, activated carbon and carbon molecular sieves.		
20/2009	Designed and constructed A pilot scale adsorption apparatus to investigate **water and ethanol adsorption/ desorption** kinetics on **3A zeolite** for the design purposes of **a fuel ethanol dehydration pressure swing adsorption (PSA)** process. A mathematical model for a bench scale adsorption bed included the linear driving force (LDF) adsorption rate model and the variation of axial velocity. A detailed heat transfer model was a necessity since the bed dynamics was affected by heat transfer in the bed wall.	Pilot scale	The breakthrough curves were utilized to study the effects of column pressure, temperature, flow rate, pellet size, and adsorbate concentration on the overall mass transfer resistance.
21 / 2008	Developed Dynamic model for a N_2-**PSA system**. The simulation studies are performed to investigate the effect of changing various process variables, such as duration of PSA steps, bed length and feed inlet velocity.	**Laboratory**	Relation between the following: 1. Time and N2 mol fraction. 2. Velocity and N2 mol fraction. 3. Bed length and N2 mol fraction.
22 / 2008	In this study they present the modeling of an adsorption process applied to **textile dye using fixed bed columns**. This model permits the prediction of the dye concentration at the adsorption column outlet, considering the influence of various operation parameters. The adsorption isotherms were determined experimentally through a comprehensive series of tests.	Laboratory	Breakthrough curves were determined with variation in feed rate, feed concentration , diameter of the column and mass transfer coefficient.
23 / 2007	Studied model and simulation for two cases (O2-N2) on **zeolite 5A** and **(CO2-C2H6-N2)** on linde **5A molecular sieve**. Rigorous model is recommended for use to validate the	Laboratory-data collected from literature	Relation between the following: • First model - Time and O2 mol fraction at different flow

	model, that's because LDF model does not match experimental data as well.		rates and initial conditions. • second model - C2H6 mol fraction and various variables (time , bed length and temperature)
24 / 2007	Developed model to simulate breakthroughs of **a methane/carbon dioxide mixture** over a 5 A zeolite and of a 2,2-dimethylbutane/2-methylpentane mixture over a silicalite molecular sieve.	Pilot plant	Relation between the following: 1- Time and mol fraction of component. 2- Time and temperature. 3- Repeat 1 & 2 at different pressures.
25 / 2006	Predicted breakthrough curves for the adsorption isotherms of **water vapor on cornmeal** and the breakthrough curves at 82–100°C were measured in a fixed-bed apparatus for ethanol dehydration.	Laboratory	Relation between the following: - Breakthrough time and C/CF at different velocities and temperatures at fixed bed lengths.
26 / 2006	Developed the solution of diffusion parabolic partial differential equations. It was applied in the **modeling of mass balance for adsorption process**. The method is proposed as the basis for developing generalized linear driving force for adsorption and desorption of **multi-component mixtures** in a single particles.	literature	Two models of homogenous diffusion equations and dusty gas model were compared to drive the equation used for the simulation, optimization and control of cyclic adsorption process.
27 / 2006	This paper concentrates on the development of simulation techniques needed to accurately **estimate dehydration efficiency** to control hydrate in a supercritical flow using **supersonic nozzles**. A simulation model linked to a thermodynamics property generator is needed to predict the water removal efficiency under various flow conditions. Intensive water dew point down to about -50 to -60 °C can be achieved without any cryogenic cooling or use of solid adsorption techniques.	Simulation by hysys-data assumed	- Hysys software was developed to predict the performance of supersonic nozzles for dehydration of natural gas. - Temperature distribution along the nozzles. - Velocity distribution, pressure difference and water content distribution along the nozzles.
28 / 2006	In this study a **review** is made for	laboratory	1- O_2 concentration

	sorption kinetics of O_2 from air by CMS used PSA process single column. Also N2 production from air by CMS-HP (O_2) used PSA process two columns.		variation in column at different pressure.
29 / 2006	This paper studied both the transient and steady state **heat transfer behavior of a gas flowing through** a packed bed under the constant wall temperature conditions. The result could predict the axial **temperature distribution** fairly well, but the prediction is poor for radial temperature.	laboratory	1. Pressure drop of gas flows through the packed bed. 2. Temperature profiles inside the packed bed at different length of the bed.
30 / 2005	Developed a PSA cycles using CMS for **O_2 purification**. The cyclic performances such as purity, recovery and productivity were compared experimentally with theoretical values.	Laboratory	Relation between the following: 1- Breakthrough time and O_2 % 2- Desorption time and O_2 %. 3-Number of cycles and O_2 %. 4- Time and temperature. 5- Bed length and O_2 mole fraction %. 6- Effect of N_2 in feed on O_2 purity.
31 / 2002	Focused on the analysis and modeling of **styrene drying** by adsorption onto activated alumina.	Laboratory	Fixed bed column experiments were performed working with different flow rates and using different bed lengths in order to obtain experimental breakthrough curves
32 / 2000	Estimation of effective **diffusion coefficients of water on silica gel** particles by adsorption process. The range of D_p^e obtained was 0.9×10^{-10} – 2.1×10^{-10} m^2/s	Laboratory-data collected from literature	A comparison between the calculated value and the other measurement demonstrate that only molecular diffusion and not Knudsen diffusion take place.
33 / 1997	The adsorption phenomena of **oxygen and nitrogen** on a carbon molecular sieve were studied above the **critical temperature of the adsorptive** as a function of pressure in order to understand the	Laboratory	Relation between time and different variables are adsorbent weight, pressure and temperature.

	mechanism of air separation.		
34 / 1996	Measured the equilibrium and kinetic parameters for **adsorption CH_4 and N_2 on activated carbon.** The parameters are input in the mathematical model of binary breakthrough experiments using an axial dispersion model.	Laboratory	- Breakthrough curves of CH_4 and N_2 - The theoretical and experimental breakthrough curves were observed to be excellent agreement.
35 / 1994	They were applied a generalized mathematical model of isothermal adsorption on adsorption of **blue dye on chitin,** adsorption of **phenol on activated carbon** and **steam on aluminum oxide**, that take into account mass transfer on the surface of a particle, diffusion in micro and macro pores, and dispersion along the length of the apparatus.	Laboratory-data collected from literature	They obtained the concentration profiles along the bed.
36 / 1987	A mass transfer model was developed based on external film mass transfer, macro pore diffusion and micro pore diffusion to explain adsorption of **pollutants** from **aqueous solutions onto adsorbent particles**. A comparison was made for the adsorption of **acid blue 25 dye on chitin** and phenol on carbon.	Laboratory	Relation between time and inlet concentrations. Applied the sensitivity analyses to show the effect of four major factors: 1. External liquid film mass transfer coefficient. 2. Surface diffusion coefficient. 3. Pore rate diffusion coefficient. 4. Fraction of total adsorptive capacity in the macro pores.