

## **Liquid Drying by Adsorption: Theory & Practice**

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### **1. Reasons for Drying**

The need for drying and purification of liquids (including liquefied gases) has been growing consistently in the last few decades. The reasons for drying organic liquids are many and some of them are as under:

- a) **Physical effects**
- b) **Chemical effects**
- c) **Corrosion effects**
- d) **Stringent specification**

Some typical examples under these heads are given below:

a) **Physical effects:**

Due to the fact that solubility of water in most immiscible liquids decreases with temperature, there is greater physical separation of free water from organic layer as they are cooled. As these temperatures fall below 0°C, the free water would tend to freeze and create problems of flowability.

An example is Aviation Turbine Fuel, which encounters temperatures of –30 to –40°C when an aircraft flies at an altitude of 30,000 to 40,000 feet. Other applications are in cryogenic processing of paraffins and olefins for separation and purification. The examples include LPG recovery from natural gas and separation of olefins from cracked gas.

b) **Chemical effects:**

In many reactions, water hydrolyses or poisons reaction agents and catalysts and this leads to slower reactions, excessive consumptions of feeds/ utilities and corrosion of equipment. Examples include:

- i) In some esterification reactions, water promotes the reversible reaction and affects the yield.
- ii) In some other reactions, water forms by-products, which lower the product purity.
- iii) Many alkylation or acylation reactions of Friedel-Crafts type use AlCl<sub>3</sub>, BF<sub>3</sub> or similar metallic halides as catalysts. These catalysts react with water and form acidic impurities that inhibit main reaction and corrode the equipment.

Examples include:

- Toluene drying for isobutyl benzene synthesis
- Ethanol drying for glycol ether manufacture
- Ether drying for Grignard reactions
- N-hexane drying for butene-1 manufacture (Friedel Crafts reaction)
- Drying of solvents like Methylene chloride, tetra hydro furan, acetone, MEK etc. for recycle in pharma/ dyes/ rubber and intermediates plants.
- Drying of methanol for formic acid manufacture.
- Drying of feeds for polymerization processes for EPDM, isoprene, polypropylene and polyethylene.

c) **Corrosion effects:**

Corrosion effects of moisture are sometimes two-fold. Apart from corrosion due to water itself, there are situations where acids such as HCl /HF are formed as a by-product and the acid (in presence of water) is highly corrosive.

Examples include –

- Drying of benzene for chlorination reactions.

- Drying of ethyl acetate for use as solvent.

**d) Stringent specification:**

Due to increasing global competition and due to end-use requirements, specifications of more and more products are becoming tighter. Allowable impurities like moisture have to be brought down further to match international quality at competitive prices.

Examples include –

- Helektrol HT (PXE i.e. Phenyl xylyl ethane) (Herdillia)
- Refrigerant liquids (Navin Fluorine)
- Anisic aldehyde (Atul, Metrochem)
- Para-cumidene (Aryan Pesticides)
- Trichloro ethylene (DCW)
- Pyridine (Armour)
- Isobutyl benzene (Vinati)
- Ethanol for blending with transport fuels

## 2. Methods of Drying

There are various alternative and competitive methods to carry out drying of liquids.

They include:

- a) Distillation** (including azeotropic)
- b) Absorption** e.g. glycol dehydrators.
- c) Pervaporation** across a membrane
- d) Chemical reaction** with some agents e.g.  $\text{CaCl}_2$ ,  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$
- e) Adsorption** – Liquid phase or vapour phase

The first three methods are suitable for bulk removal of water and ratio of feed to product water-contents is usually less than 10. The chemical reaction method is suitable for once-through applications i.e. use and throw (or use the product formed). Adsorption is the ideal choice for trace removal of water and it is capable of giving very high ratios (like 100 to 5000) of feed concentration to product concentration of water. Moreover, adsorption is the only practical and cost effective method of removing final traces or dissolved water in organic liquids.

Conventional adsorbents like silica gel and activated alumina have been used for drying liquids. But unlike molecular sieves, they have larger sized pores and a wide distribution of pore sizes in the range 10 to 50 angstroms ( $1\text{A}^\circ = 10^{-8}\text{ cm}$ ). Molecular sieves of the type 3A, 4A, 5A & 13X have most of the pores of the size 3, 4, 5 & 10  $\text{A}^\circ$  respectively. The smaller pores and narrow distribution of pore sizes in molecular sieves help in many ways as under:

- 1) Selective removal of water or any other impurity as per design – No change in the composition of the fluid on water-free basis.
- 2) Stronger adsorption of water helps in achieving the lowest possible water-content in the product e.g. 5 ppm in immiscible liquids.
- 3) Prevention of co-adsorption of reactive and polar liquids (like alcohols, olefins, chlorinated compounds etc.) ensures minimum exothermicity and side reactions during adsorption step and minimum complications during regeneration step.
- 4) Simultaneous removal of small sized and polar molecules like water, methanol, ethanol, ethylene, mercaptans etc. by suitable selection of molecular sieves within the bed.
- 5) Easier to handle fluctuations in process parameters within a certain range. It is possible to maintain product specifications in spite of normal variations in feed flowrate, pressure, temperature and composition.
- 6) Being fully regenerable, an adsorption system can be designed for drying a variety of liquids. Multi-purpose plants are useful when these are many liquids to be dried but the tonnage for each liquid is low.
- 7) Operating cost of adsorption system is much less than that of distillation. All water and carrier liquid has to be vaporized many times over (depending on reflux ratio) for distillation. But this is not so for adsorption system, where heat has to be provided for mainly desorption of water alone and water-content itself is rather low in most cases. Please refer to Table 1 for comparison of operating costs for drying of ethanol from 8% to 0.1% water-content by

azeotropic distillation vis-à-vis adsorption. Total operating cost of this application is less than half for adsorption than for azeotropic distillation.

**Table 1**

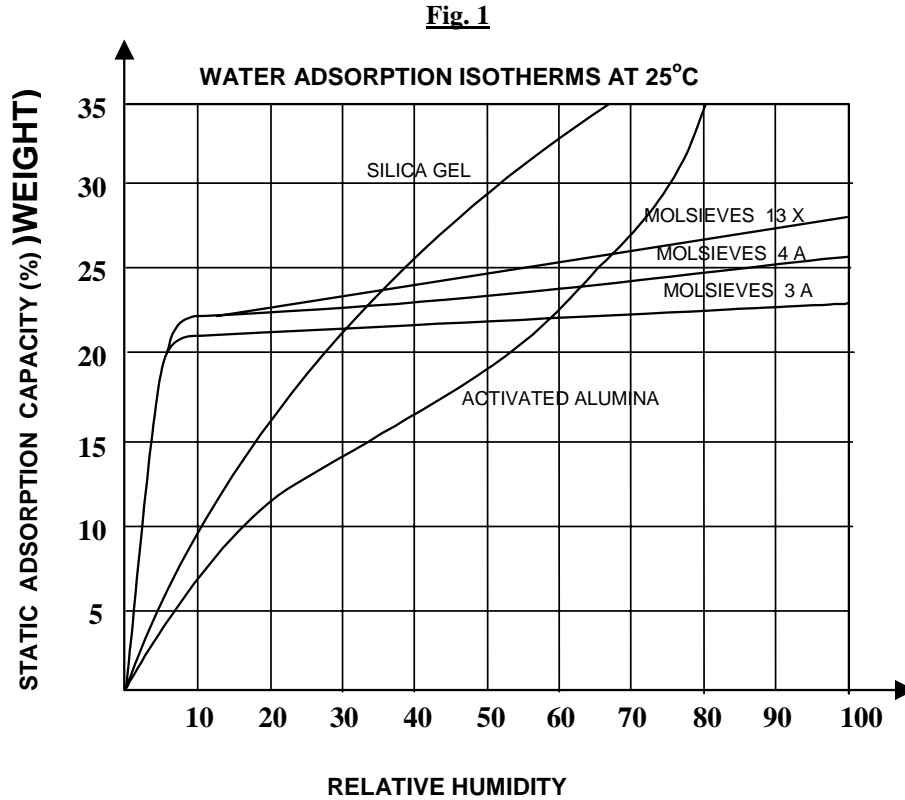
| ITEM | ADSORPTION                    |            |            |             | AZEOTROPIC DISTILLATION |            |            |             |               |
|------|-------------------------------|------------|------------|-------------|-------------------------|------------|------------|-------------|---------------|
|      | UNITS/KL                      | SPECS      | COST/UNIT  | COST RS./KL | UNIT S/KL               | SPECS      | COST/UNIT  | COST RS/KL  |               |
| 1    | STEAM                         | 0.37 T/KL  | 30 KG/CM2G | RS. 600/T   | 222                     | 1.8 T/KL   | 3 KG/CM2G  | RS. 600/T   | 1080          |
| 2    | COOLING WATER                 | 45 M3/KL   | ΔT=5 DEG C | RS.1/ M3/HR | 45                      | 80 M3/KL   | ΔT=5 DEG C | RS.1/ M3/HR | 80            |
| 3    | CHILLED WATER                 | 30 M3/KL   | ΔT=5 DEG C | RS.5/ M3    | 150                     | NIL        |            |             | NIL           |
| 4    | PROCESS WATER                 | NIL        |            |             | NIL                     | 7.5 M3 /KL |            | RS.1/ M3    | 7.5           |
| 5    | POWER                         | 50 KWH/KL  |            | RS.5/ KWH   | 250                     | 60         |            | RS.5/ KWH   | 300           |
| 6    | ENTRAINER CYCLOHEXANE         |            |            |             | NIL                     | 2 KG/ KL   |            | RS. 80 /KG  | 160           |
| 7    | NITROGEN                      | 20NM3/KL   | 99.5% PURE | RS.2/ NM3   | 40                      | NIL        |            |             | NIL           |
| 8    | MOL. SIEVES                   | 0.5 KG/ KL | 3A         | RS.200/ KG  | 100                     | NIL        |            |             | NIL           |
|      | <b>TOTAL OP. COST, RS/ KL</b> |            |            |             | <b>807</b>              |            |            |             | <b>1627.5</b> |

### 3. Fundamentals of Adsorption

#### **3.1 Principle of Adsorption:**

Adsorption is a surface phenomenon, whereby certain molecules of a fluid are preferentially attracted towards and attached to the surface of a solid. Such porous solids with very high specific surface areas are called adsorbents. Surface area ranges for 300 to 1000 m<sup>2</sup>/g i.e. somewhat like an area of one football ground in one gram of the adsorbent. Adsorbed component of the fluid is known as adsorbate.

Adsorbents are generally compared on the basis of adsorption isotherms, which represent equilibrium loadings of adsorbate on an active adsorbent at different partial pressures and a particular temperature. Please refer to Fig.1 for typical water adsorption isotherms at 25°C on well-known adsorbents like silica gel, activated alumina and molecular sieves type 3A, 4A & 13X.

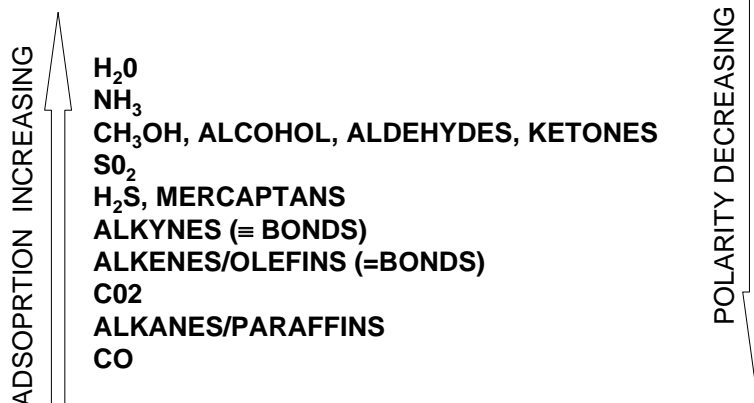


As explained earlier, molecular sieves have a narrow pore size distribution and that helps in removal or separation of components based on molecular diameter and polarity. Table 2 below gives critical diameter and relative polarity of some molecules. Table 3 gives typical properties of adsorbents.

Table 2

| MOLECULES                                    | CRITICAL DIAMETER IN Å <sup>0</sup><br>1 Å <sup>0</sup> = 10 <sup>-8</sup> CM |
|--|---|
| HELIUM                                       | 2.0   |
| HYDROGEN, ACETYLENE                          | 2.4   |
| WATER, OXYGEN, CARBON MONOXIDE AND DIOXIDE   | 2.8   |
| NITROGEN                                     | 3.0   |
| AMMONIA, HYDROGEN, SULPHIDE                  | 3.6   |
| ARGON  | 3.8   |
| METHANE                                      | 4.0   |
| ETHYLENE, ETHYLENE MONOXIDE                  | 4.2   |
| ETHANE, METHANOL, ETHANOL                    | 4.4   |
| METHYL-MERCAPTAN                             | 4.5   |
| PROPANE, nC <sub>4</sub> to nC <sub>22</sub> | 4.9   |
| PROPYLENE                                    | 5.0   |
| ETHYL-MERCAPTAN, BUTENE 1, BUTENE 2 TRANS    | 5.1   |
| DIFLUOROCHEMETHANE (R 22)                    | 5.3   |
| ISO C <sub>22</sub>                          | 5.6   |
| CYCLOHEXANE                                  | 6.1   |
| TOLUENE, PARAXYLENE                          | 6.7   |
| BENZENE                                      | 6.8   |
| CARBON TETRACHLORIDE                         | 6.9   |
| METAXYLENE                                   | 7.1   |
| TRI-ETHYLAMINE                               | 8.4   |

**TABLE :**  
**MOLECULES POLARITY**  
**DECREASING SCALE**



**Table 3: Properties of Adsorbents**

| Adsorbent Property                           | Silica Gel | Activated Alumina | Molecular Sieves             | Activated Carbon         |
|--|------------|-------------------|------------------------------|--------------------------|
| Grade  | Commercial | AD-101            | 4A 13X                       | Commercial (Shell-based) |
| Nominal pore Diameter (Å)                    | 20-50      | 20-40             | 4 10                         | 20-30                    |
| Pore Volume (cc / g)                         | 0.45-0.45  | 0.35-0.50         | 0.32 0.38                    | 0.45-0.50                |
| Specific surface area (m <sup>2</sup> /g)    | 600-800    | 300-350           | 700 800                      | 1000-1200                |
| Bulk density (Kg/m <sup>3</sup> )            | 600-700    | 850-900           | 650-750, 600-650             | 450-500                  |
| Equilibrium water adsorption capacity (%wt.) |            |                   |                              |                          |
| At 30 °C, 75%RH                              | 26-30      | 24-25             | 23 26                        | *                        |
| At 30 °C, 15%RH                              | 4-5        | 5-6               | 21 23                        |                          |
| Typical shape & size                         | Granular   | Balls             | Cylindrical Pellets Or balls | Granular                 |
|  | 4x8 mesh   | 2-5 & 5-8 mesh    | 1.5 & 3.0mm dia.             | 4x8, 8x12 mesh           |
| Regeneration temperature (T)                 | 150-160    | 180-200           | 250-300                      | 120-140                  |

\* Activated carbons do not adsorb water; typical adsorption capacities for hydrocarbons are 30-60%

### 3.2 Applications of Adsorption:

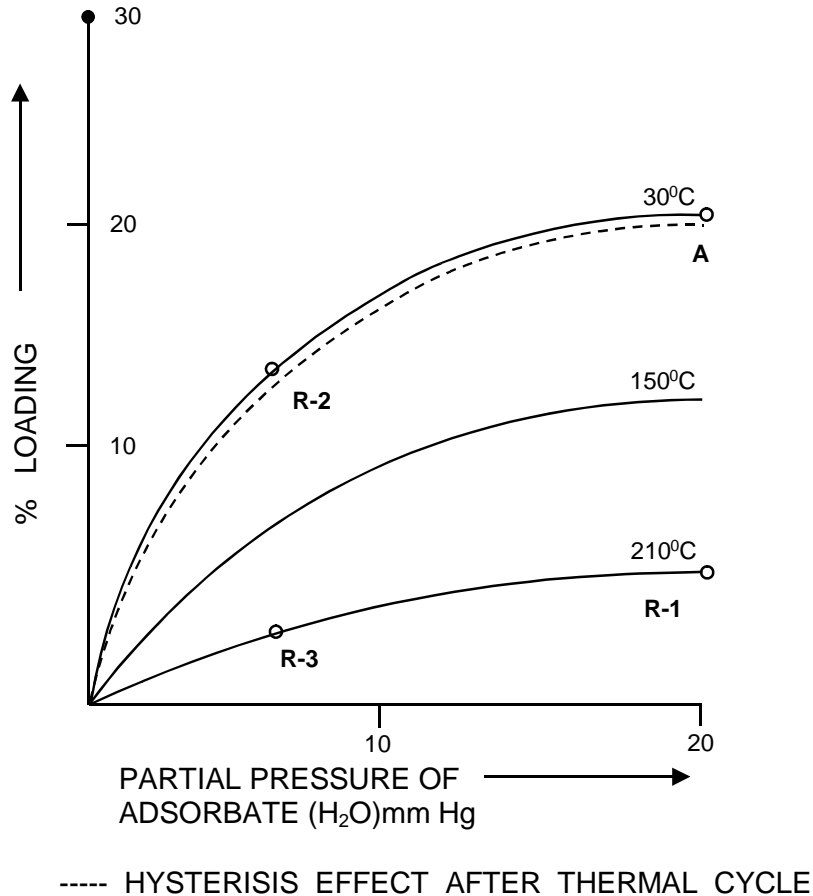
Adsorption-based processes are generally useful for the following end-uses:

- a) DRYING** : Removal of moisture from a wide variety of gases and liquids.
- b) PURIFICATION** : Removal of absorbable compounds like CO, CO<sub>2</sub>, H<sub>2</sub>S, olefins, mercaptans, alcohols, hydrocarbons etc. from gases and liquids.
- c) SEPARATION** : Generation of useful gases by PSA/VSA e.g. O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>; Separation normal and iso paraffins e.g. Molex.
- d) CATALYSIS** : Molecular sieves are used as shape selective catalysts and also as catalyst carriers for Friedel Crafts acylation, alkylation, dewaxing and isomerisation type of reactions.

### 3.3 Concept of Adsorptive Drying:

For basic understanding of cyclic drying by adsorption of water on molecular sieves, refer to Fig 2. Molecular sieves can be regenerated by increasing the temperature or by reducing the pressure or both. Fig 2 shows isotherms at 30, 150 & 210°C. Point A is the adsorption condition of 30°C and 20 mm Hg partial pressure of water. Point R-1 is the regeneration condition at 210°C with wet gas, R-3 is the regeneration condition at 210°C with dry gas and R-2 is the isothermal regeneration condition at reduced partial pressure. R-1 & R-3 represent thermal swing adsorption and R-2 represents pressure swing adsorption. Comparison of loadings against the points A vs. R-1, R-2 and R-3 gives the theoretical differential available for design.

**Fig. 2**



### 3.4 Dynamics of Adsorptive Drying:

In practical and dynamic situations, loadings of water on an adsorbent are much less than the static or equilibrium loadings as per isotherms due to:

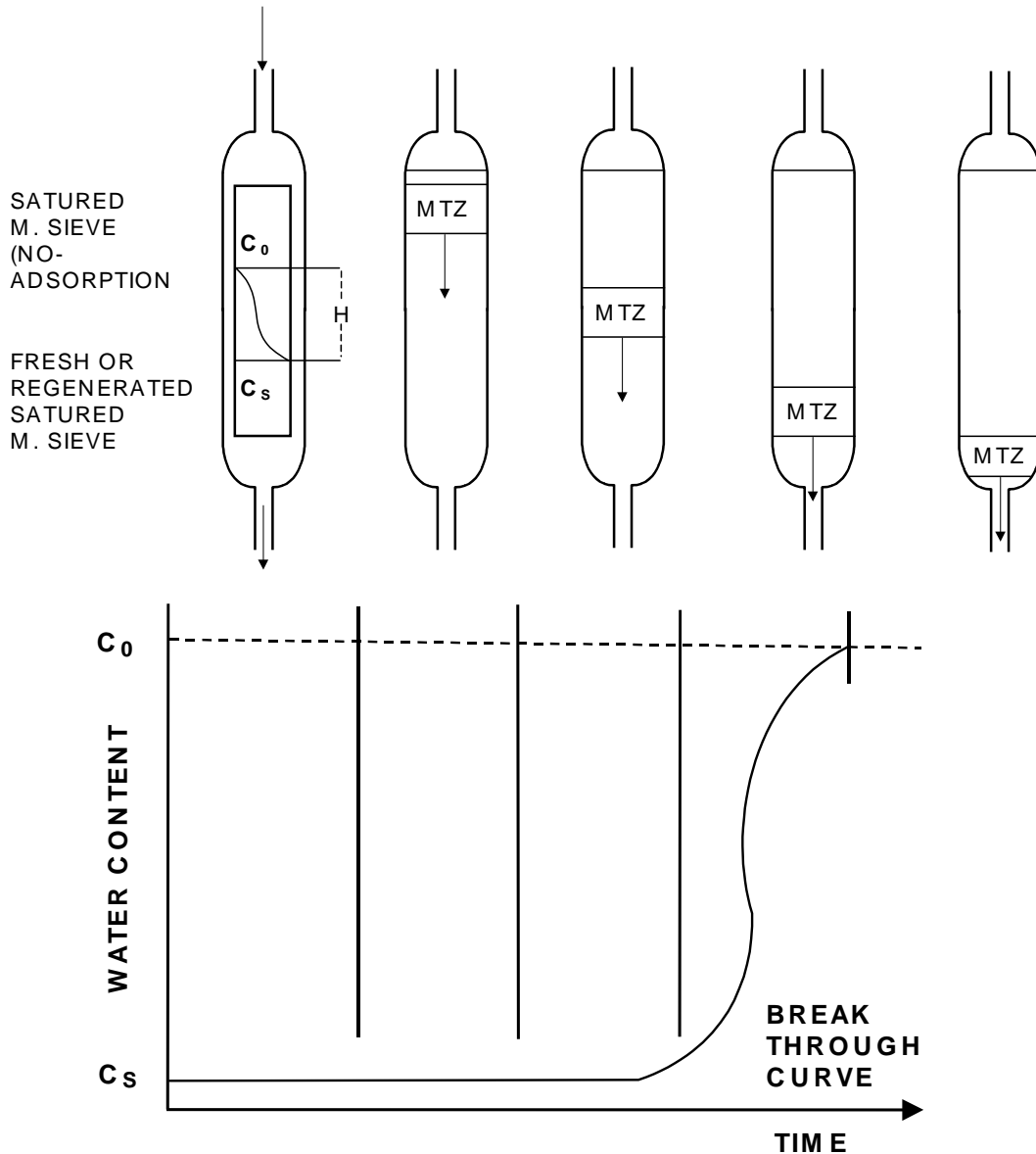
- i) Residual loadings after previous regeneration
- ii) Degradation of adsorbent due to ageing, dusting, coking, fusion etc.
- iii) Heat of adsorption effects
- iv) Co-adsorption and displacement desorption
- v) Length of mass transfer zone.

Any adsorption process is unsteady and the progress of adsorption along the length of the bed can be explained by mass transfer zone principle. In any adsorption column at any given time, there are three conceptual zones as per Fig 3.

- a) **Equilibrium zone:** which corresponds to an exhausted part of the bed.
- b) **Mass transfer zone (MTZ):** which the working zone.
- c) **Pure or dry zone:** which acts as safety factor in achieving the desired specifications.

As the time passes, MTZ moves out of the bed and outlet impurity levels start rising. The start of breach of product purity is known as break through point. The shape of the break through curve determines the length of mass transfer zone. Short MTZ lengths are good for optimum utilization of capacity.

**Fig. 3**



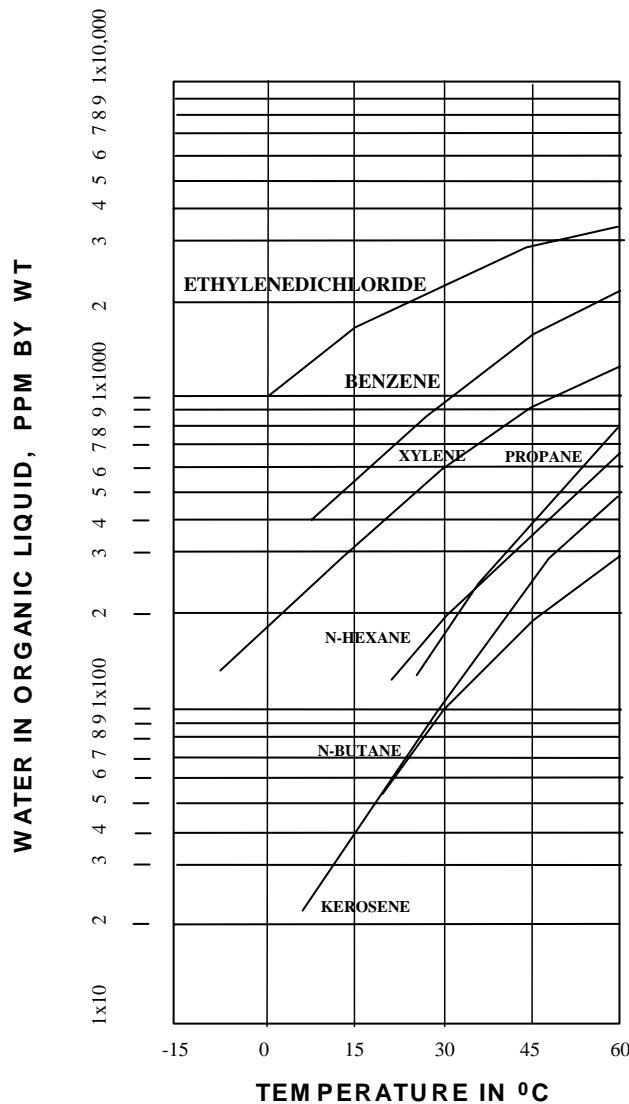
#### 4. Liquid Phase Adsorptive Drying

##### 4.1 Limits of Drying:

Organic liquids are classified in three categories:

a) **Immiscible liquids:** They form easily separable layers of aqueous and organic phases. The organic layer contains dissolved water and this solubility depends basically on temperature. It is generally not known that it also depends on pH and the type/concentration of impurities. For most liquids, solubility of water at 20°C is below 0.2% (2000 ppm). The examples are benzene, xylene, toluene, n-hexane, kerosene, Methylene chloride, carbon tetrachloride, and dichloro benzenes. Solubility of water in some of these liquids can be seen in Fig 4.

**Fig. 4**



**b) Partly Miscible Liquids:** They also form layers of aqueous and organic phases but concentration of water in the organic layer is fairly high and it can range from 1% to 20%. The examples are butanol, ethyl acetate, butyl acetate, para cumidene, MEK etc.

**c) Miscible Liquids:** They are soluble in water at any concentration and do not form any layers. The examples are methanol, ethanol, acetone, THF, DMF, pyridine etc.

**While immiscible liquids theoretically can be dried to as low as 1 ppm of water, partly and fully miscible liquids can be dried upto 100 to 500 ppm water.**

#### **4.2 Typical Process Description:**

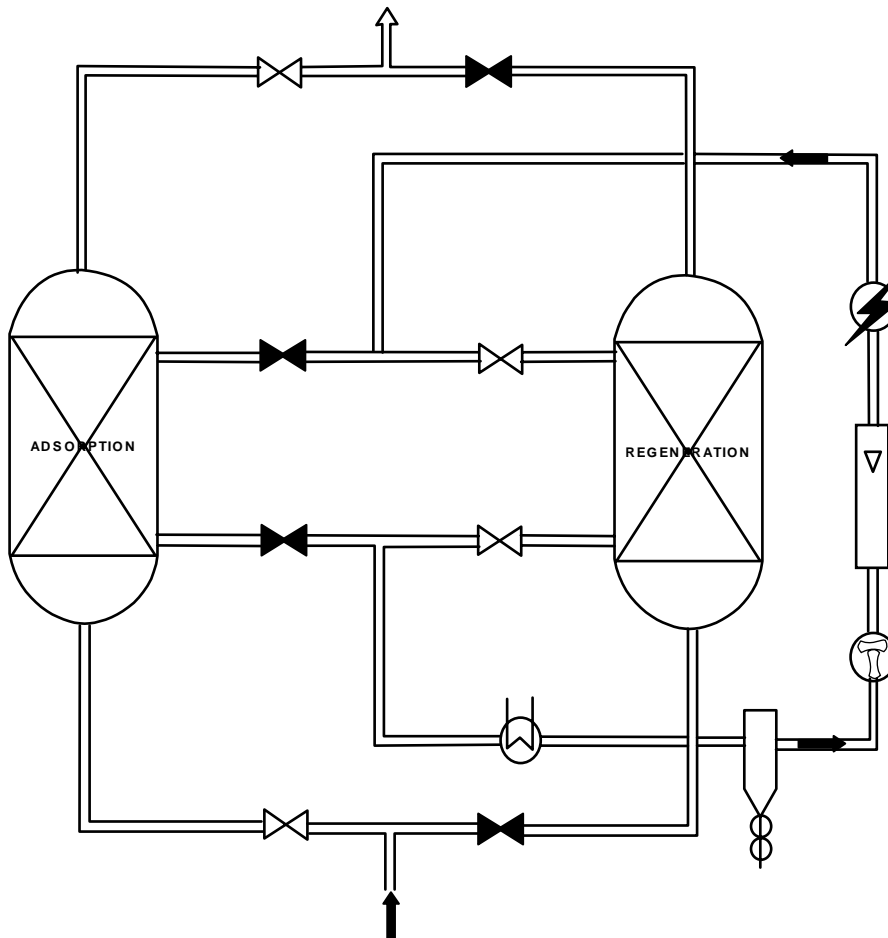
Commercial liquid drying systems can have one, two, three or more adsorption columns depending upon the capacity. The columns undergo the following cyclic operations:

- Adsorption – Usually from bottom to top (to ensure proper distribution).
- Generally single pass is enough to get the required performance.
- Draining – To remove filled liquid to a sump tank.
- Low temperature heating – To evaporate the process liquid on the surface of adsorbents – Usually upto boiling point of the liquid.
- High temperature heating upto 200°C – To desorb water from molecular sieves.
- Cooling – To bring back the bed to working temperature.
- Filling – To move to the adsorption cycle in liquid phase.

The critical step during regeneration is desorption of water. Sufficient heat at certain temperature has to be provided and there should be enough volume of purge gas to carry away the desorbed water. The most popular method is use of hot inert gas like nitrogen in a closed circuit. This method ensures maximum recovery of the process liquid, highest safety and environmental protection. A schematic flow diagram is given in Fig 5.

**Fig. 5**

*TYPICAL SCHEMATIC FLOW DIAGRAM  
(TSA/PSA CLOSED LOOP BLOWER TYPE)*



## 5. Some Case Studies

### 5.1 ETHANOL DRYER (for a glycol ether plant in Uttaranchal):

This is the largest liquid phase ethanol dryer in India. Its capacity is 20,000 LPD of the product. Water content is reduced from 8% to <0.1% on consistent basis since July 2001. Dry ethanol is used for their Glycol Ether Plant. Drying system consists of three main adsorption columns as per Fig 6. While one column is on drying duty for 6 hrs, the other two columns are on regeneration cycle (with one heating and one cooling). This 3-column design enables achievement of energy conservation as heat recovered during cooling is utilized for heating step.

### 5.2 DIETHYL ETHER DRYER (for a bulk drug plant in Gujarat):

This is 20,000 LPD ether dryer for reducing water-content from 1% to less than 0.05% for use in Grignard reaction. Recovered ether from the process plant is first neutralized with caustic soda and

