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# An experimental study of adsorption and variable temperature desorption of ethanol-water, propane-propylene and hydrogen sulfide-carbon dioxide-propane

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# AN EXPERIMENTAL STUDY OF ADSORPTION AND VARIABLE TEMPERATURE

## DESORPTION OF ETHANOL-WATER, PROPANE-PROPYLENE

## AND HYDROGEN SULFIDE-CARBON DIOXIDE-PROPANE

BY

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# ABSTRACT

An ideal adsorption only removes the desired components. Many times one or more other components are also adsorbed. If two or more components are adsorbed, an adsorption separation may not be satisfactory or may require additional separation procedures, even though one is highly preferentially adsorbed. In such cases it may be possible to get additional separation during the desorption stage by using variable temperature desorption.

To study such problems, two experimental apparatus were set up, one for adsorption for ethanol and water mixtures on activated carbon and silicalite, the other for propane-propylene mixtures, and hydrogen sulfide-carbon dioxide-propane mixtures both on molecular sieves (5A and 13X). Both types of adsorption were followed by a stepwise desorption process with increasing temperatures.

The study indicates that, in the desorption process the above three separations are significantly improved, with the more weakly adsorbed components being desorbed first at lower temperatures followed by desorption of the more strongly adsorbed components at higher temperatures.

The method of variable temperature desorption may have useful applications in many adsorption separations.

# ACKNOWLEDGEMENT

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## I. INTRODUCTION

Adsorption-desorption processes are widely used in industry especially in the petroleum refining and petrochemical industries.

Adsorption is usually used to remove low concentrations of impurities or small amounts of valuable products from liquids or gases. Adsorption is often not suitable to use for removal of high volume products because the use of solids makes it more difficult and complex in continuous processes and multiple stages and high adsorbent costs may be necessary unless an almost complete separation can be obtained in one stage.

There are many potential uses for adsorption as a separation method due to the fact that relatively specific interaction forces exist at interfaces and these produce very selective separations. However, most adsorptions are not 100 percent selective for the components to be removed. Due to the complexities of staging for increasing the separation, the applications of adsorption have not been as widespread as distillation, extraction and gas absorption which involve liquids and gases, even though the latter separations usually require more energy consumption. Improvements in adsorption-desorption techniques have a good possibility of permitting increased use of these techniques.

The purpose of this research was to determine whether the use of adsorption with the desorption process carried out in multiple steps at different temperatures could be used in industrially important separations. As examples of possible industrial applications of this method, the separations of ethanol and water, propane and propylene, and hydrogen sulfide, carbon dioxide and propane were investigated.

## II. LITERATURE REVIEW

### A. ADSORPTION-DESORPTION PROCESSES

1. _Adsorption Process_. Adsorption is the concentration, due to surface forces existing on a solid, of gases, vapors, liquids solutes, dispersed materials or colloids. The extent of the adsorption may be large or small, and depends on the nature and character of the adsorbent and the adsorbate, the material concentrated, localized, fixed, or separated.

The adsorbent may be employed only once or it may be used once and then be removed and treated to eliminate the adsorbate and be rendered fit for reuse, a process termed "reactivation" or "regeneration", or it may be used in such a manner that adsorption, reactivation in place, and re-use occur in cyclic procedures.

Adsorbents are specific in their nature and properties. According to Mantell, applications of adsorption are often subdivided into the following (1):

"1. Separation of gases from gases, as deodorization of air, elimination of toxic gases.

2. Separation of vapors from gases, as recovery of solvents, drying of gases, dehumidification.

3. Separation of solutes from solutions, as decolorizing and clarifying of liquids.

4. Separation of ions from solutions, as concentration of metal ions on adsorbents (ion exchange).

5. Separation of dissolved gases or suspended solids from liquids, as in water treatment.

6. Concentration of dissolved materials, often toxic in nature, to eliminate them from liquids, as in the case of medicinal carbons, which take up poisonous chemical compounds.

7. Fractionation by selective adsorption of gases from gases, vapors from gases, vapor from vapors, liquids from liquids, dissolved materials from other solutes, and then concentration of these."

Adsorption should be sharply differentiated from absorption. Adsorption involves the concentration of an adsorbate at an interface between phases, with physical or chemical interactions between the adsorbent and the adsorbate, while absorption refers to a component in one phase dissolving or penetrating throughout the volume of another phase. A gas or vapor

brought into contact with a solid substance may tend to collect on the surface of the solid. This phenomenon is known as "adsorption". The term "absorption", on the other hand, is used to describe the phenomenon that occurs when a gas or vapor penetrates a solid or liquid producing a solid or liquid solution. Adsorption may occur simultaneously with chemical reaction or the solution of the gas in the mass of the solid. The general term "sorption" may be used when a gas or vapor is taken up by a solid.

The adsorbing solid, or adsorbent, is generally extremely porous with large internal surfaces, its external surface comprising only a small part of the total surface. Diffusion of adsorbate into ultramicroscopic pores and capillaries is easily confused with absorption into a solid solution in the interior of the solid. However as long as the gas does not penetrate into the structure and bonding of the atoms, ions, or molecules inside the solid, it is considered adsorbed on the surface of the solid.

The adsorbed atoms or molecules may be bound to the surface by a weak interaction between solid and gas, similar to condensation, or by a strong interaction, similar to chemical reaction. The former is called physical or van der Waals adsorption, and the latter is termed "chemisorption". This type of adsorption requires activation energies in the same range as do chemical reactions. In physical adsorption the adsorbed gases may be easily pumped off under low pressure, particularly if the temperature is raised. In chemisorption, generally a much higher temperature may be necessary either to adsorb or to remove the gases and the process may be irreversible. The binding between the adsorbed material and the solid may be sufficient so that the gas originally adsorbed, acts as if in a different state (e.g., as atoms instead of molecules, or as compounds with the atoms of the adsorbent) and thus may act as a catalyst in speeding up reactions (2).

During the 1970s due to the escalation of energy prices, which made the separation of close boiling components by distillation a costly and less economical process, interest in adsorption separations increased. It was desired to determine whether certain distillations could be replaced by a more economic adsorptive separation. However, for adsorption processes to be developed on a commercial scale requires a suitable adsorbent in tonnage quantities at an economic cost. This has stimulated research in adsorption and the development of new adsorbents. The potential of adsorption as a separation process led to the development of

molecular sieve adsorbents, which first became available on a commercial scale in the late 1950s (3).

Physical adsorption generally decreases with increasing temperature, and it is to be expected that it should take place with the evolution of heat (i.e. it is an exothermic process). The general magnitude of the heat evolved distinguishes in some degree between physical adsorption and chemisorption. In physical adsorption, heats of adsorption are similar to heats of liquefaction of gases, and in chemisorption, they are similar to heats of chemical reaction.

Adsorption occurs practically instantaneously in some cases, in others at a measurable rate until a state of equilibrium is reached.

The amount of gas adsorbed at equilibrium is dependent upon the temperature, the pressure, and the adsorbent, and the preparation and history of the adsorbent. The quantity of a gas adsorbed by a given weight of adsorbent varies greatly from one adsorbent to another. Amorphous solids are generally more adsorbent than crystalline materials (4).

The Langmuir theory regards the surface of an adsorbent as containing different kinds of sites on the surface arranged in a pattern that has been compared to a checkboard. When a molecule from a gas phase strikes an unoccupied site on the surface, the molecule will be adsorbed instead of rebounding. It does not adhere indefinitely, and depending upon the thermal energy and on the strength of the attractive forces, the adsorbed molecule may reenter the fluid phase. When the surface is bare, the number of molecules adhering exceeds the number of those leaving. As the surface becomes covered, the rate of adsorption of other gas molecules decreases, and there is also an increase in the number of molecules escaping from the surface. When the rate of escape equals the rate of adsorption, equilibrium is reached. The amount adsorbed at equilibrium is a function of the several factors, some of which are interrelated. These factors, as described by Hassler (5), are as follows:

"1. The time lag i.e., the average period between the moment the molecule condenses and its subsequent evaporation.

2. The total area of the solid surface.

3. The proportion of the total surface which has specific attractive power for the molecules in the gas phase, and also the accessibility of such surface.

4. The number of adsorbable molecules in the gas state, i.e., the pressure (in the case of solutions, the concentration).

5. The number of layers of adsorbed molecules."

In early studies of gas adsorption, it was observed that the more condensable gases are usually adsorbed in larger quantities. However, adsorption will occur when the physical attraction of the gas molecules for the surface is sufficiently great. Gas molecules can condense on solid surfaces by physical adsorption under conditions that would normally cause them to remain in the gas phase, even above their critical temperature.

2. <u>Desorption Process</u>. Desorption is used to remove adsorbed components from the adsorbent and regenerate the adsorbent for repeated use. High temperatures, low pressures, a flow of a diluent gas or liquid or a combination of these can be used for desorption.

In general practice, desorption is accomplished by providing conditions that diminish the adsorbability of the adsorbate which is recovered as a gas or liquid, pure or diluted. This usually is done by elevating the temperature, and in some cases a vacuum is also applied. Gases differ to some extent in their response to elevated temperatures. For this reason, the selection of a suitable temperature can contribute to the efficiency of desorption methods. A higher temperature will generally increase the rate and amount desorbed, but may or may be not selective with respect to components desorbed from a multicomponent adsorbed phase. Variable temperature stepwise desorption can sometimes improve the separation by removing a high concentration of one adsorbed component first at low temperatures and then removing other components later at higher temperatures.

A patent application on this method has been filed by Dr. Marshall E. Findley, Dr. A. I. Liapis, and H. T. Nguyen, at the University of Missouri-Rolla.

3. <u>Temperature Dependence of Adsorption and Desorption</u>. The simplest and most useful theoretical isotherm, for both physical adsorption and chemisorption, is the Langmuir isotherm.

The Langmuir isotherm for monolayer adsorption or homogeneous surfaces is based on the following assumptions (according to Yang) (6):

"1. The adsorbed molecule or atom is held at definite, localized sites.

2. Each site can accommodate one and only one molecule or atom.

3. The energy of adsorption is a constant over all sites, and there is no interaction (for example, via Van der Waals attraction) between neighboring adsorbates."

The isotherm equation is derived based on the concept of dynamic equilibrium between the rates of adsorption and desorption. The sites already occupied are assumed to be unavailable for adsorption, and the rate of adsorption per unit surface equals $\alpha v(1 - \Theta)$, where $v$ is the collision frequency of gas molecules striking the surface, $\alpha$ is the probability that a molecule will stick to the surface, or the accommodation coefficient for adsorption. The variable $\Theta$ is the fractional coverage. As given by the kinetic theory of gases:

$$v = \frac{P}{(2\pi mKT)^{1/2}} \tag{1}$$

where: P = Pressure

m = Molecular mass

K = Boltzmann constant

T = Temperature

The rate of desorption per unit surface area based on physical adsorption is:

$$\beta\Theta e^{-E_d/RT} = \beta\Theta e^{-Q/RT}$$

where: $\beta$ = the rate constant for desorption

$E_d$ = the activation energy for desorption which is assumed to be the heat of adsorption $(-\Delta H)$ for physically adsorbed species, Q.

At equilibrium the following equations apply (7):

$$\Theta = \frac{BP}{1 + BP} \tag{2}$$

$$B = \frac{\alpha}{\beta(2\pi mKT)^{1/2}} e^{Q/RT} \tag{3}$$

equation(2) is the Langmuir isotherm and B is the Langmuir adsorption constant. The variable $\Theta$ is the fraction of monolayer coverage. The temperature dependence of B is $e^{Q/RT}T^{-1/2}$ , and its values decrease rapidly with increasing temperature, because Q is positive for physical adsorption. For small pressures, equation (2) gives a coverage proportional to pressure similar to Henry 's Law. For high pressures, $\Theta$ equals 1, or the adsorptivity is constant and the sites are completely filled.

For the multicomponent systems studied, each component would have a different temperature dependence due to different values of Q for each component. Also most adsorbents probably are not uniform in surface characteristics, and at some sites Q will be different than other sites. For these reasons, the theoretical treatment of adsorption and desorption equilibria is highly complex and requires considerable data beyond the scope of this investigation.

This study was under taken in order to determine experimentally whether changes in temperature during desorption can produce effects leading to improvements in separating propylene from propane, and mixtures of propane, hydrogen sulfide and carbon dioxide, and ethanol-water solutions. All these separations are utilized in industry and are important potential applications for adsorption-desorption techniques.

## B. <u>ACTIVATED CARBON</u>

Activated carbon, a microcrystalline, nongraphitic form of carbon, has been processed to develop internal porosity. Activated carbons are characterized by a large specific surface area of 300-2500 $m^2/g$ which allows the physical adsorption of gases and vapors. Commercial grades of activated carbon are designated as either gas-phase or liquid-phase adsorbents. Liquid-phase carbons are generally powdered or granular in form; gas phase, vapor-adsorbent carbons are hard granules or hard, relatively dust-free pellets. Activated carbons are widely used to remove impurities from liquids and gases and to recover valuable substances such as solvents contaminants, or pollutants from gas streams.

Surface area and its availability are the most important physical property of activated carbon. For specific applications, the surface available for adsorption depends upon the molecular size of the adsorbate and the porous structure of the activated carbon. Generally,

liquid-phase carbons are characterized as having a majority of pores of 3 nm diameter and larger, whereas most of the pores of gas-phase adsorbents are less than 3 nm in diameter. Larger pores are used with liquids because of the need for rapid diffusion in the liquid and because of the larger size of many dissolved adsorbates. Methods of testing adsorbency employ substances having a range of molecular sizes. Liquid-phase carbons are usually characterized by phenol, iodine, and molasses numbers. Gas phase carbons are characterized by carbon tetrachloride and benzene adsorption activities.

The bulk density or apparent density of an activated carbon, together with its specific adsorptive capacity for a given substance, can be used to determine bed capacity in the design of an adsorption system or to determine grades of carbon required for an existing system. The range of particle sizes of activated carbon is important, and the rate of adsorption has been shown to depend inversely upon the particle size (small particles having the fastest rates). However, in fixed beds pressure drop increases as particle size decreases.

The most important chemical properties of activated carbon are the ash content, ash composition, and pH of the carbon. Discrepancies between the expected performance of an activated carbon, based upon surface area and pore-size distribution data, and actual adsorptive capacity, can often be explained by oxygen-containing groups on the surfaces of the carbon. The pH or pKa of the carbon, as a measure of surface acidity or basicity of the oxygen-containing groups, assists in predicting hydrophilicity and anionic or cationic adsorptive preferences of the carbon (8).

Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700 − 1000°C). The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The actual distribution and the total pore volume associated with each pore sizes range are sensitive to the condition of the initial pyrolysis and activation procedures. Typical ranges are given in Appendix A, Table V, but by special procedures it is possible to prepare activated carbons with even higher porosity, surface area, and adsorptive capacity. The surface of carbon is essentially nonpolar although a slight polarity may arise form surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic.

They are widely used for the adsorption of organics in decolorizing sugar, water purification, and solvent recovery systems as well as for the adsorption of gasoline vapor and as a general purpose adsorbent in air purification systems (9).

Some typical physical properties of activated carbons are shown in Appendix A, Table VI. These are approximate values, and properties vary by grade and manufacture within each raw material type (10).

## C. ZEOLITES

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium, and calcium, represented by the stoichiometry $M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$ where x and y are integers with y/x equal to or greater than 1, n is the valence of cation M, and z is the number of water molecules in each unit cell. The cations are necessary to balance the electrical charge of the $AlO_2$ groups, each having a net charge of -1. The water molecules can be removed with ease upon heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are usually interconnected by six windows in each cage. The cages can imbibe or occlude large amounts of guest molecules in place of water. The size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 Å to 10 Å. The sorption may occur with great selectivity because of the size of the aperture (and to a lesser extent because of the surface property in the cages)-hence the name "molecular sieve". More than 150 types of zeolites have been synthesized; they are designated by a letter or group of letters-Type A, Type X, Type Y, Type ZSM and so on. The primary structural units of zeolite are the tetrahedra of silicon and aluminum, $SiO_4$ and $AlO_4$. These units are assembled into secondary polyhedral building units such as cubes, hexagonol prisms, octahedra, and truncated octahedra. The silicon and aluminum atoms, located at the corners of the polyhedra, are joined by a shared oxygen. The final zeolite structure consists of assemblages of the secondary units in a regular three-dimensional crystalline frame work. The ratio Si/Al is commonly one to five. The aluminum atom can be removed and replaced by silicon in some zeolites, thereby reducing the number of cations, and the cations can be exchanged. The inner atoms in the windows are

oxygen. The size of the windows depends, then, on the number of oxygen atoms in the ring four, five, six , eight, ten, or twelve. The aperture size, as well as the adsorptive properties, can be further modified by the number and type of exchanged cations. The characteristics of the major commercial zeolite sorbents in the pelletized forms are given in Appendix A, Table VII (11).

The important gas separation processes using zeolite adsorbents are: air separation for the production of oxygen and nitrogen, hydrogen purification, recovery of n-paraffins from branched-chain and cyclic hydrocarbons, aromatic hydrocarbon separation, and drying. These and other uses have been discussed by Collins (12). Except for the n-paraffin and aromatics separations, these processes employ the preferential adsorption of certain components. For example, nitrogen is preferentially adsorbed over oxygen (by approximately three fold in 5A zeolite) as a result of its quadruple moment, which forms a strong bond with the polar surface (13).

## D. SILICALITE

The pentasil zeolites comprise a family of silica-rich zeolite with structure based on the double five-ring unit. By stacking such layers in different sequences a variety of related structures may be obtained. More detailed descriptions have been given by Kokatailo, Meier, Olson, and co-workers (14,15).

The channel systems of the two end members, ZSM-5 and ZSM-11, which are characterized by a ten-membered oxygen ring of free diameter about 6 Å , which is intermediate between the small-port sieves with 8-ring channels and the large-port sieves with 12-ring channels. The Si/Al ratio is typically about 30 but wide variation is possible and the structures may be prepared in essentially aluminum-free form. The aluminum free form of ZSM-5 is often referred to as silicalite. These materials are characterized by great thermal and hydrothermal stability and show a number of useful catalytic properties, including the ability to catalyze the conversion of methanol to gasoline range hydrocarbons without excessive coke formation. The affinity for water is low while the affinity for linear parafins and para-substituded aromatic

hydrocarbons is surprisingly high. These adsorbents are therefore potentially useful as an alternative to activated carbon for removal of organics from aqueous streams (16).

## III. EXPERIMENTAL

### A. MATERIALS AND EQUIPMENT

#### 1. Materials.

- Ethanol

- Water

- Propane

- Propylene

- Hydrogen sulfide

- Carbon dioxide

- Activated carbon (granular, Calgon F-200)

- Molecular sieves 5A and 13X (Union Carbide Company)

- Silicalite (Union Carbide Company)

#### 2. Equipment.

- Copper and stainless steel U-tubes were used to contain the adsorbents.

- A water bath was used to keep temperature constant in the adsorption process.

- An oil bath was used to heat up the adsorbent column in adsorption and desorption processes.

- A condenser was used to condense the liquid solution from vapor in the desorption process.

- A pump was used to circulate vapor from the liquid solution to the adsorbent column in the adsorption process, and to circulate vapor from column to condenser in the desorption process.

- A vacuum pump was used for evacuating gases.

- A heater was used to heat up the oil bath.

- Gas chromatographs, Hewlett Packard model-5890A and Aerograph model-A-90-P, were used for analytical purposes.

- An integrator, Hewlett Packard model-3390A, was used to integrate plot results from the gas chromatograph (model HP-5890A).

- Pressure gauges are used to measure pressure.

- Gas tanks were used to contain propane-propylene, carbon dioxide-hydrogen sulfide-propane, pure propane, pure propylene in various composition.

- Flasks for solutions.

- Vials and syringe for taking samples.


## B. EXPERIMENTAL PROCEDURE FOR ETHANOL-WATER

The experimental apparatus for adsorption-desorption processes for ethanol and water mixtures is shown in Figure 1.

A U-tube filled with adsorbent was used as an adsorbent column.

The water bath is used to maintain the approximately 150 ml of a 6 weight percent ethanol solution, contained in the flasks, at 40°C (104°F) during adsorption processes.

The heater in the oil bath is used to keep the adsorbent column at 44°C in adsorption processes, and to heat up the adsorbent column to various temperatures (from 50 to 140°C) in desorption processes. In the adsorption process, the adsorber is kept at a slightly higher temperature than the solution flask to avoid condensation in the adsorbent interstices, which would greatly reduce the efficiency of any separation acheived.

In the adsorption process used, vapor from the liquid solution is stripped from the flask and passed through the adsorbent column with the gas pump. The vapor is circulated through the adsorber for approximately 3 hours, saturating the adsorbent with vapor from the liquid solutions. To approach saturation by adsorption, the column temperature is maintained at higher temperature for 1 hour and then decreased to the desired temperature for 2 hours. To approach saturation by desorption, the column is maintained at a lower temperature for 1 hour and then increased to the desired temperature for 2 hours.
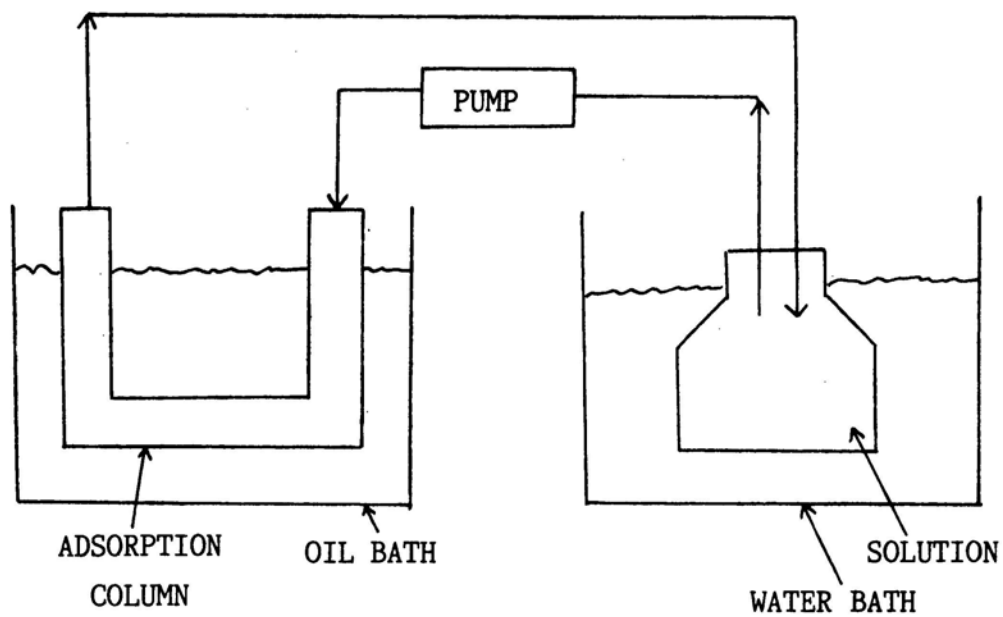
(a): ADSORPTION
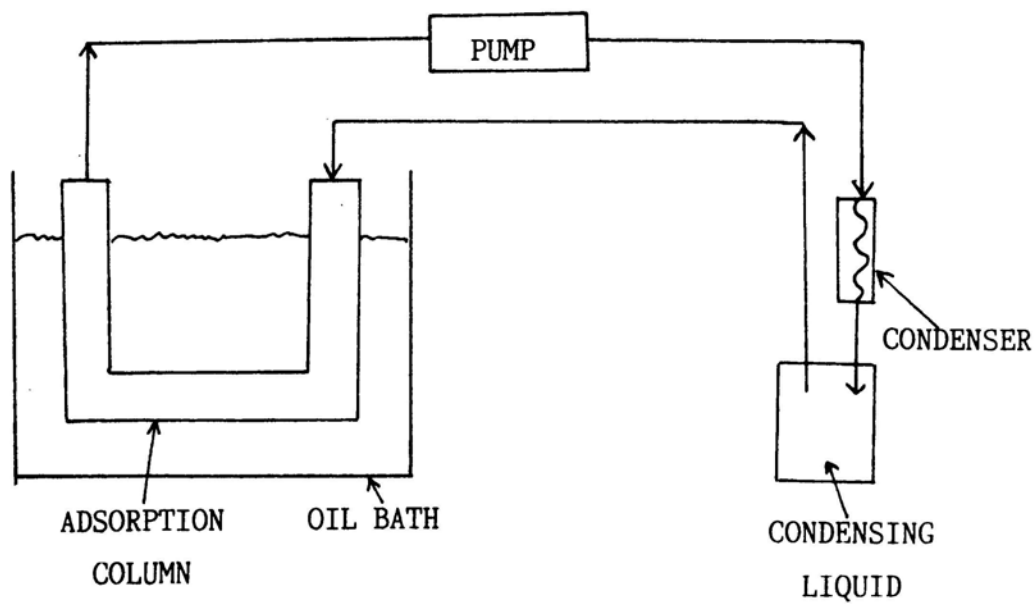


(b): DESORPTION

Figure 1.    Experimental apparatus for ethanol-water.

The liquid mixture was recovered from the adsorber by stripping at up to 140°C (284°F) and the vapor mixture is pumped out from the adsorber with the gas pump and is passed through the condenser at 21 °C. The liquid is collected in a sample bottle and the vapor stream is recirculated to the adsorbent column.

In some runs the vapor is removed from the adsorber at a starting temperature of 50 °C, and the temperature is then increased whenever there is no further condensation from the condenser. This continues until the desired highest temperature is reached.

The condensing liquids are weighed and samples were injected into the gas chromatograph (Aerograph model-A-90-P) for analysis.

To determine vapor pressure in equilibrium with an adsorbent holding a fixed amount of adsorbed phase a system such as Figure 1 (b), with no reservoir and no condenser was used. After recirculation of gas at the desired conditions, gas samples were taken and analyzed on a gas chromatograph.

## C. <u>EXPERIMENTAL PROCEDURE FOR PROPANE-PROPYLENE</u>

The experimental apparutus for the adsorption-desorption process of propane-propylene mixture is shown in Figure 2.

1. <u>Adsorption Step</u>. Before performing initial adsorptions, a vacuum was applied while heating the column up to 160 °C, in order to desorb the column. The column was then cooled to room temperature. In many cases the column was heated to 160 °C at 1 atmosphere for desorption.

Adsorption of a propane-propylene mixture was tested by allowing a mixture of 50 mole % propane-50 mole % propylene to flow through an appropriate adsorbent column. For adsorption, the column was at 25 °C, and the gas mixture was passed through the column into a chamber that was alternately evacuated and filled to atmospheric pressure with the column out flow.

From volume, pressure, and temperature, the outflowing number of moles were calculated, and samples of each filling were analyzed. Equilibrium of the adsorbent with the gas mixture was assumed when the out flow was essentially equal in composition with the inflow and after isolation, the pressure remained constant at 1 atmosphere and 25 °C.

2. <u>Desorption Step</u>. The gas mixture was desorbed by heating the adsorbent column, first to 50 °C and later to higher temperatures. The gas desorbed after heating was released from the column to an evacuated chamber for measurement by pressure, volume and temperature. Gas was released until there was no change in the atmospheric pressure of the column at a given temperature. This indicated the complete desorption at this temperature.

The desorbed gas was sampled and analyzed with a gas chromatograph (model HP-5890A). The column was then heated to 80 °C and the quantity and composition of the desorbed gas was measured as before.
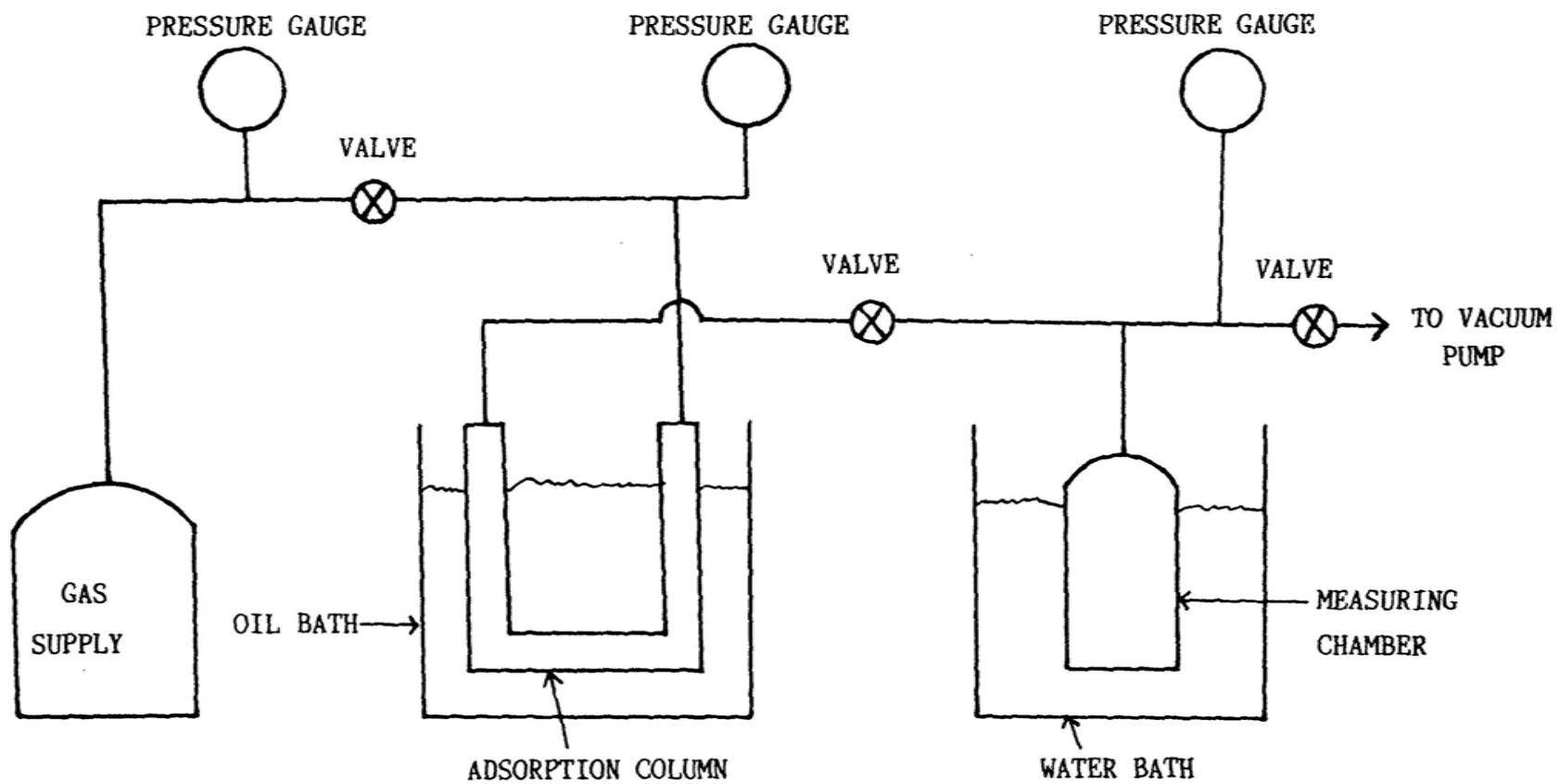
Figure 2.    The experimental apparatus for propane-propylene and propane-hydrogen sulfide-carbon dioxide.

This procedure was repeated at various steps in temperature up to 160 °C. At each temperature, the pressures of the column and the chamber were recorded for quantity measurements, and after each desorption temperature the measuring chamber was evacuated by the vacuum pump. In some cases the entire desorption was at 1 atmosphere to simulate possible industrial conditions. In other cases, the first desorption occurred by dropping the pressure to 1 atm, and the last step was to reduce the pressure to about -730 mm Hg at the highest temperature of desorption.

Similar procedures were used when molecular sieves 5A and 13X, silicalite and activated carbon were used in the adsorption columns.

## D.  EXPERIMENTAL PROCEDURE FOR CARBON DIOXIDE-HYDROGEN SULFIDE-PROPANE

The experimental apparatus and procedure for the $CO_2 - H_2S - C_3H_8$ adsorption-desorption process were almost the same as the experimental procedure for the propane-propylene mixture.

The composition for $CO_2 - H_2S - C_3H_8$ was 80 mole % $C_3H_8$, 10 mole % $CO_2$ and 10 mole % $H_2S$. Also a mixture of 50 mole % $C_3H_8$, 25 mole % $CO_2$ and 25 mole % $H_2S$ was tested. During the desorption step, desorbed gas was sampled and analyzed by gas chromatograph (Aerograph model A-90-P).

## E.  SAMPLE CALCULATIONS

Sample calculations are shown in Appendix E. Results are in the Results and Discussion section.

F. ANALYSIS

1. Propane-Propylene Mixtures. For chromatography (model HP-5890A), a column packed with n-octane polasil C 80/100 mesh from Supelco, inc, was used with a flame ionization detector.

In the gas chromatograph (model HP-5890A):

- The temperature (degree Celsius) were:

For the oven, constant temperature of 65, 120 for the injector, 120 for the detector.

- The time was 4 minutes.

- Nitrogen was the carrier gas with hydrogen and compressed air used for the flame ionization detector.

- The nitrogen flow was 25 ml/minutes through a 1/8 inch x 6 ft. packed length stainless steel column.

- Data recorded: A sample was analyzed on the gas chromatograph. A calibration test was performed in each series of tests. The mole ratios of the components were calculated as proportional to the area ratios from the gas chromatograph intergrator (HP-3390A) for samples at each desorbing temperature. The proportionality was based on a constant from calibration runs.

2. Ethanol-Water Mixtures.

- Packing = Porapak Q.

- Temperature = 100°C.

- Column 1/8 inch x 3 ft. packed length.

- Detector = thermal conductivity.

3. <u>Hydrogen sulfide-Carbon dioxide-Propane</u>.

        - Packing = Porapak Q.

        - Temperature = 100°C.

        - Column 1/8 inch x 3 ft. packed length.

        - Detector = thermal conductivity.

# IV.  RESULTS AND DISCUSSION

The results for the adsorption-desorption separation of ethanol and water were tabulated in Appendix C, Tables XXXVII-XXXLII.  Adsorption-desorption data on propane and propylene from molecular sieve 5A and 13X were tabulated in Tables I, II, and in Appendix B, Tables XIII-XXXI, XXXIII-XXXVI and adsorption-desorption data on propane-hydrogen sulfide-carbon dioxide on molecular sieve 13X were tabulated in Appendix B, Table XXXII.

The important possibilities of separation by variable temperature desorption were discovered by Mr. Hoa Tri Nguyen under the direction and supervision of Drs. M. E. Findley and A. I. Liapis in attempts to improve the possibilities of producing ethanol for fuel by a combined fermentation and adsorption process using activated carbon.  Mr. James Langston and the author continued this work by preliminary studies under different conditions and with a different adsorbent, silicalite.  The results on silicalite are given in Appendix C, Tables XLI-XLII.  In the adsorption on both activated carbon and silicalite, water desorbed more at lower temperatures followed by more ethanol adsorption at higher temperatures.  This is the reverse of the normal vaporization of ethanol and water from liquids, where ethanol vaporizes at lower temperatures than water.  The results with silicalite were less significant, and the adsorptive capacity was low.  However, the results on activated carbon indicated that it might be feasible to preferentially adsorb ethanol along with some water.  Then a variable temperature desorption could be used to desorb water at lower temperatures into one stream, and then desorb ethanol at higher temperatures into another stream.

From Figures 3, 4, and 5, the results for ethanol-water showed that, with activated carbon adsorbents, most of the water is desorbed and condensed up to about 80°C to 90°C. Ninety six percent of the water desorbed and was condensed and collected at adsorbent bath temperatures from 50°C to 90°C . The ethanol concentration in all the condensate up to 90°C was 4.7 %.  At temperatures from 90°C to 140°C,  the total condensate was 91.1 % ethanol. This condensate included 88 % of the total ethanol that was desorbed.

Figure 6 shows the results obtained when the natural log of ethanol vapor pressure was plotted against inverse temperature in the desorption step for constant adsorbed quantities.
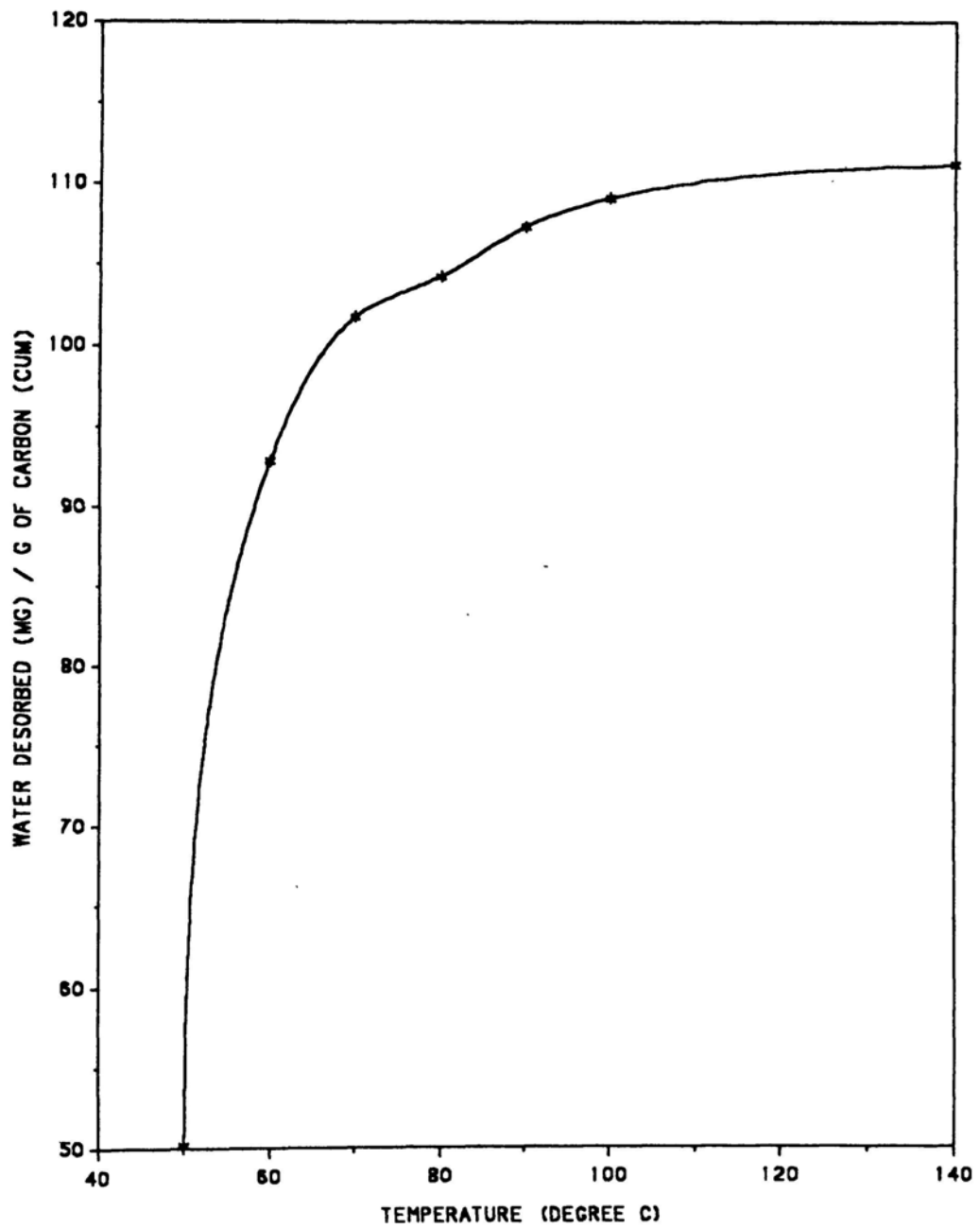
Figure 3.    Cummulative amount of water desorbed and condensed per gram of carbon vs. temperature.
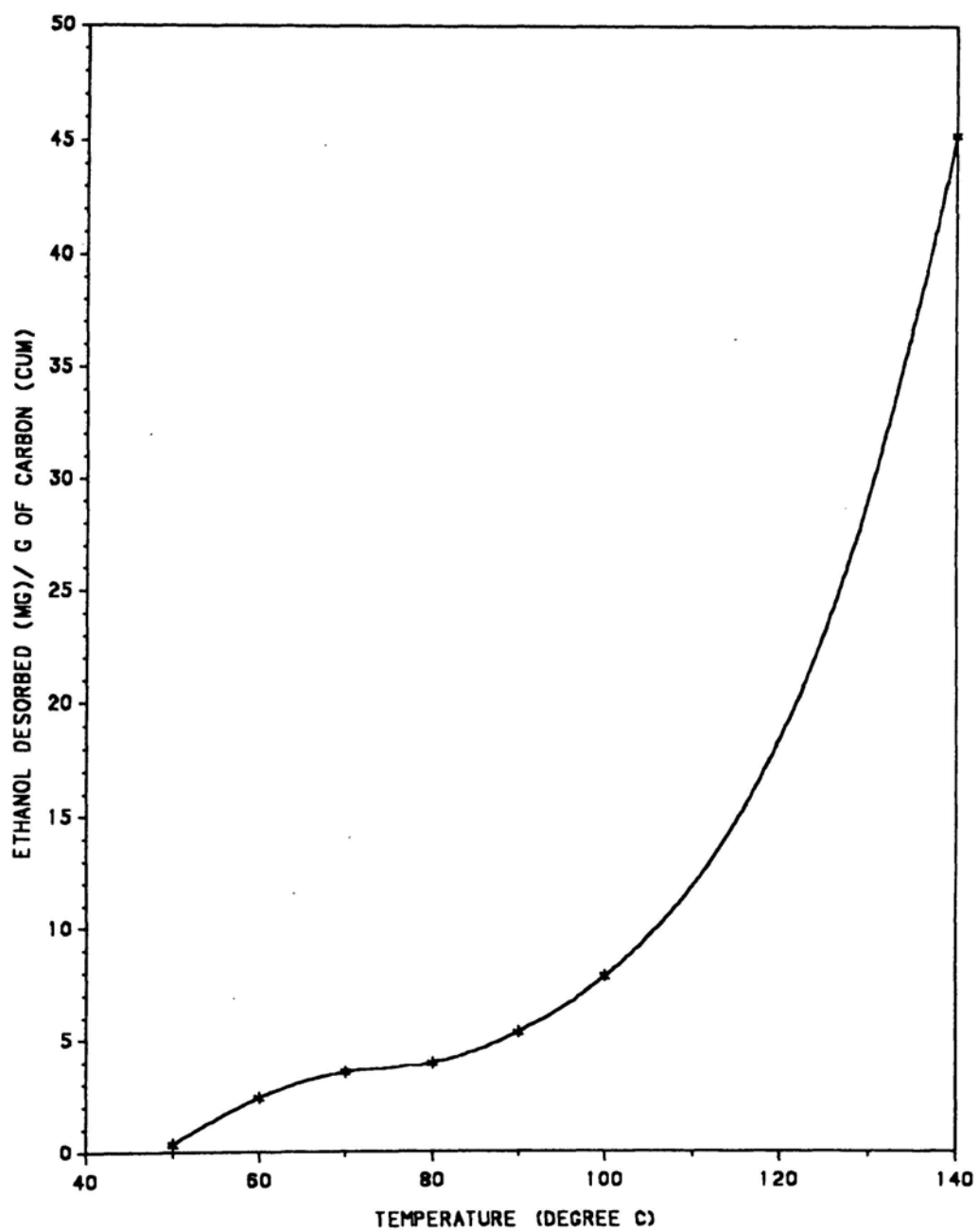
Figure 4.    Cummulative amount of ethanol desorbed and condensed per gram of carbon vs. temperature.
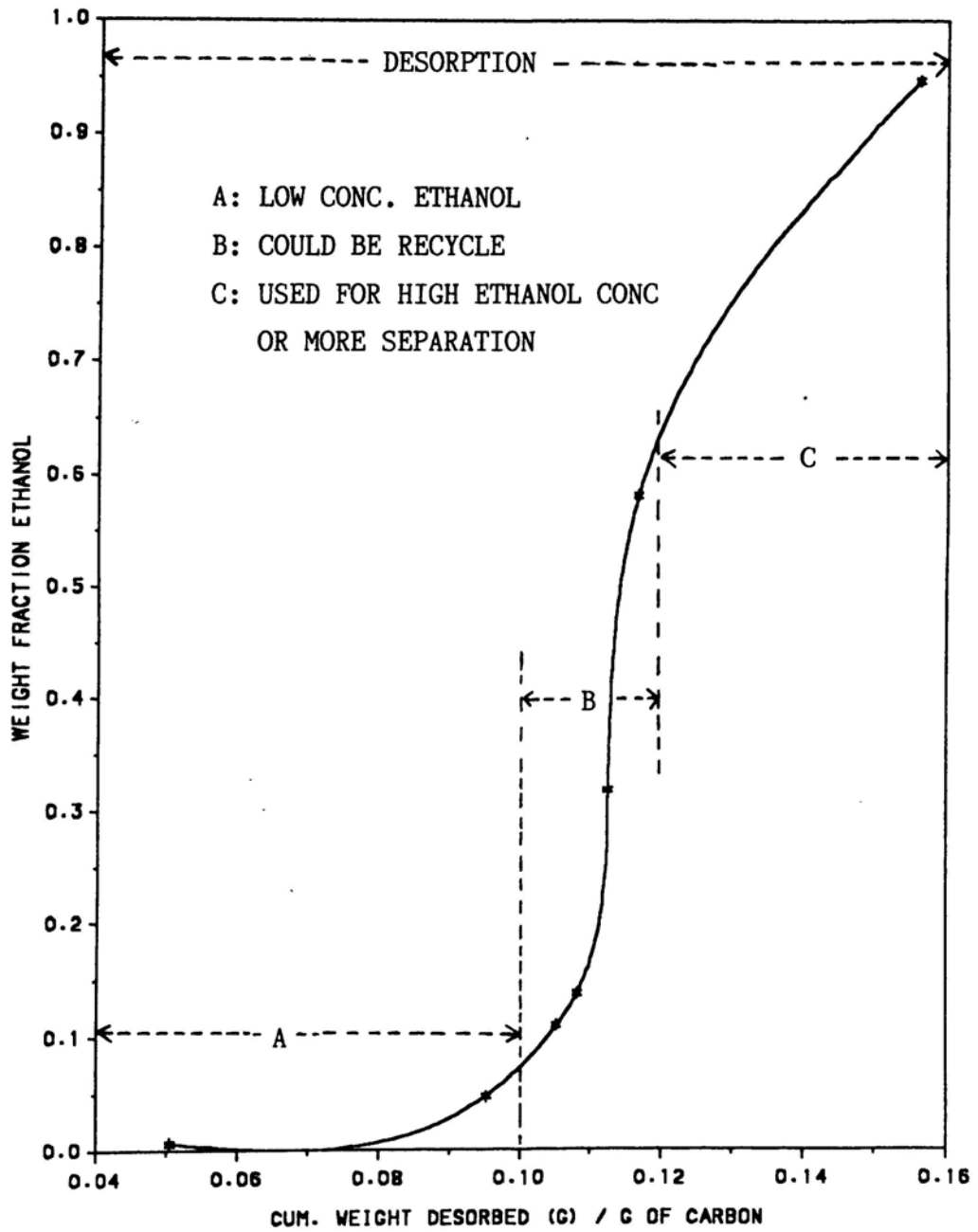
Figure 5.    Weight fraction of ethanol vs. cummulative weight desorbed per gram of carbon. Ethanol and water were previously adsorbed from air and vapor at 44 degree C. Air and vapor were in equilibrium with 6 wt % of ethanol in water solution at 40 degree C.
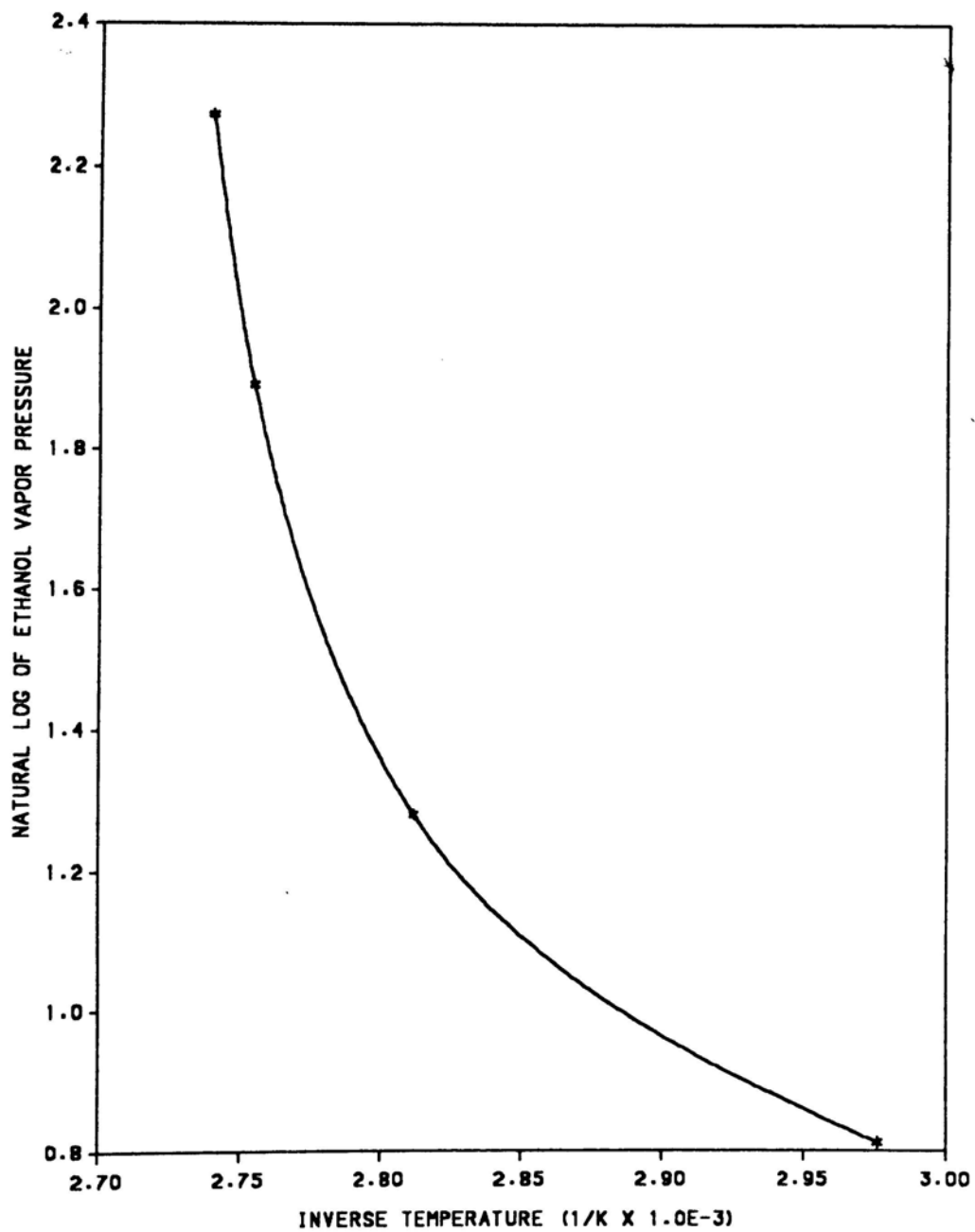
Figure 6.    Natural log of ethanol vapor pressure vs. inverse temperature.

The plot shows that the relationship is not linear, which implies that $\Delta H_{Ads.}$ and $\Delta H_{Des.}$ are not constant, but change with temperature, or that adsorption and desorption are not reversible and equilibrium was not reached within the 2-3 hours of the experiments. This data suggested that hysteresis might occur, yielding different adsorption and desorption component compositions at a constant temperature. To obtain this data, the column was brought to apparent equilibrium at a series of different temperatures for adsorption (with temperature decreasing to the desired level) and desorption (with temperature increasing to the desired level). Then the column was stripped at 120°C and the column exit was condensed and analyzed. The amount of ethanol (grams) adsorbed (or remaining after desorption) on the column per gram of carbon was plotted against temperature (°C). This graph is shown in Figure 7, and reveals a definite hysteresis occurs for ethanol with the desorption curve lying above that for ethanol adsorption. This phenomena may be due to the fact that adsorption and desorption equilibrium was not reached in the experiment time of 2 hours. A similar plot was done for water adsorption and desorption (Figure 8), which showed that the water exhibited negligible hysteresis effects, or adsorption and desorption are almost reversible. Tests showed that weights of adsorbent were essentially constant after 2 hours so any changes taking place at the end of the experiments must have been very slow. These results show that water desorbs at low temperature, leaving a relatively high concentration of ethanol on the column, which desorbs at high temperatures. The apparent irreversibility of ethanol adsorption-desorption contributes to the separation by requiring higher temperatures to desorb ethanol.

The cumulative amount (grams) of water and ethanol desorbed and condensed at each temperature is shown in Figures 3 and 4. In Figure 3, the amount of water desorbed rises quickly, then begins to level out at approximately 80°C. Figure 4 shows that the amount of ethanol desorbed with the water does not increase significantly below 80°C. Therefore, we could desorb most of the water at a low temperature, then recover the ethanol at a higher concentrations at a higher temperature.

A proposed method of fermentation, adsorption and variable temperature desorption for ethanol production is given in Appendix D.
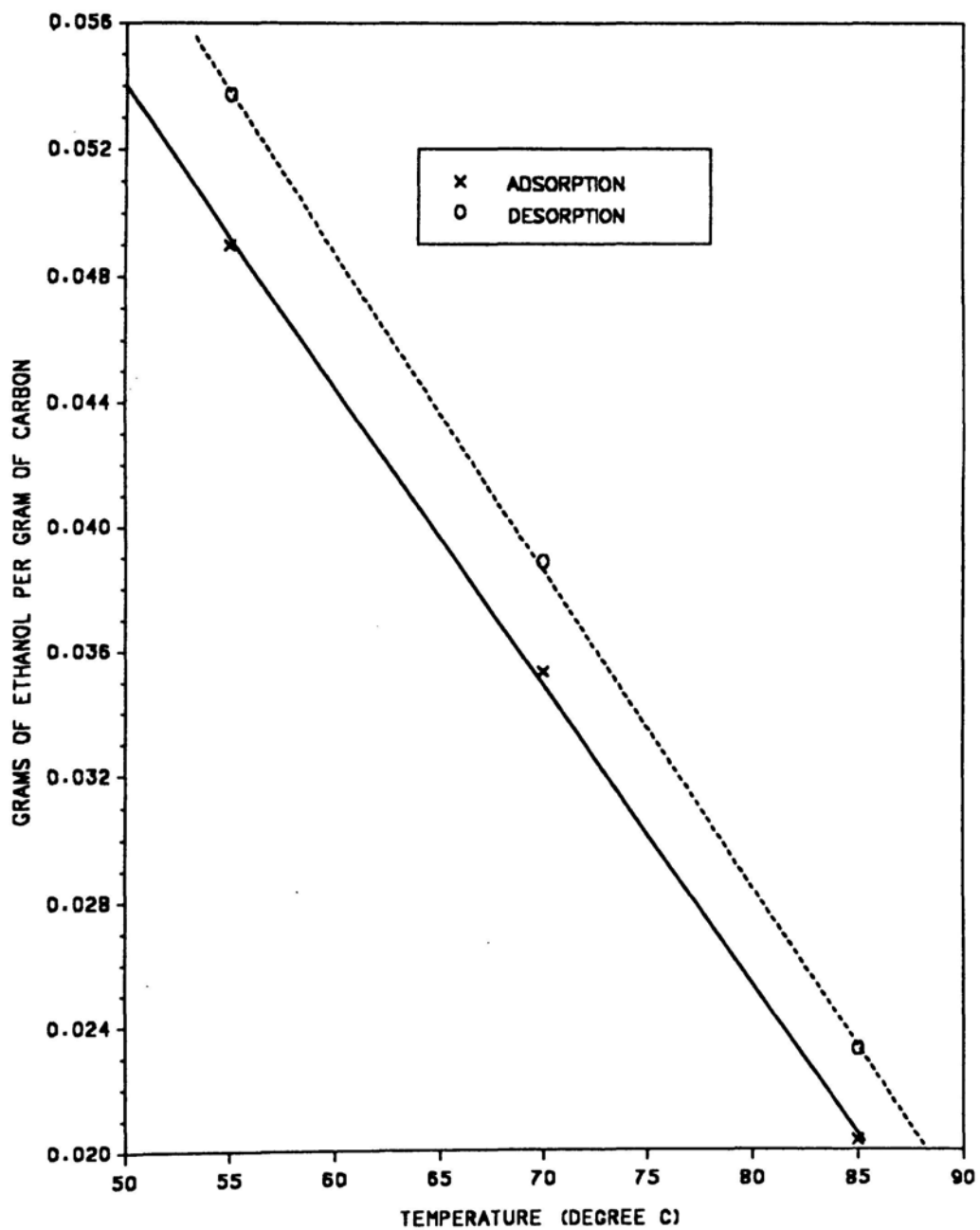
Figure 7.    Grams of ethanol adsorbed or remaining after desorption per gram of carbon vs. temperature.
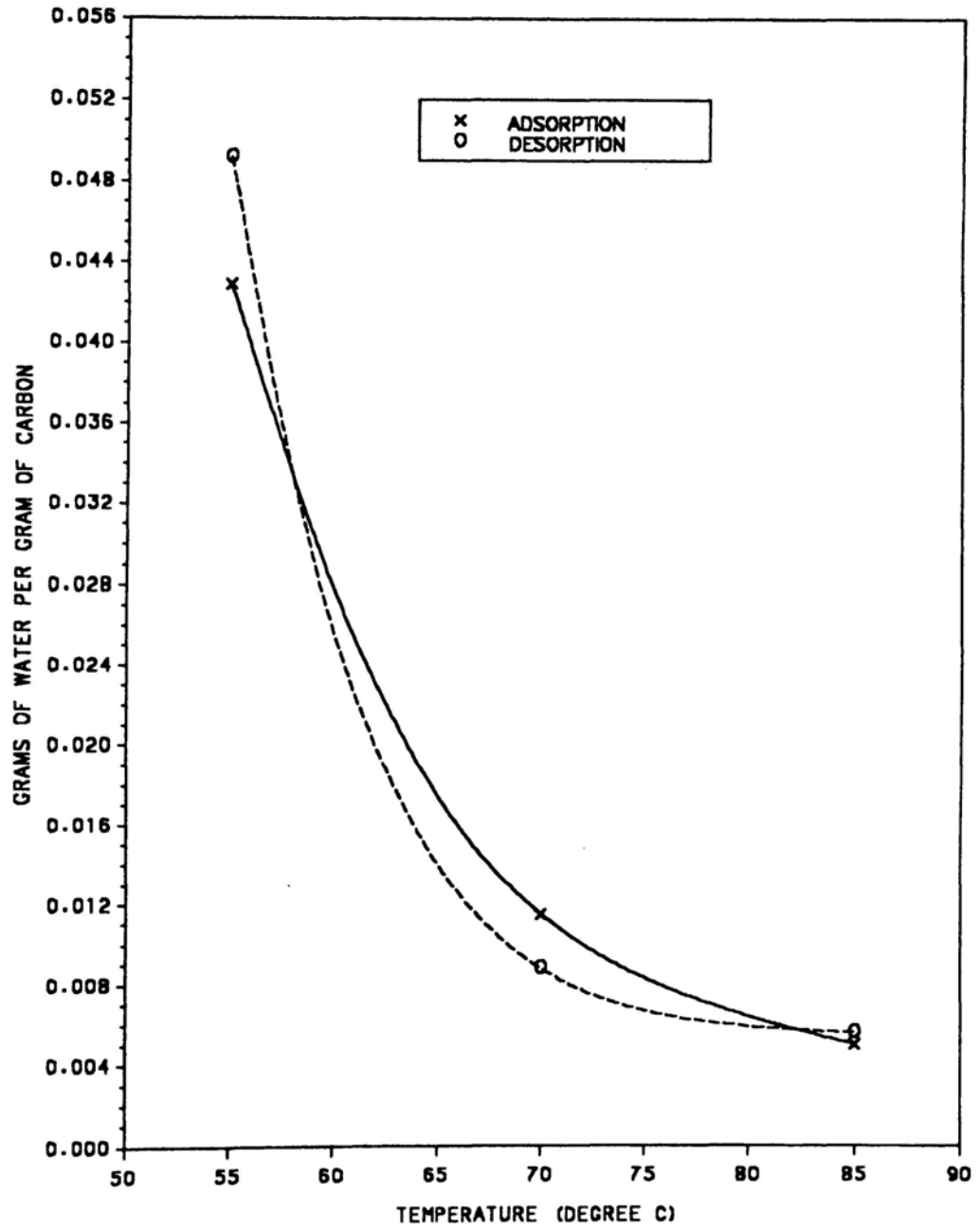
Figure 8. Grams of water adsorbed or remaining after desorption per gram of carbon vs. temperature.

In the propylene-propane systems similar phenomenon occur as in the ethanol-water system. Adsorption of a 50 mole % propylene, 50 mole % propane gas on 13X molecular sieves was carried out in 2 ways. In the first (Table I), adsorption was carried out at a constant temperature of 51°C onto a desorbed adsorbent and 0.477 mg moles of propylene were adsorbed per gram of adsorbent (adsorption was occurring throughout the experiment). In the second test (Table II), adsorption was carried out at 26.1°C for 1 hour and then at 50°C for 2 hours (desorption was occuring the last 2 hours). In this case, the final adsorbed amount was 0.542 mg moles per gram of adsorbent. On the other hand, in the first case or adsorption, 0.23 mg moles of propane were adsorbed, while in the second case 0.242 mg moles of propane were adsorbed at the final conditions. These results show that propylene adsorption and desorption did not reach equilibrium, while on the contrary, propane adsorption-desorption was almost reversible or almost reached equilibrium. This apparent irreversibility is important in removing propane first, then removing propylene later as temperatures are increased in desorption.

Figure 9 shows a plot of propylene concentration and desorption temperatures for differing adsorption pressures using 13X molecular sieves (see Appendix B, Tables XXVIII-XXX). Adsorption pressure does not seem to be an important factor in the concentration obtained.

Figure 10, is a similar plot at different temperatures of adsorption from 25°C to 70°C at a constant pressure of 0 psig (see Table I and Appendix B, Tables XXVIII and XXXI). This plot reveals that higher concentrations are obtained by a lower temperature of adsorption followed by variable temperature desorption, and that the same effects cannot be obtained by adsorption at a higher temperature as by desorption at increasing temperatures. This is another indication of hysteresis or nonequilibrium.

Figures 11 and 12 show mg moles of gases remaining on the adsorbent column versus concentration of gas during desorption. These two figures show similar characteristics which indicate that in the range from 50°C to 80°C both propylene and propane seem to desorb more than in the temperature range of 80°C to 100°C. Above 100°C the desorption for both components with temperature then increases. This indicates that two types of desorption, perhaps from two layers or types of active sites, are occurring. In Figure 11, the composition

Table I.    Results of Adsorption-Desorption Run 19

Adsorption-Desorption of 50 mole% $C_3H_6$ , 50 mole% $C_3H_8$ on molecular sieve 13X adsorbent (18.831 grams).
At 0 psig and 51°C adsorption, 0 psig desorption.  After final desorption temperature (160°C). The column was heated to 161°C, 29 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 161°C and 29.0 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | Each Increment | | | | Cumulative | |
| --- | --- | --- | --- | --- | --- | --- |
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 51 | 37.63 | 1.99830 | 0.48174 | 1.99830 | 0.96266 | 0.48174 |
| 51 | 37.91 | 2.01317 | 0.49848 | 4.01147 | 1.96618 | 0.49014 |
| Desorption Run | | | | | | |
| 80 | 2.6900 | 0.14285 | 0.55135 | 0.14285 | 0.07876 | 0.55135 |
| 100 | 2.6900 | 0.14285 | 0.60038 | 0.28570 | 0.16452 | 0.57587 |
| 120 | 2.6900 | 0.14285 | 0.66419 | 0.42855 | 0.25940 | 0.60531 |
| 140 | 2.6900 | 0.14285 | 0.76733 | 0.57140 | 0.36880 | 0.64544 |
| 160 | 2.5600 | 0.13595 | 0.79692 | 0.70735 | 0.47735 | 0.67485 |

Table II.        Results of Adsorption-Desorption Run 21

Adsorption-Desorption of 50 mole% $C_3H_6$, 50 mole% $C_3H_8$ on molecular sieve 13X adsorbent (18.831 grams).
At 0 psig and 26.1 − 50°C adsorption, 0 psig desorption.  After final desorption temperature (160°C). The column was heated at 160°C, 29 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 160°C and 29.0 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 26.1-50 | 37.97 | 2.01636 | 0.48960 | 2.01636 | 0.98722 | 0.48960 |
| 26.1-50 | 37.97 | 2.01636 | 0.49740 | 4.03272 | 1.99016 | 0.49350 |
| Desorption Run | | | | | | |
| 80 | 4.0700 | 0.21613 | 0.55473 | 0.21613 | 0.11990 | 0.55473 |
| 100 | 2.7100 | 0.14391 | 0.60969 | 0.36004 | 0.20764 | 0.57670 |
| 120 | 2.3000 | 0.12214 | 0.69430 | 0.48218 | 0.29244 | 0.60649 |
| 140 | 2.9800 | 0.15825 | 0.81040 | 0.64043 | 0.42068 | 0.65687 |
| 160 | 2.7000 | 0.14338 | 0.84526 | 0.78381 | 0.54187 | 0.69133 |
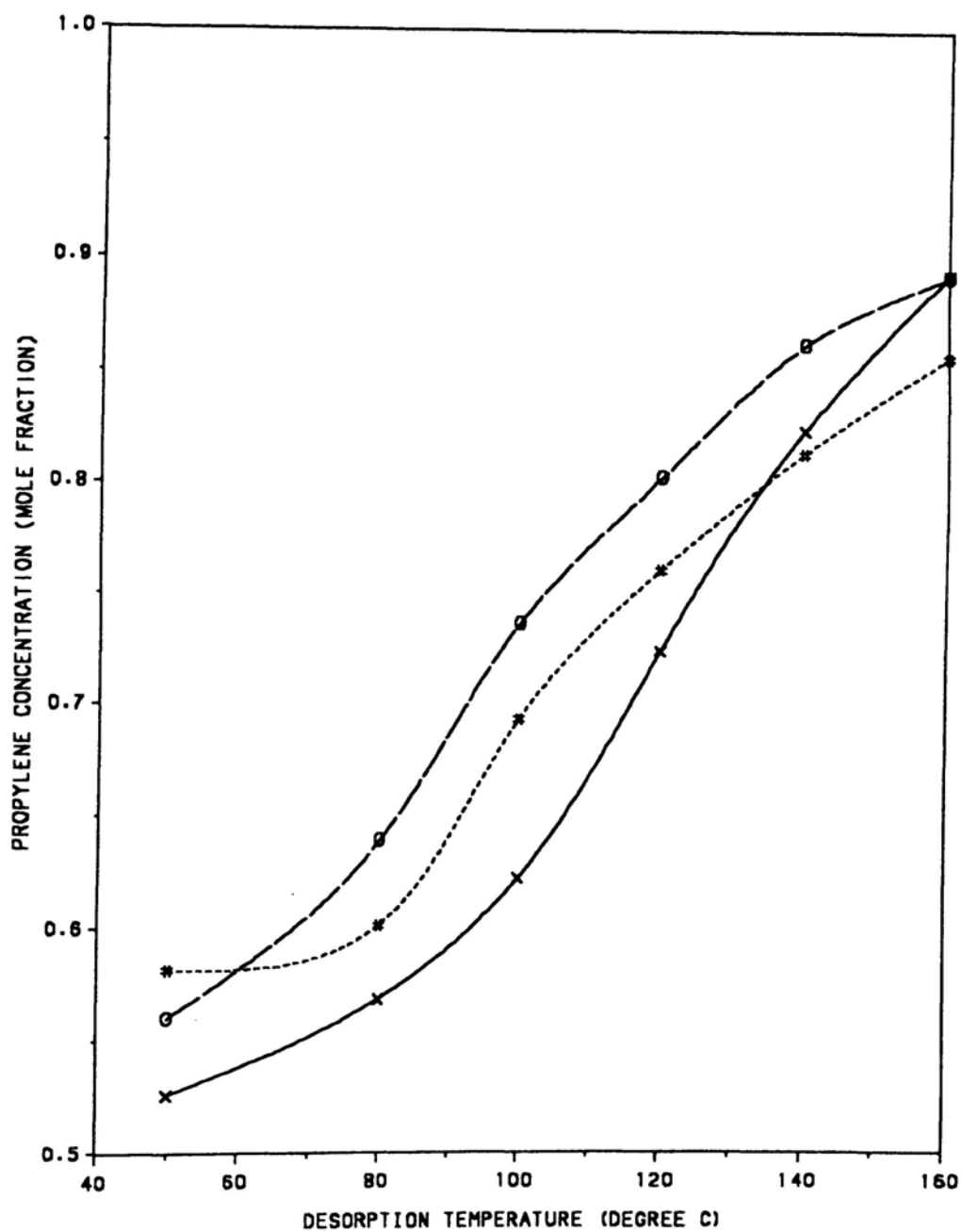
Figure 9.    Propylene concentration vs. desorption temperature.  After adsorption of 50 mole
% propane, 50 mole % propylene on molecular sieves 13X, Des. at 0 psig.
X  Ads. at  0 psig, 25 C, Adsorp. .03170 g C3H6/g adsb., .01069 g C3H8/g.
#  Ads. at 10 psig, 25 C, Adsorp. .02884 g C3H6/g adsb., .01400 g C3H8/g.
O  Ads. at 20 psig, 25 C, Adsorp. .03337 g C3H6/g adsb., .01535 g C3H8/g.
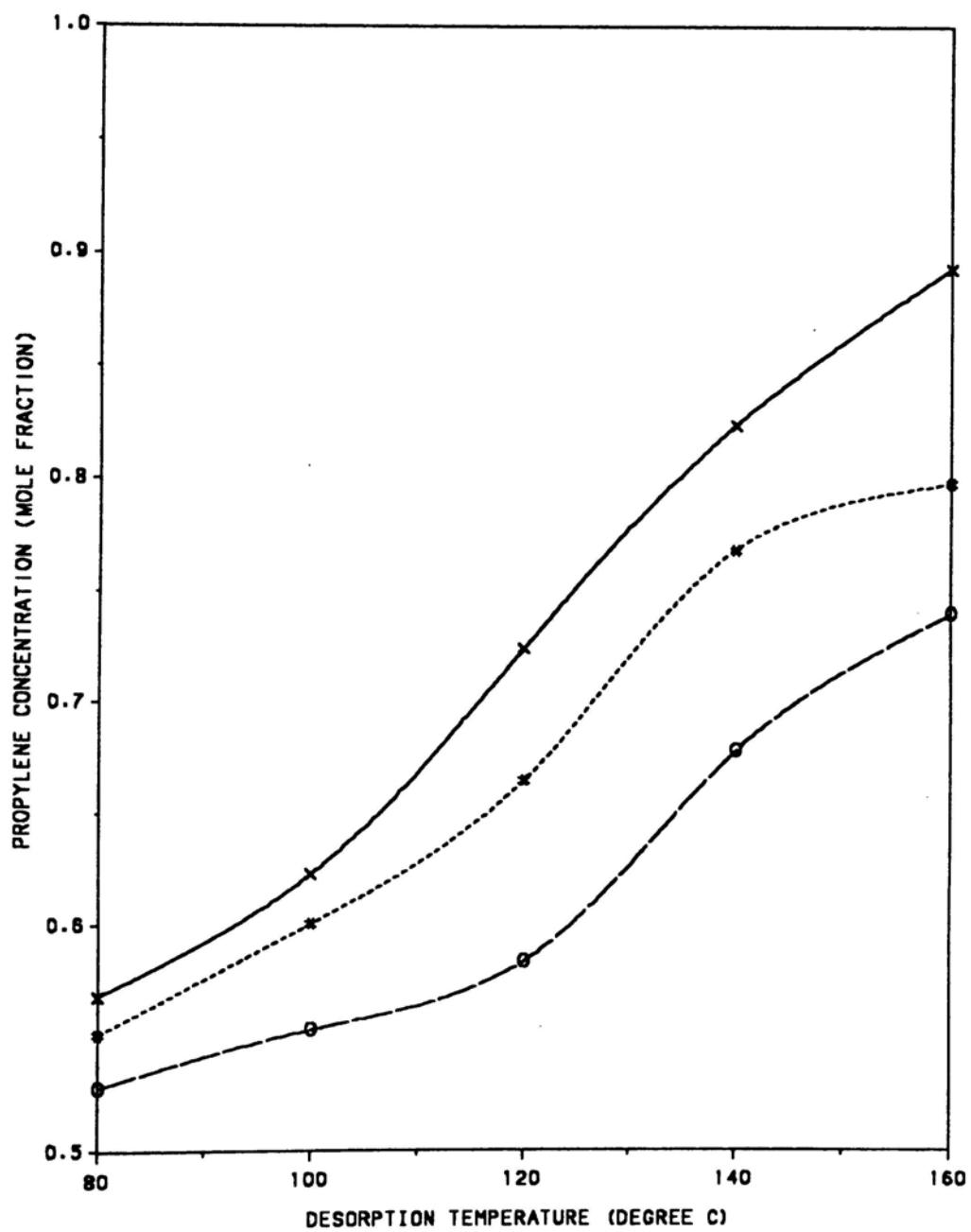
Figure 10.   Propylene concentraion vs. desorption temperature.  After adsorption of 50 mole
% propane, 50 mole % propylene on molecular sieves 13X, Des. at 0 psig.
X  Ads. at 0 psig, 25 C, Adsorp. .03170 g C3H6/g adsb., .01070 g C3H8/g.
#  Ads. at 0 psig, 51 C, Adsorp. .02009 g C3H6/g adsb., .01014 g C3H8/g.
O  Ads. at 0 psig, 70 C, Adsorp. .01581 g C3H6/g adsb., .00991 g C3H8/g.
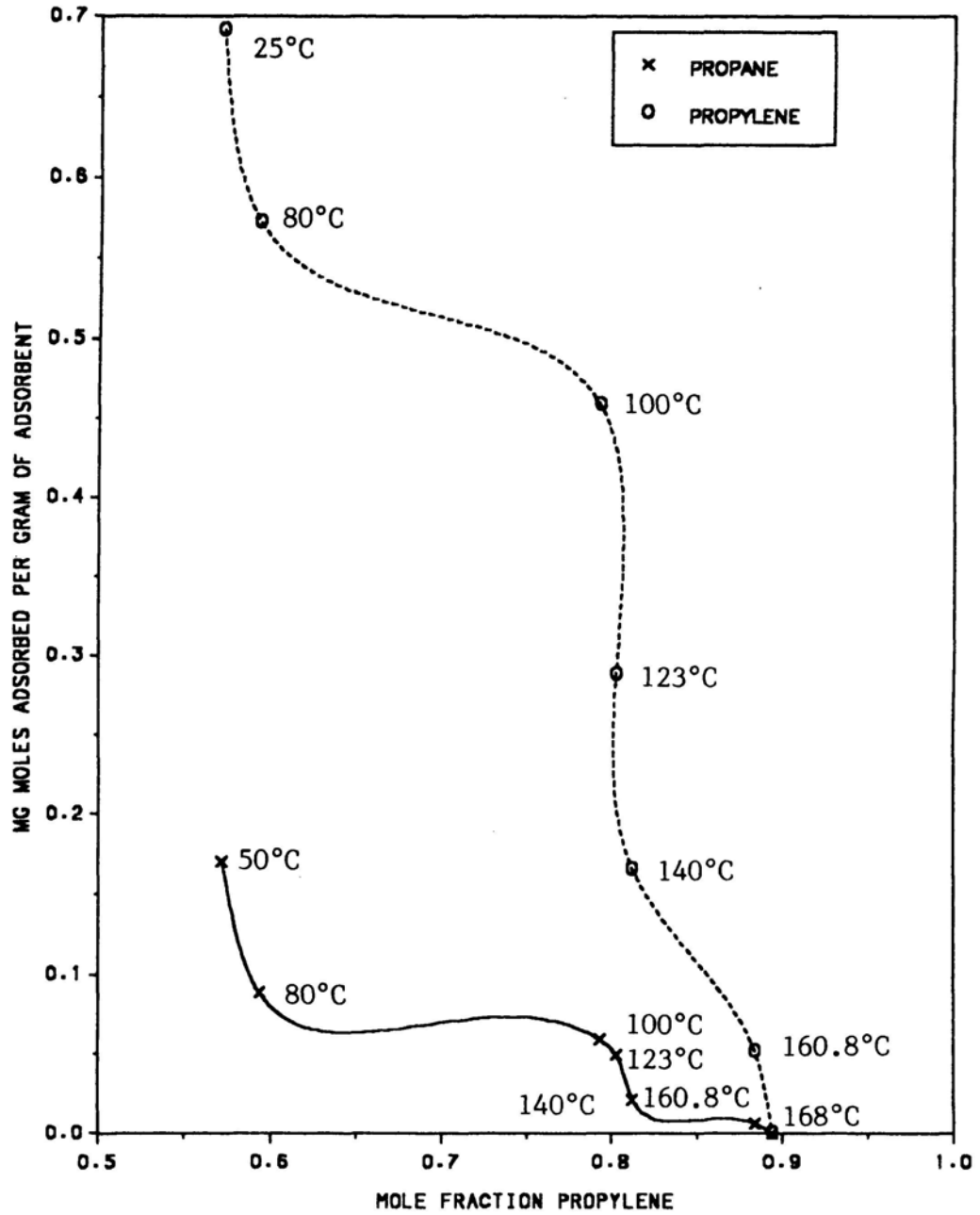
Figure 11.  Mole fraction propylene vs. mg moles adsorbed (remaining on column) per gram of adsorbent after ads. at 0 psig. After adsorption and desorption of 50 mole % propylene, 50 mole % propane at 25 degree C on molecular sieves 13X, adsorption at 0 psig, desorption at 0 psig but last point desorption at 27.5 in Hg vacuum pressure (see Appendix B, Table XXVIII).
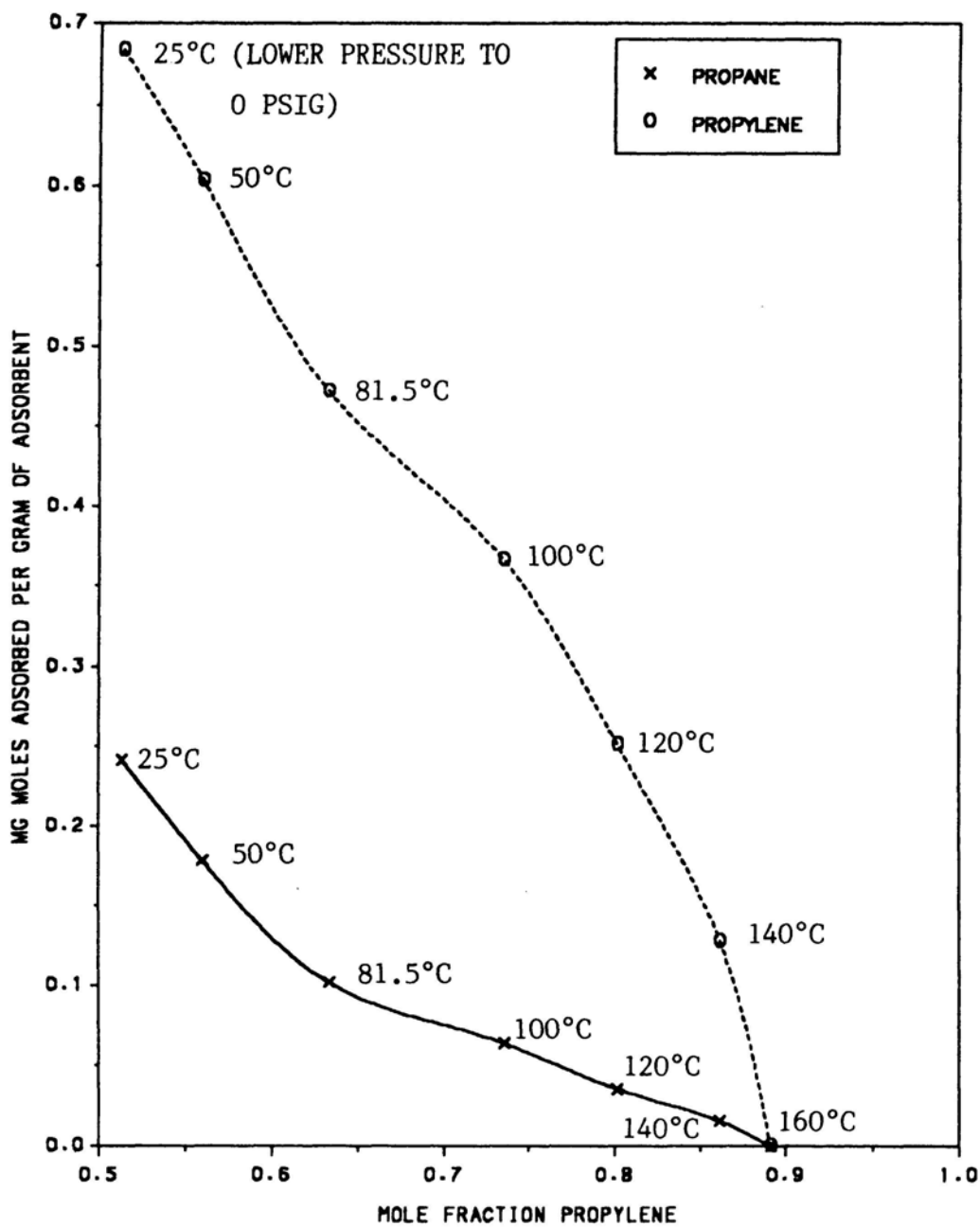
Figure 12. Mole fraction propylene vs. mg moles adsorbed (remaining on column) per gram of adsorbent after ads. at 20 psig. After adsorption and desorption of 50 mole % propylene, 50 mole % propane at 25 degree C on molecular sieves 13X, adsorption at 20 psig, desorption at 0 psig but for the first point the pressure is lowered from 20 psig to 0 psig (see Appendix B, Table XXX).

desorbed does not appear to change during each of these two types of increased desorption.

In Figure 13, propylene concentration was plotted versus the number of mg moles through the adsorber with a feed of 50 mole % propylene, 50 mole % propane at 27°C on molecular sieves 5A at 0 psig, for both adsorption and desorption. Separation can be obtained by using part A for a low concentration of propylene product, part B for recycle, and part C for high propylene concentration product or for further separation.

Runs were made on propane-propylene at 75 %-25 %, 50 %-50 %, 25 %-75 %, 5 %-95 % respectively, and the data are in Appendix B. In all cases of variable temperature desorption, the propane concentrations were higher at the earlier lower temperature desorptions and were followed by higher temperature desorption of high concentrations of propylene. Since propane-propylene separations are important in industry to produce 99 % propylene for polymerization, and because such mixtures are usually separated by distillation, a difficult and expensive separation, the variable temperature desorption method has important industrial possibilities.

Another system that was studied was the adsorption-variable temperature desorption of propane-carbon dioxide-hydrogen sulfide using molecular sieves 13X (80%-10%-10% respectively). This simulates the separation of hydrogen sulfide and carbon dioxide from petroleum gases. The results are shown in Figure 14. The $H_2S$ can be completely removed from most of the adsorption output flow, and after a low temperature desorption the $H_2S$ can be obtained at over 50 % concentration. The intermediate concentrations can be recycled. Since $H_2S$ separated from petroleum is usually converted to sulfur, this method could be useful in increasing $H_2S$ concentration for processes converting $H_2S$ to sulfur such as the Claus process.
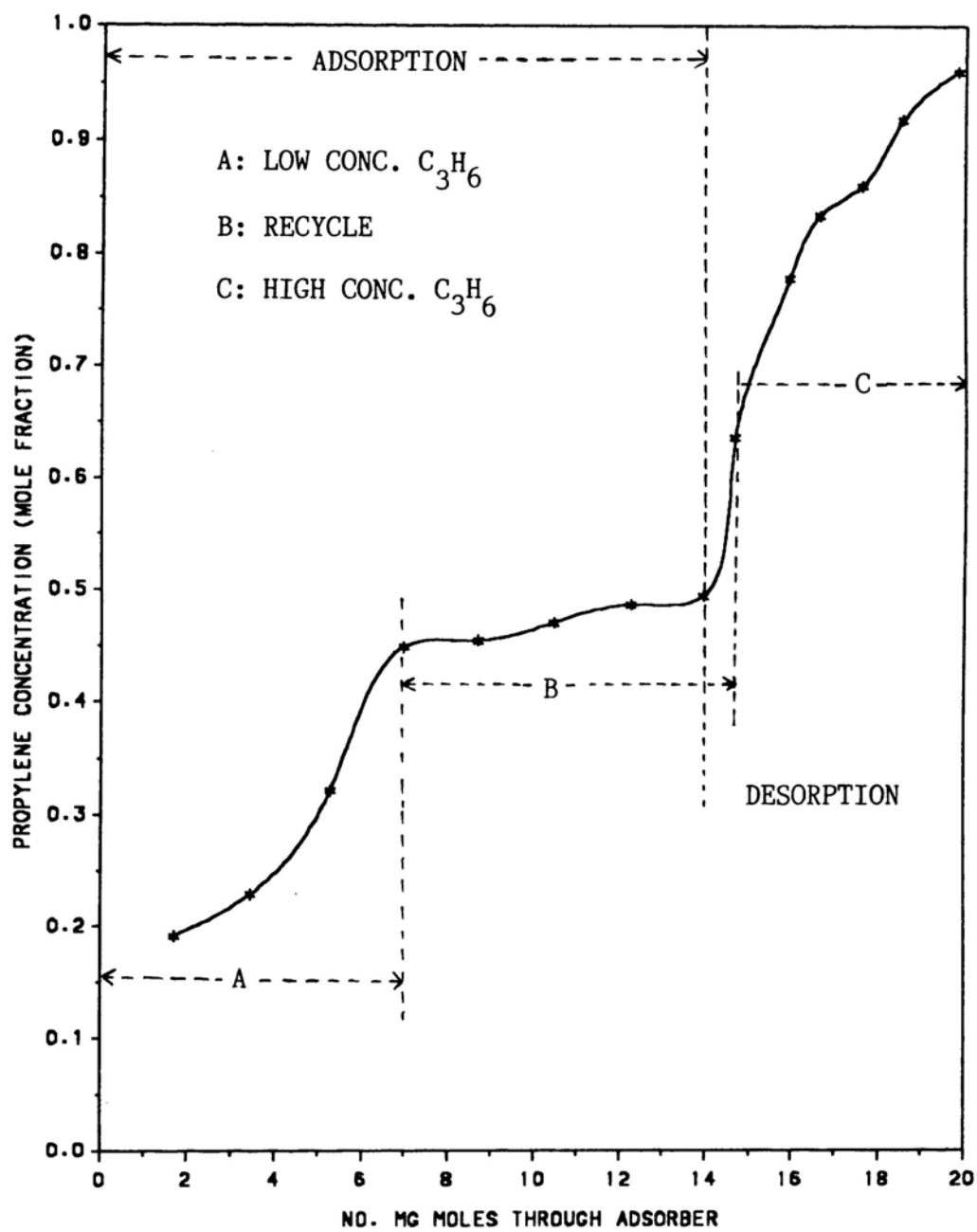
Figure 13. Propylene concentration vs. no. mg moles through adsorber. After adsorption and desorption of 50 mole % propylene, 50 mole % propane at 27 degree C on molecular sieves 5A, adsorption at 0 psig, desorption at 0 psig.
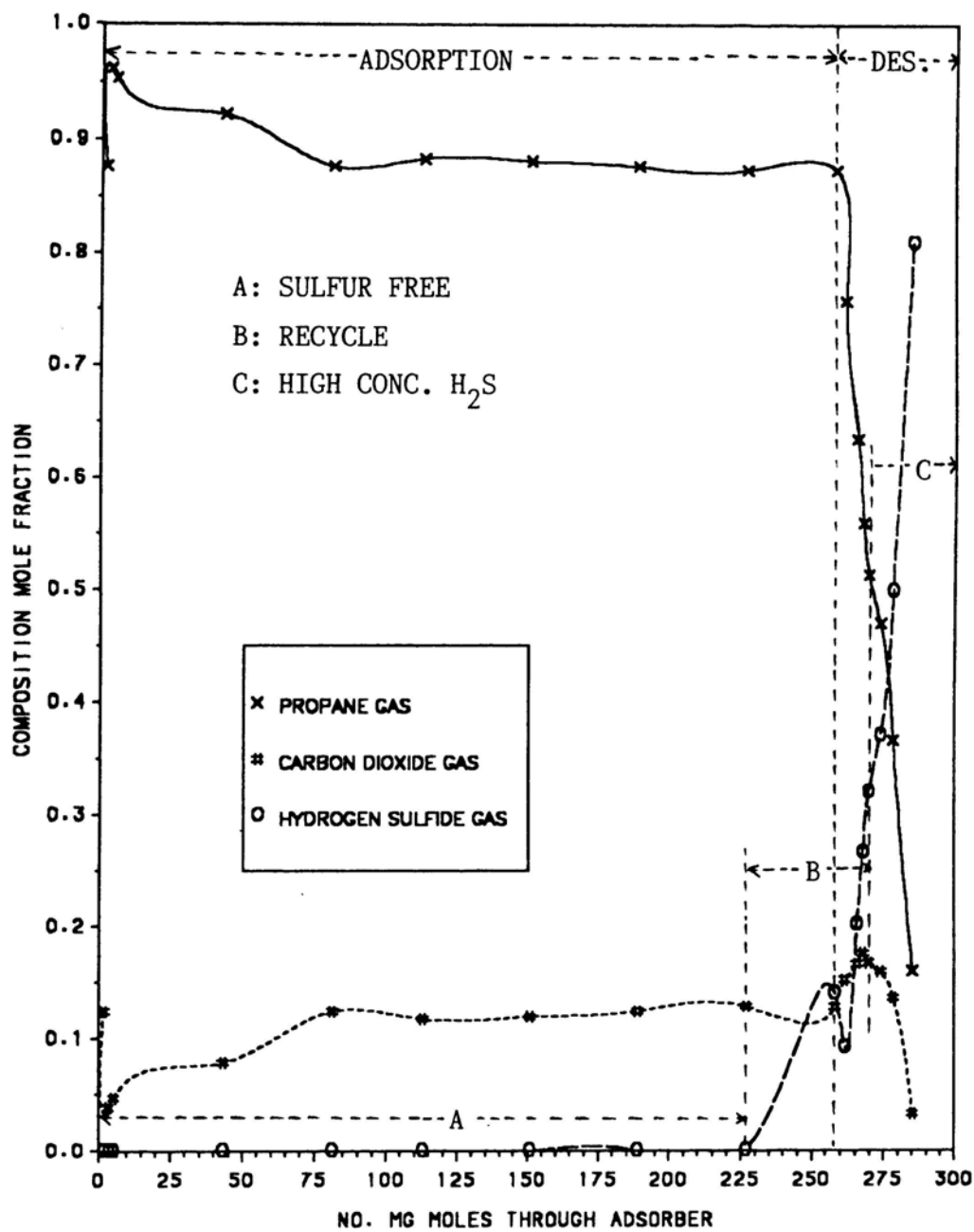
Figure 14.    Composition mole fraction vs. no. mg moles through adsorber.  After adsorption
and desorption of 80 mole % propane, 10 mole % carbon dioxide, 10 mole % on
molecular sieves 13X, adsorption at 25 degree C, 0 psig, desorption at 0 psig (see
Appendix B, Table XXXII).

# V. ECONOMIC EVALUATION COMPARING ADSORPTION AND DISTILLATION
## OF PROPYLENE FROM PROPANE

In order to determine the practicality of using adsorption with variable temperature desorption an economic comparison with distillation was calculated.

This economic evaluation is based on a total feed rate of 100 lb moles per hour (21.26 lb moles of propylene and 78.74 lb moles of propane per hour). The separation achieved was based on an experimental run made by C. M. Shu, (see Appendix B, Tables XXXV and XXXVI). The distillation system was calculated to give the same separation.

The distillation method was calculated using Aspen Plus (17) computer simulation using short cut distillation models "DSTWU" which performs a Winn-Underwood-Gilliland short cut design calculation for a single-feed, two-product distillation column with a partial or total condenser. For the specified recovery of the light and heavy key components, DSTWU estimates the minimum reflux ratio and the minimum number of theoretical stages. DSTWU can then either estimate the required reflux ratio for the specified number of theoretical stages, or as in this case, it estimates the required number of theoretical stages for the specified reflux ratio. DSTWU also estimates the optimum feed stage location and the condenser and reboiler duties. The following data were used as inputs:

Input data for distillation calculation:

| | |
|---|---|
| Feed stream pressure | = 175 psi |
| Mole-flow of feed | = 100 lb moles/hr |
| Mole-flow of propylene | = 21.26 lb moles/hr |
| Mole-flow of propane | = 78.74 lb moles/hr |

Recovery of propylene in distillate (moles propylene in distillate/ mole propylene in feed)

= 0.9409

Recovery of propane in distillate (moles propane in distillate/ mole propane in feed)

= 0.0507

| | |
|---|---|
| Condenser pressure | = 175 psi |
| Reboiler pressure | = 175 psi |

| | |
|---|---|
| Desired reflux ratio | = 1.2 x minimum |
| Tray-efficiency | = 90 % |
| Tray-space | = 1.5 ft. |
| Cooling water temperature into condenser | = 75°F |
| Cooling water temperature out of condenser | = 80°F |
| Price of cooling water | = $ 0.15 / 1000 gallon |
| Price of steam | = $ 5.00 / 1000 lb |

Thermodynamics property models using Wilson/Redlich-Kwong

The results of the calculations were as follows:

| | |
|---|---|
| Diameter of distillation column | = 5 ft. |
| Height of distillation column | = 122.5 ft. |
| Number of trays (sieve) | = 73 |
| Reboiler area | = 58.78 sq. ft. |
| Reboiler heat duty | = 4.1173 million BTU/hr |
| Condenser area | = 4823.3 sq. ft. |
| Condenser duty | = 4.6091 million BTU/hr |

The adsorber was calculated based on 100 lb moles feed per hour (21.26 lb moles/hr propylene, 78.74 lb moles/hr propane), with the same recoveries as the distillation system after allowing for recycle.

Moles feed / lb of adsorbent = 10.885 g moles / 1650 g adsorbent.

= 0.006597 lb mole /lb adsorbent

Assume 1.5 hour cycle time for adsorption and desorption step.

so;  amount of adsorbent = 22,738 lbs

Assume 1.5 inch tubes for adsorber

Area of tubes = 18220 sq. ft., divided into 4 units, each unit has 4555 sq. ft.

Pressure = 1 Atmosphere, 29 inches Hg vacuum in final desorption step.

Vacuum pump horse power = 22.2 HP

The adsorber cost was calculated as a heat exchanger. For both systems, distillation and adsorption, equipment and investment costs were calculated by Capital Cost

Estimating (18) using bare module factors, with buildings, yard improvements, service facilities and land, plus contingency and contactor fee from Peters & Timmerhaus (19).

The results in Tables III and IV indicate that separation of mixtures with low concentration propylene may be more economical by adsorption with variable temperature desorption than by distillation. At high concentrations of propylene, distillation appears to be more economical than adsorption with variable temperature desorption if propylene is preferentially adsorbed. This is due to the large amount of adsorbent required per mole of feed. If an adsorbent were used that preferentially adsorbed propane, high concentration propylene might be separated more economically by adsorption. The results suggest that the high propane end (bottom) of a propane-propylene distillation might be economically replaced by an adsorption with variable temperature desorption process.

Table III.    Cost comparision between distillation and adsorption (1988) method 1.

A. Counting molecular sieves as an investment.

|  | Distillation | Adsorption | |
|---|---|---|---|
| **Equipment Cost** | | | |
| Column | $ 115,337.00 | | |
| Adsorber | | $ 274,315.02 | |
| Heat Exchanger | $ 75,904.21 | | |
| Vacuum pump | | $ 31,172.16 | |
| **Equipment Cost With Bare Module Factor** | | | |
| Column | $ 417,395.23 | | |
| Adsorber | | $ 902,496.41 | |
| Heat Exchanger | $ 249,724.86 | | |
| Vacuum pump | | $ 96,883.08 | |
| Buliding & service (104 % Equip.) | $ 198,890.86 | $ 317,706.67 | |
| Total direct & indirect cost | $ 866,010.96 | $1,317,086.16 | |
| Contingency & contractor's fee (15%) | $ 129,901.64 | $ 197,562.92 | |
| Total fixed capital investment (less molecular sieves) | $ 995,912.60 | $1,514,649.08 | |
| Molecular sieves cost | $ | $ 113,690.00 | |
| Total fixed-capital investment | $ 995,912.60 | $1,628,339.08 | |
| Increased in investment | | | $ 632,426.00 |
| Steam cost/yr. | $ 177,897.60 | $ 40,521.60 | |
| Cooling cost/yr. | $ 141,782.40 | $ 28,857.60 | |
| Electric cost/yr. | $ | $ 6,480.00 | |
| Depreciation/yr. (10%) | $ 99,591.26 | $ 162,833.91 | |
| Total variable operating cost/yr. | $ 419,271.26 | $ 238,693.11 | |
| Change in variable operating cost/yr. | | | $-180,578.15/year |
| Change in profit after tax (33%) | | | $ 120,988.00 |
| ROI after 33 % tax | | | 19.13 % |
| Change in cash flow after tax | | | $ 184,230.00 |
| Cash flow payout time | | | 3.43 yr |
| Net present value basis 15% (after tax) | | | $ 292,182.00 |
| Net present value basis 20% (after tax) | | | $ 139,953.00 |
| Net present value basis 25% (after tax) | | | $ 25,368.00 |
| Approximate discount cash flow rate | | | 26.1 % |

Table IV.        Cost comparision between distillation and adsorption (1988) method 2.

B. Counting molecular sieves as an operating cost, replacement once/year.

|  | Distillation | Adsorption | |
|---|---|---|---|
| **Equipment Cost** | | | |
| Column | $ 115,337.00 | | |
| Adsorber | | $ 274,315.02 | |
| Heat Exchanger | $ 75,904.21 | | |
| Vacuum pump | | $ 31,172.16 | |
| **Equipment Cost With Bare Module Factor** | | | |
| Column | $ 417,395.23 | | |
| Adsorber | | $ 902,496.41 | |
| Heat Exchanger | $ 249,724.86 | | |
| Vacuum pump | | $ 96,883.08 | |
| Buliding & service (104 % Equip.) | $ 198,890.86 | $ 317,706.67 | |
| Total direct & indirect cost | $ 866,010.96 | $1,317,086.16 | |
| Contingency & contractor's fee (15%) | $ 129,901.64 | $ 197,562.92 | |
| Total fixed-capital investment | $ 995,912.60 | $1,514,649.08 | |
| Increased in investment | | | $ 518,736.48 |
| Steam cost/yr. | $ 177,897.60 | $ 40,521.60 | |
| Cooling cost/yr. | $ 141,782.40 | $ 28,857.60 | |
| Electric cost/yr. | $ | $ 6,480.00 | |
| Molecular sieves replace once/yr. | $ | $ 113,690.00 | |
| Depreciation/yr. (10%) | $ 99,591.26 | $ 151,464.91 | |
| Total variable operating cost/yr. | $ 419,271.26 | $ 341,014.11 | |
| Change in variable operating cost/yr. | | | $- 78,257.15/year |
| Change in profit after tax (33%) | | | $ 52,432.00 |
| ROI after 33 % tax | | | 10.10 % |
| Change in cash flow after tax | | | $ 104,306.00 |
| Cash flow payout time | | | 7.46 yr |
| Net present value basis 12% (after tax) | | | $ 70,616.00 |
| Net present value basis 15% (after tax) | | | $ 4,752.00 |
| Approximate discount cash flow rate | | | 15.2 % |

# VI. CONCLUSIONS AND RECOMMENDATIONS

In adsorption separations where more components are adsorbed than desired, it is sometimes possible to further separate the adsorbed components by desorbing in steps, with increasing temperatures. The more weakly adsorbed components will normally be desorbed first at lower temperature and the more strongly adsorbed will desorb at the higher temperatures.

Adsorption with variable temperature desorption is capable of improving separations in certain multicomponent adsorption systems. This method can significantly improve separation by adsorption for ethanol-water on activated carbon, propane-propylene, and $H_2S - CO_2$ -hydrocarbon systems on molecular sieves.

In the ethanol-water system, water is desorbed at lower temperatures, while propane desorbs at lower temperatures for the propane-propylene system. Hydrogen sulfide is much more strongly adsorbed in the $H_2S - CO_2 - C_3H_8$ system and desorbs at the higher temperatures.

In the case of propane and propylene, there is evidence that two types of desorption occur at two different temperature levels.

In the case of ethanol-water and propylene-propane adsorptions, hysteresis or non-equilibrium effects on ethanol and propylene appear to increase the separation obtained, by decreasing the desorption of these two components at a given temperature, while water or propane desorbs more readily. This could be due to the effect of desorption rates.

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# VITA

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# APPENDIX A

## TABLES OF PHYSICAL PROPERTIES

Table V.        Pore Sizes in Typical Activated Carbons

|  | Micropore | Mesopores or Transitional Pores | Macropores |
|---|---|---|---|
| Diameter (Å) | < 20 | 20-500 | > 500 |
| Pore volume (cm³/$g$ ) | 0.15-0.5 | 0.02-0.1 | 0.2-0.5 |
| Surface area (m²/$g$ ) | 100-1000 | 10-100 | 0.5-2 |
| (Particle density 0.6-0.9 g/cm³; porosity 0.4-0.6) | | | |

Table VI.        Physical Properties of Typical Activated Carbon Grades

| Property | Liquid-phase carbon | | | Gas-phase carbon | | |
|---|---|---|---|---|---|---|
| | Lignite base | Wood base | Bituminous coal base | Granular coal | Pelleted coke | Granular coconut |
| mesh (Tyler) | -100 | -100 | 8-30 | -4, + 10 | -6, + 8 | -6, + 14 |
| (mm) | (0.15) | (0.15) | (2.38-0.59) | (4.76,1.70) | (3.36,2.38) | (3.36,1.18) |
| $CCl_4$ | | | | | | |
| activity, % min | 30 | 40 | 50 | 60 | 60 | 60 |
| iodine no.,min | 500 | 700 | 950 | 1000 | 1000 | 1000 |
| bulk density, g/mL, min | 0.48 | 0.25 | 0.50 | 0.50 | 0.52 | 0.53 |
| ash, % max | 18 | 7 | 8 | 8 | 2 | 4 |

Table VII.        Characteristics of Major Synthetic Zeolite Sorbents

| Zeolite Type | Major Cation | Nominal Aperture Size,Å | Bulk Density,[a] lb/$ft^3$ | Water[b] Capacity, wt % |
|---|---|---|---|---|
| 3A (Linde) | K | 3 | 40 | 20.0 |
| 3A (Davidson) | K | 3 | 46 | 21.0 |
| 4A (Linde) | Na | 4 | 41 | 22.0 |
| 4A (Davidson) | Na | 4 | 44 | 23.0 |
| 5A (Linde) | Ca | 5 | 45 | 21.5 |
| 5A (Davidson) | Ca | 5 | 44 | 21.7 |
| 10X (Linde) | Ca | 8 | 40 | 31.6 |
| 13X (Linde) | Na | 10 | 38 | 28.5 |
| 13X (Davidson) | Na | 10 | 43 | 29.5 |

a   Based on 1/16 inch pellets or beads.

b   The dried sorbent contains < 1.5 weight-percent water in Linde products and 1.5 weight-percent in Davidson products.

Table VIII.     Physical Properties of Propane (20)

| Property | Value |
|---|---|
| Molecular Weight | 44.09 |
| Melting Point, K | 85.5 |
| Boiling Point, K | 231.0 |
| Explosivity limits, Vol% | 2.3-9.5 |
| Autoignition Temperature, K | 741.0 |
| Flash Point, K | 169.0 |
| Heat of Combustion, kJ/mol | 2202.0 |
| Heat of Formation, kJ/mol | 127.2 |
| Heat of Vaporization, kJ/mol | 18.83 |
| Vapor Pressure at 273 K, MPa | 0.475 |
| Specific Heat, J/(mol.K) | |
| at 293 K | 73.63 |
| at 373 K | 84.65 |
| Density, Kg/ m³ | |
| at 293 K | 1.984 |
| at 373 K | 1.455 |
| Critical Point | |
| Pressure, MPa | 4.24 |
| Temperature, K | 369.8 |
| Density, Kg/m³ | 220.5 |
| Triple Point | |
| Pressure, MPa | $3.0x 10^{10}$ |
| Temperature, K | 85.5 |
| Liquid Density, Kg/ m³ | 731.9 |
| Vapor Density, Kg/ m³ | $1.85x10^{-8}$ |
| Dipole Moment | 0.0 |
| Hazards | Fire |
| | Explosion |
| | Asphyxiation |

Table IX.    Physical Properties of Propylene (21)

| Property | Value |
|---|---|
| Molecular Weight | 42.081 |
| Freezing Point, K | 87.9 |
| Boiling Point, K | 225.4 |
| Critical Temperature, K | 365.0 |
| Critical Pressure, MPa | 4.6 |
| Critical Volume,cm$^3$/mol | 181.0 |
| Critical Compressibility | 0.275 |
| Pitzer's Acentric Factor | 0.148 |
| Liquid Density (at 223 K), g/cm$^3$ | 0.612 |
| Dipole Moment, $10^{-30}$ C.m | 1.3 |
| Standard Enthalpy of Formation, kJ/mol | 20.42 |
| Standard Gibbs energy of Formation for Ideal Gas (at 101.3 kPa ( = 1 atm)), kJ/mol | 62.72 |
| Heat of Vaporization at bp, kJ/mol | 18.41 |
| Lennard Jones Potential | |
| T, nm | 0.4678 |
| $\varepsilon^0/K$ ,K | 298.9 |
| Solubility (at 20 °C and 101.3 kPa), mL gas/100 ml solvent | |
| In water | 44.6 |
| In ethanol | 1250.0 |
| In acetic acid | 524.5 |
| Refractive Index, $n_D$ | 1.3567 |

Table X.        Physical Properties of Hydrogen Sulfide (22)

| Property | Value |
|---|---|
| Molecular Weight | 34.08 |
| Melting Point,°C | -85.60 |
| Boiling Point,°C | -60.75 |
| $\Delta H$ fusion, kJ/mol | |
| | 2.375 |
| $\Delta H$ vaporization, kJ/mol | |
| | 18.67 |
| Density at -60°C g/cm³ | 0.993 |
| Specific Gravity, gs (air = 1) | 1.19 |
| Critical Temperature,°C | 100.4 |
| Critical Pressure, kPa | 9020.0 |
| Critical Density, $g/cm^3$ | 0.3681 |
| $\Delta G°$formation, kJ/mol | |
| | -33.6 |
| $\Delta H°$formation at 25 °C, kJ/mol | |
| | -20.6 |
| $S°$formation at 25°C , J/(mol.K) | |
| | 205.7 |
| $C°_p$, J/(mol.K) | |
| | 34.2 |
| Autoignition Temperature in air,°C | ca 260.0 |
| Explosive range in air at 20°C , vol % | |
| Upper Limit | 46.0 |
| Lower Limit | 4.3 |
| Vapor Pressure, kPa | |
| -60°C | 102.7 |
| -40°C | 256.6 |
| -20°C | 546.6 |
| 0°C | 1033.0 |
| 20°C | 1780.0 |
| 40°C | 2859.0 |
| 60°C | 4347.0 |
| Solubility in Water at 101.3 kPa ( = 1 atm) | |
| Total Pressure, g/100 g soln | |
| 0°C | 0.710 |
| 10°C | 0.530 |
| 20°C | 0.398 |

Table XI.        Physical Properties of Carbon Dioxide (23)

| Property | Value |
|---|---|
| Sublimation Point, °C at 101 kPa (1 atm) | -78.5 |
| Triple Point, °C at 518 kPa (75.1 psia) | -56.5 |
| Critical Temperature,°C | 31.1 |
| Critical Pressure, kPa (1071 psia) | 734.0 |
| Critical Density, g/L | 467.0 |
| Latent Heat of Vaporization J/g | |
| at the Triple Point | 348.0 |
| at 0°C | 235.0 |
| Gas Density, g/L at 0°C and 101 kPa (1 atm) | 1.976 |
| Liquid Density, g/L at 0°C and 0.759 vol/vol at 25°C | |
| and 101 kPa pressure of carbon dioxide | 914.0 |
| Viscosity, mPa.s (= cP) at 25°C | |
| and 101 kPa pressure | 0.015 |
| Heat of Formation of Carbon dioxide, J/mol at 25°C | 393,700.0 |

Table XII.    Physical Properties of Ethanol (24)

| Property | Value |
| --- | --- |
| Freezing point,°C | -114.1 |
| Normal boiling point,°C | + 78.32 |
| Critical temperature,°C | 243.1 |
| Critical pressure, kPa | 6383.48 |
| Critical volume, L/mol | 0.167 |
| Critical compressibility Factor | 0.248 |
| Density, g/mL | 0.7893 |
| Refractive index, $n_D^{20}$ | 1.36143 |
| Surface tension, at 25°C , mN/m ( = dyn/cm) | 231.0 |
| Viscosity, at 20°C , mPa.s ( = cP) | 1.17 |
| Solubility in water, at 20°C | miscible |
| Heat of vaporization, at normal boiling point, J/g | 839.31 |
| Heat of combustion, at 25°C , J/g | 2967.69 |
| Heat of fusion, J/g | 104.6 |
| flammable limits in air | |
|   lower, vol % | 4.3 |
|   upper, vol % | 19.0 |
| Autoignition temperature,°C | 793.0 |
| Flash point, closed-cup,°C | 14.0 |
| Specific heat, at 20°C , J/(g.°C) | 2.42 |
| Thermal conductivity, at 20°C , W/(m.K) | 0.170 |
| Dipole moment, liq at 25°C , C.m | $5.67 \times 10^{-30}$ |
| Magnetic susceptibility at 20°C | $0.734 \times 10^{-6}$ |
| Dielectric constant at 20°C | 25.7 |

# APPENDIX B

## TABLES OF EXPERIMENTAL DATA AND CALCULATED VALUES FOR
## PROPANE-PROPYLENE, HYDROGEN SULFIDE-CARBON DIOXIDE-PROPANE

Table XIII.     Results of Adsorption-Desorption Run 1

Adsorption-Desorption of 75 mole% $C_3H_6$ , 25 mole% $C_3H_8$ on molecular sieves 5A adsorbent (9.40 grams).
At 10 psig and 25°C adsorption, 10 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | F = $\sum C \times D$ | G = F/E |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 25 | 2.9204 | 0.31068 | 0.3700 | 0.31068 | 0.11495 | 0.36999 |
| 25 | 1.3137 | 0.13976 | 0.6411 | 0.45044 | 0.20455 | 0.45411 |
| 25 | 1.2632 | 0.13438 | 0.6796 | 0.58482 | 0.29588 | 0.50593 |
| 25 | 1.2632 | 0.13438 | 0.7172 | 0.71920 | 0.39225 | 0.54540 |
| 25 | 2.9885 | 0.31793 | 0.7354 | 1.03713 | 0.62606 | 0.60365 |
| **Desorption Run** | | | | | | |
| 50 | 1.6757 | 0.17827 | 0.8678 | 0.17827 | 0.15470 | 0.86780 |
| 80 | 0.7258 | 0.07720 | 0.9237 | 0.25548 | 0.22602 | 0.88469 |
| 100 | 0.8842 | 0.09406 | 0.9285 | 0.34954 | 0.31336 | 0.89563 |
| 120 | 0.7832 | 0.08332 | 0.9434 | 0.43286 | 0.38879 | 0.89820 |
| 140 | 0.8969 | 0.09542 | 0.9582 | 0.52828 | 0.48022 | 0.90904 |
| 160 | 1.1621 | 0.12362 | 0.9725 | 0.65191 | 1.08067 | 0.92107 |

Table XIV.     Results of Adsorption-Desorption Run 2

Adsorption-Desorption of 25 mole% $C_3H_6$ , 75 mole% $C_3H_8$ on molecular sieves 5A adsorbent (9.40 grams).
At 10 psig and 26°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 10 psig pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 26 | 0.7406 | 0.07878 | 0.10826 | 0.07878 | 0.00853 | 0.10826 |
| 26 | 1.6663 | 0.17727 | 0.10858 | 0.25605 | 0.02778 | 0.10849 |
| 26 | 2.9224 | 0.31089 | 0.10979 | 0.56694 | 0.06191 | 0.10920 |
| 26 | 1.7125 | 0.18218 | 0.11697 | 0.74912 | 0.08322 | 0.11109 |
| 26 | 1.7125 | 0.18218 | 0.13879 | 0.93130 | 0.10850 | 0.11650 |
| 26 | 1.7001 | 0.18086 | 0.16693 | 1.11216 | 0.13870 | 0.12470 |
| 26 | 3.0048 | 0.31966 | 0.19973 | 1.43182 | 0.20254 | 0.14146 |
| 26 | 2.9423 | 0.31301 | 0.22168 | 1.74483 | 0.27193 | 0.15588 |
| 26 | 2.9484 | 0.31366 | 0.23597 | 2.05849 | 0.34594 | 0.16806 |
| 26 | 2.9423 | 0.31301 | 0.24405 | 2.37150 | 0.42233 | 0.17809 |
| **Desorption Run** | | | | | | |
| 50 | 1.0022 | 0.10662 | 0.3797 | 0.10662 | 0.04048 | 0.37971 |
| 80 | 1.0022 | 0.10662 | 0.5186 | 0.21323 | 0.09577 | 0.44914 |
| 100 | 0.8423 | 0.08961 | 0.6810 | 0.30284 | 0.15680 | 0.51776 |
| 120 | 0.7686 | 0.08177 | 0.7237 | 0.38461 | 0.21597 | 0.56154 |
| 140 | 1.0452 | 0.11119 | 0.7823 | 0.49579 | 0.30296 | 0.61105 |
| 160 | 1.0760 | 0.11447 | 0.8638 | 0.61027 | 0.40184 | 0.65846 |

Table XV.　　　Results of Adsorption-Desorption Run 3

Adsorption-Desorption of 50 mole% $C_3H_6$, 50 mole% $C_3H_8$ on molecular sieves 5A adsorbent (9.40 grams).
At 10 psig and 27°C adsorption, 10 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 0 psig pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 27 | 0.7870 | 0.08372 | 0.07964 | 0.08372 | 0.00667 | 0.07964 |
| 27 | 1.7093 | 0.18184 | 0.08420 | 0.26556 | 0.02198 | 0.08276 |
| 27 | 2.9607 | 0.31497 | 0.10520 | 0.58053 | 0.05511 | 0.09494 |
| 27 | 3.0044 | 0.31962 | 0.22310 | 0.90015 | 0.12642 | 0.14044 |
| 27 | 2.9169 | 0.31031 | 0.40486 | 1.21046 | 0.25205 | 0.20822 |
| 27 | 2.9169 | 0.30975 | 0.45464 | 1.52021 | 0.39288 | 0.25844 |
| 27 | 2.9662 | 0.31555 | 0.47145 | 1.83576 | 0.54164 | 0.29505 |
| **Desorption Run** | | | | | | |
| 50 | 0.9346 | 0.09426 | 0.5772 | 0.09426 | 0.05739 | 0.57723 |
| 80 | 0.8608 | 0.09155 | 0.7667 | 0.18580 | 0.12760 | 0.55698 |
| 100 | 0.8546 | 0.09092 | 0.8103 | 0.27672 | 0.20127 | 0.71373 |
| 120 | 0.7867 | 0.08369 | 0.8496 | 0.36046 | 0.27237 | 0.74479 |
| 140 | 0.9758 | 0.10413 | 0.8888 | 0.46454 | 0.36464 | 0.77663 |
| 160 | 1.3133 | 0.13971 | 0.9316 | 0.60425 | 0.49478 | 0.81216 |

Table XVI.     Results of Adsorption-Desorption Run 4

Adsorption-Desorption of 50 mole% $C_3H_6$ , 50 mole% $C_3H_8$ on molecular sieves 5A adsorbent (9.40 grams).
At 0 psig and 27°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 10 psig pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 27 | 1.7220 | 0.18319 | 0.19158 | 0.18319 | 0.03510 | 0.19158 |
| 27 | 1.7343 | 0.18450 | 0.22878 | 0.36769 | 0.07731 | 0.21026 |
| 27 | 1.8149 | 0.19308 | 0.32167 | 0.56077 | 0.13941 | 0.24861 |
| 27 | 1.7047 | 0.18135 | 0.44830 | 0.74211 | 0.22071 | 0.29741 |
| 27 | 1.7108 | 0.18200 | 0.45416 | 0.92412 | 0.30337 | 0.32828 |
| 27 | 1.7784 | 0.18919 | 0.47011 | 1.11331 | 0.39231 | 0.35238 |
| 27 | 1.7846 | 0.18985 | 0.48587 | 1.30316 | 0.48455 | 0.37183 |
| 27 | 1.7031 | 0.18118 | 0.49363 | 1.48434 | 0.57398 | 0.38669 |
| **Desorption Run** | | | | | | |
| 50 | 0.7145 | 0.07601 | 0.6351 | 0.07601 | 0.04828 | 0.63513 |
| 80 | 1.2751 | 0.13565 | 0.7768 | 0.21166 | 0.15365 | 0.72595 |
| 100 | 0.7146 | 0.07601 | 0.8334 | 0.28767 | 0.21701 | 0.75433 |
| 120 | 0.9566 | 0.10177 | 0.8598 | 0.38944 | 0.30450 | 0.78188 |
| 140 | 0.9375 | 0.09973 | 0.9180 | 0.48917 | 0.39606 | 0.80963 |
| 160 | 1.2689 | 0.13499 | 0.9594 | 0.62416 | 0.52557 | 0.84202 |

Table XVII.    Results of Adsorption-Desorption Run 5

Adsorption-Desorption of 95 mole% $C_3H_6$ , 5 mole% $C_3H_8$ on molecular sieves 5A adsorbent (9.40 grams).
At 0 psig and 25°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 25 | 0.8050 | 0.08564 | 0.69226 | 0.08564 | 0.05928 | 0.69226 |
| 25 | 1.7338 | 0.18445 | 0.86721 | 0.27008 | 0.21924 | 0.81176 |
| 25 | 1.7464 | 0.18579 | 0.93337 | 0.45587 | 0.39265 | 0.86131 |
| 25 | 1.7338 | 0.18445 | 0.94060 | 0.64032 | 0.56614 | 0.88416 |
| 25 | 1.7338 | 0.18445 | 0.94885 | 0.82477 | 0.74116 | 0.89863 |
| 25 | 1.7338 | 0.18445 | 0.95211 | 1.00922 | 0.91678 | 0.90840 |
| **Desorption Run** | | | | | | |
| 50 | 0.8610 | 0.09160 | 0.9708 | 0.09160 | 0.08893 | 0.97083 |
| 80 | 1.1150 | 0.11862 | 0.9833 | 0.21022 | 0.20557 | 0.97787 |
| 100 | 1.1208 | 0.11923 | 0.9887 | 0.32945 | 0.32345 | 0.98178 |
| 120 | 0.9534 | 0.10143 | 0.9912 | 0.43088 | 0.42399 | 0.98399 |
| 140 | 1.1887 | 0.12646 | 0.9938 | 0.55734 | 0.54966 | 0.98622 |
| 160 | 0.9718 | 0.10338 | 0.9944 | 0.66072 | 0.65246 | 0.98750 |

Table XVIII.  Results of Adsorption-Desorption Run 6

Adsorption-Desorption of 95 mole% $C_3H_6$, 5 mole% $C_3H_8$ on molecular sieves 5A adsorbent (9.40 grams).
At 0 psig and 80°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | F = $\sum C \times D$ | G = F/E |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 80 | 0.7991 | 0.08501 | 0.90107 | 0.08501 | 0.07660 | 0.90107 |
| 80 | 1.7409 | 0.18520 | 0.93089 | 0.27021 | 0.24900 | 0.92151 |
| 80 | 1.7221 | 0.18320 | 0.99486 | 0.45341 | 0.42278 | 0.93244 |
| 80 | 1.7221 | 0.18320 | 0.95205 | 0.63662 | 0.59720 | 0.93808 |
| **Desorption Run** | | | | | | |
| 100 | 0.6938 | 0.07381 | 0.96666 | 0.07381 | 0.07135 | 0.96666 |
| 120 | 1.0964 | 0.11664 | 0.98005 | 0.19045 | 0.18566 | 0.97486 |
| 140 | 1.0717 | 0.10945 | 0.98761 | 0.29990 | 0.29826 | 0.97963 |
| 160 | 1.2575 | 0.13378 | 0.99082 | 0.43368 | 0.43080 | 0.98305 |

Table XIX.    Results of Adsorption-Desorption Run 7

Adsorption-Desorption of 95 mole% $C_3H_6$, 5 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 25°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
| --- | --- | --- | --- | --- | --- | --- |
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 25 | 0.7906 | 0.04213 | 0.07443 | 0.04213 | 0.00314 | 0.07443 |
| 25 | 1.7230 | 0.09150 | 0.29581 | 0.13363 | 0.03020 | 0.22600 |
| 25 | 1.7230 | 0.09149 | 0.77506 | 0.22512 | 0.10111 | 0.44915 |
| 25 | 1.8109 | 0.09617 | 0.90000 | 0.32128 | 0.18767 | 0.58413 |
| 25 | 1.7097 | 0.09079 | 0.91611 | 0.41208 | 0.27084 | 0.65725 |
| 25 | 1.7103 | 0.09082 | 0.93608 | 0.50290 | 0.35585 | 0.70874 |
| 25 | 1.7167 | 0.09116 | 0.94301 | 0.59406 | 0.44182 | 0.74373 |
| 25 | 1.7100 | 0.09081 | 0.94541 | 0.68487 | 0.52767 | 0.77047 |
| 25 | 1.7103 | 0.09082 | 0.94906 | 0.77569 | 0.61387 | 0.79139 |
| **Desorption Run** | | | | | | |
| 50 | 3.1226 | 0.16582 | 0.95968 | 0.16582 | 0.15914 | 0.95968 |
| 80 | 3.5804 | 0.19013 | 0.97978 | 0.35595 | 0.34543 | 0.97042 |
| 100 | 2.7380 | 0.14540 | 0.98956 | 0.50135 | 0.48931 | 0.97595 |
| 120 | 3.0539 | 0.16217 | 0.99273 | 0.66352 | 0.65030 | 0.98007 |
| 140 | 3.8034 | 0.20197 | 0.99526 | 0.86550 | 0.85132 | 0.98361 |
| 160 | 4.8308 | 0.25653 | 0.99714 | 1.22031 | 1.10712 | 0.98670 |

Table XX.    Results of Adsorption-Desorption Run 8

Adsorption-Desorption of 95 mole% $C_3H_6$ , 5 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 24°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 24 | 1.7371 | 0.09225 | 0.75706 | 0.09225 | 0.06984 | 0.75706 |
| 24 | 1.7305 | 0.09190 | 0.87602 | 0.18414 | 0.15034 | 0.81644 |
| 24 | 1.7941 | 0.09527 | 0.93450 | 0.27942 | 0.23937 | 0.85667 |
| 24 | 1.7054 | 0.09056 | 0.94132 | 0.36998 | 0.32462 | 0.87740 |
| 24 | 1.8316 | 0.09727 | 0.95063 | 0.46725 | 0.41709 | 0.89265 |
| **Desorption Run** | | | | | | |
| 50 | 3.1586 | 0.16773 | 0.96390 | 0.16773 | 0.16168 | 0.96390 |
| 80 | 3.8488 | 0.20439 | 0.98052 | 0.37212 | 0.36208 | 0.97303 |
| 100 | 2.4249 | 0.12877 | 0.98897 | 0.50089 | 0.48944 | 0.97713 |
| 120 | 3.4740 | 0.18448 | 0.99425 | 0.68537 | 0.67286 | 0.98174 |
| 140 | 3.3184 | 0.17622 | 0.99567 | 0.86159 | 0.84831 | 0.98459 |
| 160 | 4.5045 | 0.23921 | 0.99569 | 1.10080 | 1.08649 | 0.98700 |

Table XXI.    Results of Adsorption-Desorption Run 9

Adsorption-Desorption of 95 mole% $C_3H_6$ , 5 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 25°$C$ adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°$C$ and 0 psig pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 25 | 1.7428 | 0.09255 | 0.76057 | 0.09255 | 0.07039 | 0.76057 |
| 25 | 1.7361 | 0.09219 | 0.87672 | 0.18474 | 0.15122 | 0.81856 |
| 25 | 1.7296 | 0.09185 | 0.92369 | 0.27659 | 0.23606 | 0.85347 |
| 25 | 1.7927 | 0.09520 | 0.93839 | 0.37179 | 0.32539 | 0.87520 |
| 25 | 1.7358 | 0.09218 | 0.94169 | 0.46397 | 0.41220 | 0.88841 |
| 25 | 1.7358 | 0.09218 | 0.94684 | 0.55615 | 0.49948 | 0.89810 |
| 25 | 1.7481 | 0.09283 | 0.94956 | 0.64898 | 0.58762 | 0.90545 |
| Desorption Run | | | | | | |
| 50 | 3.3927 | 0.18016 | 0.95520 | 0.18016 | 0.17209 | 0.95520 |
| 80 | 3.3122 | 0.17589 | 0.97806 | 0.35605 | 0.34413 | 0.96649 |
| 100 | 2.6488 | 0.14066 | 0.98972 | 0.49671 | 0.48334 | 0.97307 |
| 120 | 3.2522 | 0.17270 | 0.99342 | 0.66941 | 0.65491 | 0.97832 |
| 140 | 3.4514 | 0.18328 | 0.99560 | 0.85269 | 0.83739 | 0.98203 |
| 160 | 4.1109 | 0.21830 | 0.99679 | 1.07099 | 1.05499 | 0.98504 |

Table XXII.    Results of Adsorption-Desorption Run 10

Adsorption-Desorption of pure propane on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 25°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 25. | - | - | 0.0 | - | 0.0 | 0.0 |
| Desorption Run | | | | | | |
| 50 | 3.6350 | 0.19303 | 0.0 | 0.19303 | 0.0 | 0.0 |
| 80 | 3.9312 | 0.20876 | 0.0 | 0.40179 | 0.0 | 0.0 |
| 100 | 3.4436 | 0.18287 | 0.0 | 0.58466 | 0.0 | 0.0 |
| 120 | 3.8695 | 0.20535 | 0.0 | 0.79001 | 0.0 | 0.0 |
| 140 | 3.8016 | 0.14338 | 0.0 | 0.93339 | 0.0 | 0.0 |
| 160 | 4.0415 | 0.21462 | 0.0 | 1.14801 | 0.0 | 0.0 |

Table XXIII.    Results of Adsorption-Desorption Run 11

Adsorption-Desorption of pure propylene on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 25°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | | Cumulative | |
| --- | --- | --- | --- | --- | --- | --- |
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 25. | - | - | 1.0 | - | - | 1.0 |
| Desorption Run | | | | | | |
| 50 | 2.4462 | 0.12990 | 1.0 | 0.12990 | 0.12990 | 1.0 |
| 80 | 3.9905 | 0.21191 | 1.0 | 0.34181 | 0.34181 | 1.0 |
| 100 | 2.8286 | 0.15021 | 1.0 | 0.49202 | 0.49202 | 1.0 |
| 120 | 3.1374 | 0.16661 | 1.0 | 0.65863 | 0.65863 | 1.0 |
| 140 | 3.3227 | 0.17645 | 1.0 | 0.83508 | 0.83508 | 1.0 |
| 160 | 4.6744 | 0.24823 | 1.0 | 1.08331 | 1.08331 | 1.0 |

Table XXIV.    Results of Adsorption-Desorption Run 12

Adsorption-Desorption of 95 mole% $C_3H_6$ , 5 mole% $C_3H_8$ with adding 0.01062 g of water per g adsorbent on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 24°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | F = $\sum C \times D$ | G = F/E |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 24 | 1.7221 | 0.09140 | 0.76222 | 0.09140 | 0.06967 | 0.76225 |
| 24 | 1.7267 | 0.09169 | 0.83977 | 0.18309 | 0.14667 | 0.80108 |
| 24 | 1.7263 | 0.09167 | 0.90609 | 0.27477 | 0.22973 | 0.83608 |
| 24 | 1.7325 | 0.09200 | 0.93914 | 0.36667 | 0.31613 | 0.86193 |
| 24 | 1.7263 | 0.09167 | 0.94557 | 0.45844 | 0.40281 | 0.87314 |
| 24 | 1.7189 | 0.09128 | 0.94820 | 0.54972 | 0.48936 | 0.89020 |
| 24 | 1.7312 | 0.09193 | 0.94833 | 0.64165 | 0.57654 | 0.89853 |
| Desorption Run | | | | | | |
| 50 | 3.0308 | 0.16095 | 0.96461 | 0.16095 | 0.15525 | 0.96461 |
| 80 | 3.4637 | 0.18394 | 0.98006 | 0.34489 | 0.33552 | 0.97285 |
| 100 | 2.8447 | 0.15106 | 0.99308 | 0.49595 | 0.48554 | 0.97901 |
| 120 | 2.9802 | 0.15826 | 0.99451 | 0.65421 | 0.64293 | 0.98276 |
| 140 | 3.3388 | 0.17730 | 0.99620 | 0.83151 | 0.81956 | 0.98563 |
| 160 | 3.2460 | 0.17237 | 0.99652 | 1.00388 | 0.99134 | 0.98750 |

Table XXV.      Results of Adsorption-Desorption Run 13

Adsorption-Desorption of pure propane on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 24°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 24. | - | - | 0.0 | - | 0.0 | 0.0 |
| Desorption Run | | | | | | |
| 50 | 2.9829 | 0.15840 | 0.0 | 0.15840 | 0.0 | 0.0 |
| 80 | 5.1559 | 0.27380 | 0.0 | 0.43220 | 0.0 | 0.0 |
| 100 | 3.1725 | 0.16847 | 0.0 | 0.60067 | 0.0 | 0.0 |
| 120 | 3.4767 | 0.18463 | 0.0 | 0.78530 | 0.0 | 0.0 |
| 140 | 3.2631 | 0.17328 | 0.0 | 0.95858 | 0.0 | 0.0 |
| 160 | 3.7349 | 0.19834 | 0.0 | 1.15692 | 0.0 | 0.0 |

Table XXVI.    Results of Adsorption-Desorption Run 14

Adsorption-Desorption of pure propane on molecular sieves 5A adsorbent (9.40 grams).
At 0 psig and 25°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 25. | - | - | 0.0 | - | 0.0 | 0.0 |
| **Desorption Run** | | | | | | |
| 50 | 1.5205 | 0.16176 | 0.0 | 0.16176 | 0.0 | 0.0 |
| 80 | 1.0360 | 0.11021 | 0.0 | 0.27197 | 0.0 | 0.0 |
| 100 | 0.8932 | 0.09502 | 0.0 | 0.36699 | 0.0 | 0.0 |
| 120 | 0.9492 | 0.10098 | 110 | 0.46797 | 0.0 | 0.0 |
| 140 | 0.9922 | 0.10555 | 0.0 | 0.57352 | 0.0 | 0.0 |
| 160 | 1.0541 | 0.11214 | 0.0 | 0.68566 | 0.0 | 0.0 |

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Table XXVII.    Results of Adsorption-Desorption Run 15

Adsorption-Desorption of pure propylene on molecular sieves 5A adsorbent (9.40 grams).
At 0 psig and 24°C adsorption, 0 psig desorption.
Adsorbent condition before adsorption: Desorbed at 160°C and 1 atm pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 24. | - | - | 1.0 | - | - | 1.0 |
| **Desorption Run** | | | | | | |
| 50 | 0.8056 | 0.08570 | 1.0 | 0.08570 | 0.08570 | 1.0 |
| 80 | 1.5486 | 0.16474 | 1.0 | 0.25044 | 0.25044 | 1.0 |
| 100 | 0.9292 | 0.09885 | 1.0 | 0.34929 | 0.34929 | 1.0 |
| 120 | 0.8672 | 0.09226 | 1.0 | 0.44155 | 0.44155 | 1.0 |
| 140 | 1.0531 | 0.11203 | 1.0 | 0.55358 | 0.55358 | 1.0 |
| 160 | 1.1150 | 0.11862 | 1.0 | 0.67220 | 0.67220 | 1.0 |

Table XXVIII.  Results of Adsorption-Desorption Run 16

Adsorption-Desorption of 50 mole% $C_3H_6$ , 50 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 25°C adsorption, desorption 0 psig.  Final desorption (*) 27.5 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 160°C and 27.5 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 25 | 1.7400 | 0.09240 | 0.10495 | 0.09240 | 0.00970 | 0.10495 |
| 25 | 37.980 | 2.01689 | 0.29177 | 2.10929 | 0.59816 | 0.28358 |
| 25 | 37.980 | 2.01689 | 0.47858 | 4.12617 | 1.56340 | 0.37890 |
| 25 | 37.980 | 2.01689 | 0.50174 | 6.14306 | 2.57535 | 0.41923 |
| **Desorption Run** | | | | | | |
| 50 | 2.0300 | 0.10780 | 0.57203 | 0.10780 | 0.06166 | 0.57203 |
| 80 | 3.7900 | 0.20126 | 0.59360 | 0.30906 | 0.18113 | 0.58607 |
| 100 | 2.7000 | 0.14338 | 0.79331 | 0.45244 | 0.29488 | 0.65175 |
| 120 | 3.3800 | 0.17949 | 0.80268 | 0.63193 | 0.46497 | 0.73579 |
| 140 | 2.8400 | 0.15081 | 0.81205 | 0.78274 | 0.58744 | 0.75049 |
| 160 | 2.4400 | 0.12957 | 0.88392 | 0.91231 | 0.70197 | 0.76944 |
| 168 (*) | 1.0800 | 0.05735 | 0.89397 | 0.96967 | 0.75324 | 0.77680 |

Table XXIX. Results of Adsorption-Desorption Run 17

Adsorption-Desorption of 50 mole% $C_3H_6$, 50 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 10 psig and 25°C adsorption, 0 psig desorption. After final desorption temperature (160°C). The column was heated to 162°C, 29 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 166°C and 29.0 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | F = $\sum C \times D$ | G = F/E |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 25 | 19.63 | 1.04243 | 0.14803 | 1.04243 | 0.15431 | 0.14803 |
| 25 | 105.95 | 5.62636 | 0.49883 | 6.66879 | 2.96091 | 0.44400 |
| Desorption Run | | | | | | |
| 26.5 | 3.7600 | 0.19967 | 0.51421 | 0.19967 | 0.10267 | 0.51421 |
| 50 | 1.3500 | 0.07169 | 0.58160 | 0.27136 | 0.14437 | 0.53201 |
| 80 | 3.3800 | 0.17949 | 0.60137 | 0.45085 | 0.25231 | 0.55963 |
| 100 | 2.2900 | 0.12161 | 0.69297 | 0.57246 | 0.33658 | 0.53804 |
| 120 | 2.7000 | 0.14338 | 0.75978 | 0.71584 | 0.44551 | 0.62237 |
| 140 | 2.4300 | 0.12904 | 0.81215 | 0.90626 | 0.55032 | 0.65136 |
| 160 | 2.9700 | 0.15772 | 0.85548 | 1.06397 | 0.68524 | 0.68347 |

Table XXX.     Results of Adsorption-Desorption Run 18

Adsorption-Desorption of 50 mole% $C_3H_6$ , 50 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 20 psig and 26°C adsorption, 0 psig desorption.  After final desorption temperature (160°C). The column was heated to 161°C, 29 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 162°C and 29.0 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | Each Increment | | | Cumulative | | |
|---|---|---|---|---|---|---|
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| **Adsorption Run** | | | | | | |
| 26 | 133.24 | 7.07557 | 0.48765 | 7.07557 | 3.45040 | 0.48765 |
| **Desorption Run** | | | | | | |
| 26.5 | 4.0500 | 0.21507 | 0.49904 | 0.21507 | 0.10733 | 0.49904 |
| 50 | 2.7000 | 0.14338 | 0.55985 | 0.35845 | 0.18760 | 0.52336 |
| 80 | 3.9200 | 0.20816 | 0.63872 | 0.56662 | 0.32056 | 0.56574 |
| 100 | 2.7000 | 0.14338 | 0.73556 | 0.71000 | 0.42602 | 0.60004 |
| 120 | 2.7000 | 0.14338 | 0.80134 | 0.85338 | 0.54092 | 0.63386 |
| 140 | 2.7000 | 0.14338 | 0.86091 | 0.99676 | 0.66518 | 0.66652 |
| 160 | 2.7000 | 0.14338 | 0.89110 | 1.14014 | 0.79295 | 0.69476 |

Table XXXI.    Results of Adsorption-Desorption Run 20

Adsorption-Desorption of 50 mole% $C_3H_6$ , 50 mole% $C_3H_8$ on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 70°C adsorption, 0 psig desorption.   After final desorption temperature (160°C). The column was heated at 160°C, 29 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 161°C and 29.0 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | Each Increment | | | | Cumulative | |
| --- | --- | --- | --- | --- | --- | --- |
| A | B | C | D | E | $F = \sum C \times D$ | $G = F/E$ |
| Temperature degree C | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $C_3H_6$ (mole fraction) | Total mgmoles per g adsorbent accumulated | mgmoles $C_3H_6$ per g adsorbent accumulated | Cumulative (mole fraction) $C_3H_6$ |
| Adsorption Run | | | | | | |
| 70 | 37.98 | 2.01689 | 0.48490 | 2.01689 | 0.97799 | 0.48490 |
| 70 | 37.98 | 2.01689 | 0.50107 | 4.03378 | 1.98860 | 0.49299 |
| Desorption Run | | | | | | |
| 80 | 0.8797 | 0.04672 | 0.52739 | 0.04672 | 0.02464 | 0.52739 |
| 100 | 2.7100 | 0.14391 | 0.55319 | 0.19063 | 0.10425 | 0.54689 |
| 120 | 2.7100 | 0.14391 | 0.58335 | 0.33454 | 0.18820 | 0.56256 |
| 140 | 2.7100 | 0.14391 | 0.67748 | 0.47845 | 0.28570 | 0.59713 |
| 160 | 2.3000 | 0.12214 | 0.73912 | 0.60059 | 0.37560 | 0.62600 |

Table XXXII.    Results of Adsorption-Desorption Run 22

Adsorption-Desorption of 80 mole% $C_3H_8$ , 10 mole% $CO_2$, 10 mole% $H_2S$ on molecular sieves 13X adsorbent (18.831 grams).
At 0 psig and 25°C adsorption, 0 psig desorption.  After final desorption temperature (163°C), the column was heated to169°C, 29 inches Hg vacuum pressure.
Adsorbent condition before adsorption: Desorbed at 160°C and 29.0 inches Hg vacuum pressure.
Data on gas from adsorbent:

| | | Each Increment | | | | | Cumulative | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| A | B | C | D | E | F | $G = \sum D \times F$ | $H = \sum E \times F$ | $I = G/F$ | $J = H/F$ |
| T ( C) | Total through adsorbent or desorbed (mg moles) | Total mgmoles per g adsorbent for increment | Composition $CO_2$ mole fraction | Composition $H_2S$ mole fraction | Total mgmoles per g adsorbent accumulated | mgmoles $CO_2$ per g adsorbent accumulated | mgmoles $H_2S$ per g Adsorbent accumulated | Cumulative mole fraction $CO_2$ | Cumulative mole frac $H_2S$ |
| **Adsorption Run** | | | | | | | | | |
| 25 | 1.7300 | 0.09187 | 0.12396 | 0.0 | 0.09187 | 0.01139 | 0.0 | 0.12398 | 0.0 |
| 25 | 1.7300 | 0.09187 | 0.03852 | 0.0 | 0.18374 | 0.01493 | 0.0 | 0.08126 | 0.0 |
| 25 | 1.7300 | 0.09187 | 0.04691 | 0.0 | 0.27561 | 0.01924 | 0.0 | 0.06981 | 0.0 |
| 25 | 37.9100 | 2.01317 | 0.07815 | 0.0 | 2.28878 | 0.17659 | 0.0 | 0.07715 | 0.0 |
| 25 | 37.9100 | 2.01317 | 0.12386 | 0.0 | 4.30195 | 0.42592 | 0.0 | 0.09901 | 0.0 |
| 25 | 31.7900 | 1.68817 | 0.11718 | 0.0 | 5.99012 | 0.62374 | 0.0 | 0.10413 | 0.0 |
| 25 | 37.9500 | 2.01529 | 0.11909 | 0.0 | 8.00541 | 0.86376 | 0.0 | 0.10790 | 0.0 |
| 25 | 37.9500 | 2.01529 | 0.12386 | 0.0 | 10.02070 | 1.11335 | 0.0 | 0.11111 | 0.0 |
| 25 | 37.9500 | 2.01529 | 0.12786 | 0.0 | 12.03599 | 1.37103 | 0.0 | 0.11391 | 0.0 |
| 25 | 31.4200 | 1.66853 | 0.12740 | 0.13948 | 13.70452 | 1.58360 | 0.23273 | 0.11555 | 0.01698 |
| **Desorption Run** | | | | | | | | | |
| 51.5 | 3.4100 | 0.18108 | 0.15172 | 0.09197 | 0.18108 | 0.02747 | 0.01665 | 0.15170 | 0.09195 |
| 77 | 4.1000 | 0.21773 | 0.16596 | 0.20119 | 0.39881 | 0.06361 | 0.06046 | 0.15950 | 0.15160 |
| 89 | 2.0500 | 0.10886 | 0.17543 | 0.26585 | 0.50767 | 0.08271 | 0.08940 | 0.16292 | 0.17610 |
| 97 | 2.0500 | 0.10886 | 0.16702 | 0.32038 | 0.61653 | 0.10089 | 0.12428 | 0.16364 | 0.20158 |
| 112 | 4.1000 | 0.21773 | 0.15919 | 0.37113 | 0.83426 | 0.13555 | 0.20508 | 0.16248 | 0.24582 |
| 131 | 4.5100 | 0.23950 | 0.13565 | 0.49834 | 1.07376 | 0.16804 | 0.32443 | 0.15650 | 0.30214 |
| 163 | 6.8300 | 0.36270 | 0.03213 | 0.80831 | 1.43646 | 0.17969 | 0.61761 | 0.12509 | 0.42995 |

Table XXXIII.  Data for Figure 11.

| Desorption temperature°C | Propylene mole fraction | mg moles propane adsorbed per g adsorbent | mg moles propylene adsorbed per g adsorbent |
|---|---|---|---|
| 50.0 | 0.57203 | 0.1703 | 0.6916 |
| 80.0 | 0.59360 | 0.0885 | 0.5721 |
| 100.0 | 0.79331 | 0.0589 | 0.4584 |
| 123.0 | 0.80268 | 0.0495 | 0.2883 |
| 140.0 | 0.81205 | 0.0211 | 0.1658 |
| 160.8 | 0.88392 | 0.0061 | 0.0513 |
| 168.0 | 0.89397 | 0.0000 | 0.0000 |

Note: Data from this table are the same as Adsorption-Desorption Run 16 (Appendix B, Table XXVIII).

Table XXXIV. Data for Figure 12.

| Desorption temperature°C | Propylene mole fraction | mg moles propane adsorbed per g adsorbent | mg moles propylene adsorbed per g adsorbent |
|---|---|---|---|
| 25.0 | 0.51355 | 0.24139 | 0.68368 |
| 50.0 | 0.55985 | 0.17828 | 0.60341 |
| 81.5 | 0.63334 | 0.10196 | 0.47157 |
| 100.0 | 0.73556 | 0.06404 | 0.36610 |
| 120.0 | 0.80134 | 0.03556 | 0.25120 |
| 140.0 | 0.86091 | 0.01562 | 0.12777 |
| 160.0 | 0.89110 | 0.00000 | 0.00000 |

Note: Data from this table are the same as Adsorption-Desorption Run 18 (Appendix B, Table XXX).

Table XXXV.   Results of Adsorption-Desorption Run 23

Adsorption Data for Economic Evaluation.  Adsorption from 25 mole % propylene-75 mole % propane at 24 degree C and 0 psig pressure.

| No. | Mole fraction propylene | Mole fraction propane | No. moles propylene | No. moles propane | Total moles propylene accumulated | Total moles propane accumulated |
|-----|------|------|------|------|------|------|
| 1.  | 0.1163 | 0.8837 | 0.0133 | 0.1007 | 0.0133 | 0.1007 |
| 2.  | 0.0535 | 0.9465 | 0.0077 | 0.1356 | 0.0209 | 0.2363 |
| 3.  | 0.0398 | 0.9602 | 0.0092 | 0.2220 | 0.0301 | 0.4583 |
| 4.  | 0.0307 | 0.9693 | 0.0069 | 0.2178 | 0.0370 | 0.6761 |
| 5.  | 0.0259 | 0.9741 | 0.0062 | 0.2351 | 0.0433 | 0.9112 |
| 6.  | 0.0208 | 0.9792 | 0.0053 | 0.2511 | 0.0486 | 1.1623 |
| 7.  | 0.1588 | 0.9841 | 0.0043 | 0.2672 | 0.0529 | 1.4295 |
| 8.  | 0.0103 | 0.9897 | 0.0027 | 0.2538 | 0.0555 | 1.6832 |
| 9.  | 0.0094 | 0.9906 | 0.0024 | 0.2540 | 0.0580 | 1.9372 |
| 10. | 0.0086 | 0.9914 | 0.0021 | 0.2482 | 0.0601 | 2.1854 |
| 11. | 0.0075 | 0.9925 | 0.0016 | 0.2096 | 0.0617 | 2.3950 |
| 12. | 0.0078 | 0.9922 | 0.0007 | 0.0898 | 0.0624 | 2.4848 |
| 13. | 0.0077 | 0.9922 | 0.0012 | 0.1556 | 0.0636 | 2.6404 |
| 14. | 0.0062 | 0.9938 | 0.0009 | 0.1439 | 0.0645 | 2.7843 |
| 15. | 0.0049 | 0.9951 | 0.0008 | 0.1591 | 0.0653 | 2.9433 |
| 16. | 0.0057 | 0.9943 | 0.0014 | 0.2400 | 0.0667 | 3.1834 |
| 17. | 0.0043 | 0.9957 | 0.0009 | 0.2163 | 0.0676 | 3.4000 |
| 18. | 0.0011 | 0.9989 | 0.0002 | 0.2170 | 0.0678 | 3.6166 |
| 19. | 0.0046 | 0.9954 | 0.0008 | 0.1817 | 0.0687 | 3.7967 |
| 20. | 0.0015 | 0.9985 | 0.0001 | 0.0663 | 0.0688 | 3.8630 |
| 21. | 0.0015 | 0.9985 | 0.0004 | 0.2651 | 0.0692 | 4.1281 |
| 22. | 0.0015 | 0.9985 | 0.0005 | 0.3343 | 0.0697 | 4.4624 |
| 23. | 0.0016 | 0.9984 | 0.0005 | 0.3464 | 0.0702 | 4.8087 |
| 24. | 0.0014 | 0.9986 | 0.0006 | 0.4006 | 0.0708 | 5.2094 |
| 25. | 0.0013 | 0.9987 | 0.0004 | 0.3465 | 0.0712 | 5.5559 |
| 26. | 0.0012 | 0.9988 | 0.0004 | 0.3465 | 0.0716 | 5.9023 |
| 27. | 0.0010 | 0.9990 | 0.0004 | 0.3465 | 0.0720 | 6.2489 |
| 28. | 0.0010 | 0.9990 | 0.0004 | 0.3466 | 0.0723 | 6.5954 |
| 29. | 0.0008 | 0.9992 | 0.0003 | 0.3677 | 0.0726 | 6.9632 |
| 30. | 0.0008 | 0.9992 | 0.0003 | 0.3316 | 0.0729 | 7.2947 |
| 31. | 0.0008 | 0.9992 | 0.0003 | 0.3617 | 0.0732 | 7.6564 |
| 32. | 0.0454 | 0.9546 | 0.0093 | 0.1958 | 0.0825 | 7.8522 |
| 33. | 0.1605 | 0.8395 | 0.0542 | 0.2836 | 0.1367 | 8.1359 |
| 34. | 0.2246 | 0.7754 | 0.0745 | 0.2573 | 0.2112 | 8.3932 |
| 35. | 0.2448 | 0.7552 | 0.0776 | 0.2392 | 0.2888 | 8.6323 |
| 36. | 0.2512 | 0.7488 | 0.1061 | 0.3162 | 0.3949 | 8.9486 |
| 37. | 0.2540 | 0.7460 | 0.0705 | 0.2070 | 0.4654 | 9.1556 |

Table XXXVI.   Results of Adsorption-Desorption Run 24

Desorption Data for Economic Evaluation.   Desorption from 25 mole % propylene-75 mole % propane at 0 psig pressure.

| T degree C | Mole fraction propylene | Mole fraction propane | No. moles propylene | No. moles propane | Total moles propylene accumulated | Total moles propane accumulated |
|---|---|---|---|---|---|---|
| 36.8 | 0.3907 | 0.6093 | 0.1591 | 0.2481 | 0.1591 | 0.2481 |
| 61.3 | 0.4891 | 0.5109 | 0.1697 | 0.1772 | 0.3288 | 0.4254 |
| 89.2 | 0.5848 | 0.4152 | 0.1464 | 0.1039 | 0.4752 | 0.5293 |
| 107.0 | 0.6432 | 0.3568 | 0.1203 | 0.0667 | 0.5955 | 0.5960 |
| 123.3 | 0.8703 | 0.1297 | 0.2650 | 0.0395 | 0.8605 | 0.6356 |
| 141.7 | 0.9703 | 0.0297 | 0.2898 | 0.0887 | 1.1503 | 0.6444 |
| 182.0 | 0.9703 | 0.0297 | 0.5093 | 0.0156 | 1.6596 | 0.6600 |
| 212.5 | 0.9646 | 0.0354 | 0.2008 | 0.0074 | 1.8604 | 0.6674 |
| 233.2 | 0.9673 | 0.0327 | 0.3064 | 0.0103 | 2.1667 | 0.6778 |
| 254.0 | 0.9673 | 0.0327 | 0.1692 | 0.0057 | 2.3360 | 0.6834 |

APPENDIX C

TABLES OF EXPERIMENTAL DATA AND CALCULATED VALUES FOR

ETHANOL-WATER

Table XXXVII. Data for Figure 3 and 4.

| Temperature°C | Cummulative amount of ethanol Desorbed per g of carbon (mg/g) | Cummulative amount of water Desorbed per g of carbon (mg/g) |
|---|---|---|
| 50 | 0.328 | 50.19 |
| 60 | 2.400 | 92.84 |
| 70 | 3.540 | 101.70 |
| 80 | 3.940 | 104.19 |
| 90 | 5.300 | 107.27 |
| 100 | 7.830 | 109.06 |
| 140 | 45.230 | 111.11 |

Table XXXVIII. Data for Figure 5.

Data on desorption of activated carbon with adsorbed ethanol and water per gram activated carbon. Ethanol and water were previously adsorbed from air and vapor at 44°C. Air and vapor were in equilibrium with 6 wt % of ethanol in water solution at 40°C.

|  | Total weight per g A.C. | Cum. wt. desorbed per g A.C. | Wt. Fraction Ethanol | Wt. Ethanol per g A.C. | Wt. $H_2O$ per g A.C. |
|---|---|---|---|---|---|
| Desorbed 50°C bath Temp. | 0.0505 | 0.0505 | 0.006 | 0.0003 | 0.0502 |
| Desorbed 50°C to 60°C | 0.0447 | 0.0952 | 0.047 | 0.0021 | 0.0426 |
| Desorbed 60°C to 70°C | 0.0100 | 0.1052 | 0.110 | 0.0011 | 0.0089 |
| Desorbed 70°C to 80°C | 0.0029 | 0.1081 | 0.138 | 0.0004 | 0.0025 |
| Desorbed 80°C to 90°C | 0.0044 | 0.1125 | 0.318 | 0.0014 | 0.0031 |
| Total desorbed to 90°C | 0.1125 | - | 0.047 | 0.0053 | 0.1073 |
| Desorbed 90°C to 100°C | 0.0043 | 0.1168 | 0.581 | 0.0025 | 0.0018 |
| Desorbed 100°C to 140°C | 0.0395 | 0.1563 | 0.947 | 0.0374 | 0.0021 |
| Total desorbed 90°C to 140°C | 0.0438 | - | 0.911 | 0.0399 | 0.0039 |
| Total desorbed | 0.1563 | - | 0.289 | 0.0452 | 0.1112 |

Table XXXIX.   Data for Figure 6.

| Natural log of ethanol vapor pressure | Inverse temperature x $10^3$ |
|---|---|
| 0.8112 | 2.976 |
| 1.2800 | 2.812 |
| 1.8920 | 2.755 |
| 2.2720 | 2.740 |

Table XL.     Data for Figures 7 and 8.

| Condition | Temperature°C | Grams of ethanol / Grams of carbon | Grams of Water / Grams of carbon |
|---|---|---|---|
| Adsorption | 55 | 0.0490 | 0.0429 |
| Desorption | 55 | 0.0537 | 0.0492 |
| Adsorption | 70 | 0.0353 | 0.0115 |
| Desorption | 70 | 0.0388 | 0.0088 |
| Adsorption | 85 | 0.0203 | 0.0050 |
| Desorption | 85 | 0.0232 | 0.0056 |

Table XLI.    Experimental Data for Ethanol-Water on Silicalite

| Run | Condition | Wt. % EtOH adsorbed | g taken off | g of EtOH / g adsorbent | g of water / g adsorbent |
|---|---|---|---|---|---|
| 1. | Ads. 44°C 2 hrs | 12.70 | 2.9516 | 0.37485 | 2.57675 |
| 2. | Des. 40°C 1 hr 44°C 2 hrs | 19.56 | 4.9525 | 0.96856 | 3.98394 |
| 3. | Ads. 50°C 1hr 44°C 2 hrs | 27.44 | 3.9897 | 1.09490 | 2.89480 |
| 4. | Ads. 50°C 1 hr 44°C 2 hrs | 19.12 | 4.5993 | 0.87923 | 3.72007 |
| 5. | Ads. 70°C 1 hr 60°C 2 hrs | 35.0 | 2.6525 | 0.93066 | 1.72184 |
| 6. | Des. 50°C 1 hr 60°C 2 hrs | 53.12 | 3.2554 | 1.72940 | 1.52600 |
| 7. | Des. 50°C 1 hr 60°C 2 hrs | 52.19 | 3.3282 | 1.73704 | 1.59116 |
| 8. | Des. 40°C 1.5 hr 44°C 2 hrs | 29.92 | 6.0384 | 1.80643 | 4.23197 |

Note: Weight of silicalite in copper U-tube approximately 70 grams.

Table XLII.  The Cumulative Amount of Ethanol and Water Desorbed at Various Temperature (Silicalite Adsorbent)

| Run | Temperature degree C | g ethanol / g adsorbent | g water / g adsorbent |
|---|---|---|---|
| Run 4. Adsorbed at 44°C | | | |
| | 60 | 0.06704 | 2.09216 |
| | 80 | 0.15240 | 2.76490 |
| | 100 | 0.28192 | 3.20098 |
| | 120 | 0.57128 | 3.53672 |
| | 140 | 0.87923 | 3.72007 |
| Run 5. Adsorbed at 60°C | | | |
| | 80 | 0.12680 | 0.89910 |
| | 100 | 0.27671 | 1.31899 |
| | 140 | 0.93066 | 1.72184 |

Note: Weight of silicalite in copper U-tube approximately 70 grams.

APPENDIX D

PROPOSED METHOD OF FERMENTATION, ADSORPTION AND VARIABLE
TEMPERATURE DESORPTION FOR ETHANOL PRODUCTION

Previous studies (25) have indicated that it is possible to remove ethanol from a fermentor into the gas phase and concentrate the ethanol by adsorption, without the use of high temperatures that destroy yeast activity, and without disturbing the fermentation. This is accomplished by circulation of carbon dioxide through the fermentor and an activated carbon adsorber. Recent studies have indicated that stepwise desorption at variable increasing temperatures can provide an ethanol concentration of 90 to 95 % from an adsorber saturated with vapor from a fermentor, and an application for a patent has been submitted for this separation method.

The above methods permit the design of a system of fermentation, adsorption, and variable temperature desorption, with the following advantages:

1. The fermentor can be operated continuously with continuous removal of ethanol, with no yeast accompanying the ethanol removed.

2. No high temperatures are required for distillation which may inactivate and decompose yeast, organics, and carbohydrates, and may produce undesirable wastes.

3. By one adsorption and one multiple step desorption of the ethanol and part of the water, 90 to 95 % ethanol can be produced.

4. The major significant requirement for heat is for desorption of ethanol and part of the water, one time, with minimal requirement for recycle and no reflux as in distillation. Much of the heat could be waste heat from power generation.

5. Yeast must be removed from the fermentor only with the discharge of water containing relatively small amounts of ethanol. Some of this yeast can probably be settled out and recycled to maintain a high yeast concentration in the fermentor.

6. Because ethanol can be continuously removed from the fermentor, lower ethanol concentrations can be maintained in the fermentor reducing the inhibiting effects of ethanol.

7. If higher concentrations of ethanol are desired, a dessicant adsorber could be used to remove water vapor from the high-ethanol vapor desorbed. The requirement for dessicant would be similar to that for a distillation product.

8. The process and equipment are relatively simple and could probably be controlled by automatic sequencing techniques.

The proposed method of fermentation, adsorption, and variable temperature desorption is described below based on conditions which have been studied, but are not necessarily optimal or possibly not even near optimal.

Fermentation should be carried out continuously with continuous inflow of sugar solution and perhaps dilution water, as shown in Figure 15. The fermentor, A, should be operated at a level of about 6 % ethanol by weight, and at a temperature of about 40°C. If other variables are maintained constant, and if the fermentor volume is adequate, the ethanol concentration can be maintained by adjusting the sugar addition rate.

Ethanol and water vapor are removed from the fermentor by a flow of recirculated carbon dioxide, which is produced by the fermentor. This $CO_2$ passes through an activated carbon adsorption column, B1, at 45°C where the ethanol is preferentially adsorbed along with some water. The higher temperature should prevent condensation. Carbon dioxide, water vapor, and perhaps some ethanol is pumped by a blower, C, to a bleed line taking off excess $CO_2$ produced in the fermentor, and to a recirculation stream. The recirculation stream goes through a stripping column, D, that removes ethanol from the discharge liquid flow from the fermentor. The $CO_2$ stream with some ethanol from the discharge is then passed through the fermentor to pick up additional ethanol and then is returned to the adsorption column. The discharged liquid from the fermentor, after stripping, can be passed through a settling tank, E, to separate out sludge containing yeast. A desired fraction of this yeast could be returned to the fermentor to maintain high yeast concentration and high fermentation rates. The portion of the sludge that is not returned could be processed to an animal feed product or other uses.

As has been demonstrated by variable temperature desorption studies, the activated carbon in the adsorption column containing adsorbed ethanol and water can be desorbed in 2 steps by circulating $CO_2$ (from the fermentor loop) through the heated column to a condenser where water and ethanol is condensed, and the $CO_2$ is returned to the column. In the first step

Figure 15.    Proposed fermentation, adsorption, variable temperature desorption process.

A - Fermentor
B - Carbon Adsorber
C - Blower
D - Stripper
E - Settling Tank

F - Condensers or Coolers
G - Dessicant Adsorber
H - Heating Fluid
CW - Coolant
J - Pump

K - Liquid Vapor Separator
L - Feed
M - Ethanol Product
N - Discharge Water
P - Air

Q - Excess $CO_2$
R - Sludge

of desorption, B2, at temperatures up to 80 or 90°C, mostly water would be desorbed with around 5 % ethanol and condensed or cooled in F1 (see Appendix C, Table XXXVIII). This stream could be recirculated as either a cooled vapor to the adsorbing column, B1, or as a liquid to the fermentor. In the second step of desorption at up to 140°C, $CO_2$ circulation is used to desorb mostly ethanol at concentrations of about 90 to 95 % ethanol and this ethanol is condensed in a condenser, F2, if desired. If a higher purity ethanol is desired, the logical method would be to pass the 90 to 95 % ethanol and 5 to 10 % water vapors through an adsorption column, G1, containing a dessicant to adsorb water such as starch (26), cellulose (25), silica gel or, molecular sieves. After passing through this column, a high purity ethanol could be condensed from the $CO_2$ stream before recirculation to the desorbing column B3. The dessicant adsorber could be regenerated by heat and air as shown for G2.

Various possibilities exist for heat recovery in the above processing steps. The heat released on adsorption in adsorber B1 could be transferred to a cooling-heating water stream that could then transfer the heat to the fermentor where some heat is needed for evaporating ethanol and water, although fermentation heat might supply much of this requirement. Heat would be required in desorption in adsorbers B2 and B3, and heat is released in the associated condensers. Heat from the outlet $CO_2$-vapor stream from B3 could be transferred to supply some heat for desorption in B2. Similar possibilities might exist for adsorption of water on the dessicant in adsorbers G1 and G2, depending on the temperatures used.

APPENDIX E

SAMPLE CALCULATIONS

1. To prepare the mixture of propylene and propane gas in the tank, use a basis of 50 mole % propylene-50 mole % propane and total pressure in the tank equal to 20 psig.

First, apply vacuum to the tank until close to 29 inches Hg vacuum.

Second, measure tank pressure $P_G$ = 28.6 inches Hg vacuum.

$\Delta P$ at 20 psig = psi = 20 psi - (-28.6 in Hg)(14.7 psi/29.92 in Hg) = 34.051 psi

Partial P of 50 mole % propylene = (34.051 psi)(0.5) = 17.026 psi

Propylene psig = (17.026 psi)-{28.6 in Hg(14.7 psi/29.92 in Hg)} = 2.975 psig

Add propylene to the tank until pressure on the gauge equals 2.975 psig, and add propane till the pressure equals to 20 psig. Maintain constant temperature for both steps.

The calculation procedure for 95 mole % propylene-5 mole % propane, 75 mole % propylene-25 mole % propane and 25 mole % propylene-75 mole % propane were made in the same way as the above.

2. The number of mg moles desorbed for propane-propylene, propane-hydrogen sulfide-carbon dioxide runs was calculated as follow:

The volume of the measuring chamber, temperature of the water bath and pressure of measuring chamber were measured.

The volume of the measuring chamber (U-Tube)    =    45.12 ml.

The volume of the measuring chamber (Cylinder)    =    942.00 ml.

Total volume of both measuring chambers    =    987.12 ml.

From N = PV/RT, $\Delta N = (V/RT)\Delta P$ if volume and temperature are constant.

P = pressure of measuring chamber (atm)

V = volume of measuring chamber (ml)

R = gas constant (82.06 ml-atm/gmol.K)

T = temperature of water bath (K)

For example, if pressure rises from 26.5 in Hg Vac to 10.1 psig in the U-tube measuring chamber, with U-tube volume = 45.12 ml and temperature of water bath = 73°F,

$$N = \frac{\left[(\frac{26.5 inHgVac}{29.92 inHgVac} + 10.1 psi(1 atm/14.7 psi))(45.12 ml)(1000 mg/g)\right]}{82.06 \frac{ml.atm}{gmol.K} \times \frac{(73 + 460)}{1.8}K}$$

$$= 2.9204 \text{ mgmol}$$

Sometimes the cylinder was used with the U-tube chamber and the measuring cylinder.

3. Calculate mole % of propane and propylene in a gas sample.

For the mixture of 50 mole % of propylene and 50 mole % propane.

Calibrating, we have:

$$[N_{C_3H_6}/N_{C_3H_8}] = K \times [A_{C_3H_6}/A_{C_3H_8}]$$

or

$$K = \frac{[N_{C_3H_6}/N_{C_3H_8}]}{[A_{C_3H_6}/A_{C_3H_8}]}$$

where;    K    = calibrating constant

$N_{C_3H_6}$ = mole % of propylene in sample gas

$N_{C_3H_8}$ = mole % of propane in sample gas

$A_{C_3H_6}$ = area of propylene in sample gas from chromatograph

$A_{C_3H_8}$ = area of propane in sample gas from chromatograph

For calibration, $A_{C_3H_6}$ = 51.496 and $A_{C_3H_8}$ = 48.505 with the sample gas of 50 mole % propylene, then

K = (0.5/0.5)/(51.496/48.505) = 0.9419

For a gas sample with $A_{C_3H_6}$ = 85.00 and $A_{C_3H_8}$ = 15.00

we have:

$$(N_{C_3H_6}/N_{C_3H_8}) = K(A_{C_3H_6}/A_{C_3H_8})$$

where:  K  =  calibrating constant

$$[N_{C_3H_6}/N_{C_3H_8}] = K[A_{C_3H_6}/A_{C_3H_8}] = 0.9419(85.00/15.00) = 5.3374$$

To find the mole fraction from the mole ratio the following equation is used:

$$[N_{C_3H_6}/[N_{C_3H_8}+N_{C_3H_6}]] = [N_{C_3H_6}/N_{C_3H_8}]/[1+N_{C_3H_6}/N_{C_3H_8}]$$

$$N_{C_3H_6}/N_{C_3H_8} = 5.3374$$

Mole fraction $C_3H_6$ =  5.3374/(1 + 5.3374)  =  0.8422

Mole % $C_3H_6$ = 84.22%

Mole % propane  =  100 -84.22  =  15.78 %

K values were determined for various ranges prior to analyzing samples.

4. Calculate the adsorptivities of propane and propylene per gram of adsorbent.

   Process with molecular sieves (5A) adsorbent (weight  =  9.4 g)

   Calculate weight of desorbing gas per weight of adsorbent.

   (mg mole desorbed / g adsorbent)  =  (2.9204)/(9.4)  =  0.3107 mg mole/g